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Effect of Salt and Surfactant on Aqueous Solution Properties of Pyrene-Labeled Poly(3-dimethyl (methylmethacryloyl ethyl) ammonium propane sulfonate)

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Summary: Photophysical and solution properties of pyrene-labeled poly(3-dimethyl(methylmethacryloyl ethyl) ammonium propane sulfonate), poly(DMAPS/Py), were studied in terms of fluorescence emission measurement. The I_E/I_M was shown as a function of polymer concentration in deionized water. I_E/I_M value decreases with an increase in the salt concentration. The addition of surfactants to the aqueous solution of poly(DMAPS/Py) can either induce the mixed micelle of intra- polymer and its surrounding surfactants and/or mixed micelle of inter-polymers and their surrounding surfactants. Models of interactions between poly(DMAPS/Py) and surfactant or divalent salt in aqueous solution are proposed.

Introduction

Recently, commercial applications of water-soluble polymers have been introduced, particularly as dispersing agents, surface-modifiers, and for other uses in the textile, pharmaceutical and related industries.[1~6)] Numerous research groups have studied the aqueous solution properties of polybetaines.[1~6)] Osada *et al.* studied the effects of polyelectrolyte complexation on UCST of zwitterionic polymer.[1)] Wu *et al.* reported on the static and dynamic laser light-scattering studies of zwitterionic polybetaine in aqueous solution.[2)] Kang *et al.* further reported that the adhesive-free adhesion between two polymer films can be achieved with surface graft copolymerization water-soluble betaine.[3,6)] Recently, many investigators have focused their attention on fluorescent labeled water-soluble polymers to correct the microscopic, photophysical response with a macroscopic event such as phase separation, aggregation, or latex film formation.[7,8)] Previously, researchers have examined a series of polybetaines and their corresponding cationic polyelectrolytes with different electron-

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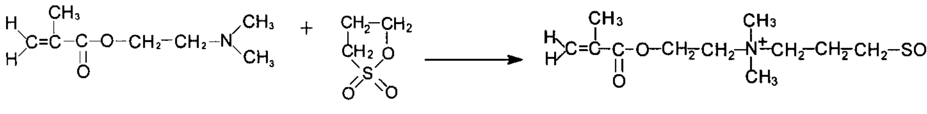
withdrawing groups, varying ethylene units between the charge group.[9)] Some studies have been conducted with dilute aqueous solution properties of the cationic polyelectrolytes, anionic polyelectrolytes and polybetaines.[10~14] Dilute aqueous solution properties such as viscosity and degree of binding have provided a reasonable assessment of the macroscopic solution; however, a detailed analysis requires the use of a more sensitive characterization. Previously, the synthesis, viscometrics, and the fluorescence properties of these water-soluble pyrene-labeled acrylamide-based copolymers have been reported.[11,12)] The behavior of the dilute aqueous solution properties of the water-soluble acrylamide-based copolymer can be clearly defined from their viscometrics and photophysical studies. Moreover, attention in recent years has focused on aqueous solution properties, photophysics, photochemistry, and the applications of the water-soluble copolymers containing hydrophobic residues such as styrenic, lauryl, cyclododecyl and admantyl groups, as well as charged units[13~15)]. The intramolecular hydrophobic aggregation of the styrene residues occurs only when the styrene content in the copolymer exceeds a critical value (estimated to be ca. 50 mole%).[16)] Furthermore, the content of the residues is adjusted to 50 mole% to secure the formation of the microphase structure consisting of the styrene aggregates. The synthesis, viscometrics, cloud point and fluorescence measurement of the ampholytic styrene-based copolymer has been reported.[13,14)] Furthermore, a series of new phenyl-containing cationic water-soluble monomers and their polymers, such as cationic poly(trimethylmethacrylamidophenyl ammonium methylsulfate) (TMMAPhAMS) and zwitterionic poly(N,N-dimethylmethacrylamidophenyl ammonium propane sultone) (DMMAPhAPS), were previously synthesized.[17)] Also, the solubilities, viscometrics, surface activity and hydrodynamic diameter of these water-soluble polymers have been discussed.[17)] A series of copolymers of methacrylamide (MAA) with phenyl-containing monomers (TMMAPhAMS or DMMAPhAPS) were prepared.[18)] The monomer reactivity ratios were calculated by the Fineman-Ross and Kelen-Tüdos methods.[18)]

In this study, pyrene-labeled poly(DMAPS/Py) was prepared. The effects of salt and surfactants on photophysical and aqueous solution properties of poly(DMAPS/Py) are discussed, particularly in aqueous poly(DMAPS/Py) solution and mixed aqueous solution of poly(DMAPS/Py) and surfactant.

Experimental Part

Synthesis of N,N-Dimethylacryl ammonium propane sultone (DMAPS)

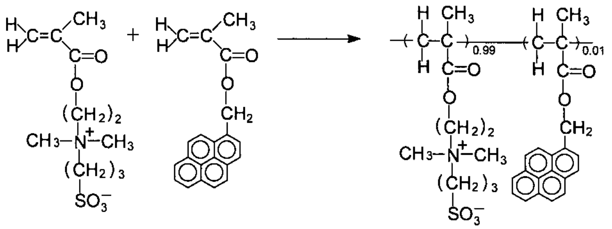
The monomer, N,N-dimethylacryl ammonium propane sultone (DMAPS), was prepared as described previously.19) The procedure is listed as following :19)



(DMAPS)

Preparation of Pyrene Labeled Polymers

In a 100 mL flask equipped with a stirrer, thermometer, 1-pyrene methanol (0.001 mol), NaOH (0.001 mol) and dried THF(20 mL) were charged under argon atmosphere and the contents were stirred below 5□. A mixture of methacryloyl chloride (0.0011 mol) and dry THF was added dropwise for 1 hr. Following this addition, the mixture was stirred for 10 hr at the same temperature. The solution was then condensed under reduced pressure to remove THF. Methanol was added to precipitate the desired product. The contents were poured into a large excess of water to precipitate the resulting compound. The precipitated white crystals were collected by filtration and dried under reduced pressure for 24 hrs, yielding methacryloyl pyrene (MAOPy). The pyrene-labeled polymers were prepared by free radical polymerization initiated by $K_2S_2O_8$. The procedure for the polymer was as follows. A glass ampoule containing DMAPS (0.01 mol) (99 mol% on the basis of the monomers) and pyrene containimg monomer (MAOPy) (10^{-4} mol) (1 mol% on the basis of the monomers) and $K_2S_2O_8$ (10^{-4}mol) in N,N-dimethylformamide (30 mL) and water(10 mL) (3/1) cosolvent was degassed by three freeze-pump-thaw cycles on a vacuum line. The sealed ampoule was maintained at 60□ in a water bath. After polymerization, the mixture was poured into a large excess of acetone to precipitate the resulting polymers. The polymers were purified by three repreciptations from H_2O into acetone and dried under vacuum at 70□. (Scheme 1) The corresponding pyrene-labeled polymers poly(DMAPS/Py) were obtained. Poly(DMAPS/Py) consisted of 99.1 mole% DMAPS and 0.9 mole% MAOPy, with yield of 94%. The ^{1}H NMR peaks of polymer were attributed to the acrylic group of monomer at 5.48 and 5.70 ppm were disappeared.[18)]



Scheme 1. Preparation of Pyrene Labeled Polymers

Characterization Methods

NMR spectra were recorded using a JEOL EX400 (^{1}H NMR at 399.96 MHz). The fluorescence spectra were recorded by a Shimadzu RF-5031 spectrophotometer. All the fluorescence measurements were performed at room temperature.

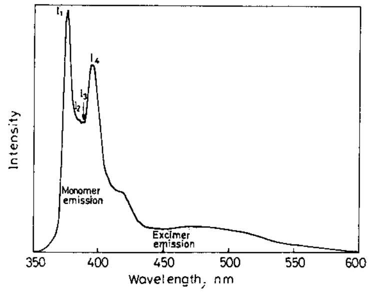


Figure 1. Excimer emission (I_E) and monomer emission (I_M) of poly (DMPAPS/Py) in deionized water. Excitation wavelength: 330 nm.

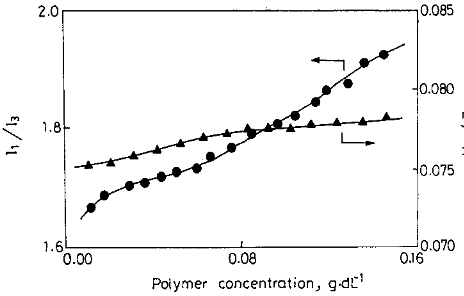


Figure 2. I_1/I_3 and I_E/I_M of poly(DMAPS/Py) in aqueous solution with different polymer concentration. Excitation wavelength: 330nm.

Results and Discussion

Pyrene-labeled poly(DMAPS/Py) excimer emission was investigated by fluorescence measurement to determine the aqueous solution's behavior. When the fluorescent hydrophobe (pyrene group) was incorporated into the sulphobetaine polymer poly(DMAPS/Py), the photophysical response may effectively probe the aqueous solution behavior on the microscopic level. As the hydrodynamic volume decreases, interactions between the isolated, covalently bound fluorescent hydrophobias allow the formation of dimeric, sandwich-like conformations that subsequently lead to excimer formation. The maximum peak at 377 nm arises from the fluorescence emission of the isolated pyrene (monomer emission) **(Figure 1)**. The broad band centered at 472 nm results from emission of excited dimeric pyrene (excimer emission) **(Figure 1)**. The interpolymer hydrophobic association is observed together with an increase in "excimer" emission relative to that of "monomer" emission, where I_E/I_M is the ratio of intensities of the excimer and the monomer fluorescence and reflects the intra- and inter- molecular interactions of pyrene groups and microscopic conformation of polymers in solution. Furthermore, the ratio of the first to the third vibronic bands (I_1/I_3) in fluorescence spectra of pyrene is known to depend on the polarity of microenvironment in media with pyrene, the I_1/I_3 ratio being lower in less polar media.7,8) Previous studies have addressed the photophysical properties of the naphthalene-labeled acrylamide-sulphobetaine copolymer, naphthalene-labeled poly(acrylamide/ N,N-dimethyl-maleimido propyl ammonium propane sulfonate copolymer), poly(ADMMAPS)/NA12) and naphthalene-labeled cationic copolymer, naphthalene-labeled poly(dimethyl sulfate quaternized acrylamide/N,N-dimethyl aminopropyl maleiimido copolymer), poly(DSQADMAPM)/NA.11) The ratio of intensity of the excimer emission and monomer emission I_E/I_M steadily increases with the increase in the polymer concentration, which was observed for both naphthalene-labeled acrylamide-based ampholytic poly(ADMMAPS)/NA and cationic poly(DSQADMAPM)/NA. The addition of salt to the polymer shielded the ionic condition of the naphthalene-labeled acrylamide-based water-soluble polymers. The I_E/I_M values of the ampholytic poly(ADMMAPS)/NA decreases with an increase in the salt concentration. The effect of the I_E/I_M values increasing with an increase in the salt concentration for cationic poly(DSQADMAPM)/NA is contrary to that of ampholytic poly(ADMMAP)/NA. 11,12)

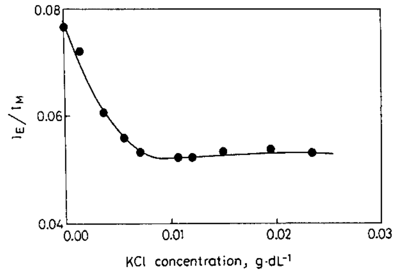


Figure 3. I_E/I_M of poly(DMAPS/Py) in aqueous solution with different KCl concentration. Excitation wavelength: 330nm. [poly(DMAPS/Py)]: 0.01 g/dL.

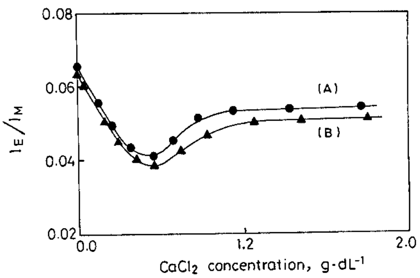


Figure 4. I_E/I_M of poly(DMAPS/Py) in aqueous $CaCl_2$ solution with different polymer concentration. (A)[poly(DMAPS/Py)]: 0.1 g/dL; (B) [poly(DMAPS/Py)]: 0.01 g/dL. Excitation wavelength: 330nm.

Fluorescent hydrophobes (pyrene group) are incorporated into the sulphobetaine polymer poly(DMAPS/Py), and the photophysical response may effectively indicate the aqueous solution behavior on the microscopic level. As the degree of hydrophobic association increases, interactions between the isolated fluorescent hydrophobes allow the formation of dimeric conformations which subsequently lead to excimer formation. I_E/I_M is the ratio of intensities of the excimer and the monomer fluorescence and it reflects the intra- and inter- chain interactions of pyrene groups. I_E/I_M is a function of polymer concentration in deionized water, and it steadily increases with an increase in the poly(DMAPS/Py) concentration(**Figure 2**). As the polymer concentration increases, the formation of entanglement and population of excited pyrene dimers increases with the intermolecular hydrophobic associations between the hydrophobes (pyrene groups). Hence, an increase in the I_E/I_M occurs. Also, the concentrations of zwitterionic groups increase with increasing poly(DMAPS/Py) concentration. Concurrently, an increase of I_1/I_3 occurs. Moreover, the water-soluble poly(DMAPS/Py) with a low content of pyrene labels showed a positively sloping plot and the steepness of the positive slopes reflects the extent of excited pyrene dimer formation. The excited pyrene dimers were formed in poly(DMAPS/Py) chains due to the hydrophobic self-aggregation of the aromatic units (pyrene labels) in the entangled poly(DMAPS/Py) chains.

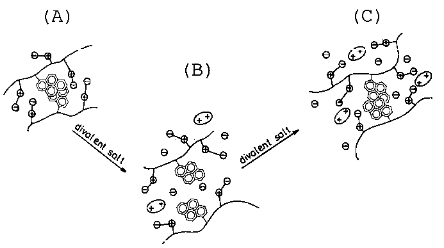


Figure 5. Proposed model of the interaction poly(DMAPS/Py) both in water and in divalent salt solution.

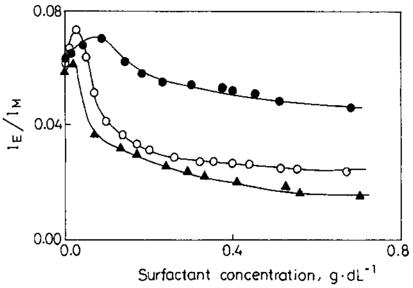


Figure 6. I_E/I_M of poly(DMAPS/Py) in aqueous solution with different surfactant concentration. (●): SDS;(○): CTAB; and (▲): Brij 35. Excitation wavelength: 330nm. [poly(DMAPS/Py)]: 0.01 g/dL.

The I_E/I_M ratio was a function of the KCl concentration in the poly(DMAPS/Py) solution(**Figure 3**), and the I_E/I_M values decrease with an increase in low KCl concentration. This decrease indicates that the positive charges and the negative charges in the poly(DMAPS/Py) are shielded and the polymer chain gets expanded conformation as more KCl salt is added. As this takes place, the distance between the pyrene groups on the same polymer chain also increases, and the formation of excimer becomes more difficult. That is, the expanded polymer chain conformation enhanced as charge-to-charge interactions between the R_4N^+ groups and SO_3^- are effectively shielded in the presence of more KCl salt addition. This fact suggests that the pyrene groups within the pyrene-labeled polysulfobetaine can be separated from one another, in addition to a decrease in the excimer emission relative to monomer emission. The interaction between divalent electrolytes ($MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$) and polybetaine, poly(DMAPS/Py), in aqueous solutions was studied herein. It was revealed that the addition of divalent electrolytes($MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$) to aqueous solutions of pyrene-labeled polysulfobetaine not only shields the zwitterionic groups but also disrupts the entangled conformation. In addition, the distance between the pyrene groups of poly(DMAPS/Py) will be increased, and therefore I_E/I_M values will be decreased (**Figure 4**). Further addition of divalent electrolytes results in the ionic association among divalent cation and sulfonate groups at polymer side chains. This ionic association increases with increasing the divalent electrolyte concentration, and the formation of dimer will be increased with the divalent electrolyte concentration in aqueous polymer solution. I_E/I_M values increase with enhancing the formation of excimer, as illustrated in **Figure 5**. From **Figure 3**, when KCl salt is added, the I_E/I_M ratio decreases with increasing KCl salt concentrations. The addition of KCl can shield the R_4N^+ group and/or SO_3^- group of poly(DMAPS/Py) chains and expand the conformation of poly(DMAPS/Py) in aqueous solution. While more KCl salt was added, the positive charge of R_4N^+ group and the negative charge of SO_3^- group within the polymer conformation were effectively screened out. The I_E/I_M ratio would stay constant at higher salt concentration (**Figure 3**). In case of salts with divalent cations (such as, $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$), the divalent salt can also shield the R_4N^+ group and/or SO_3^- group of poly(DMAPS/Py) chains and expand the conformation of poly(DMAPS/Py) in an aqueous solution [**Figure 5(A)**]. As more divalent salt was added, the divalent cation and anionic SO_3^- groups within the polymer side chains contribute to ionic bridging conformation, and the I_E/I_M ratio increases with the concentrations of divalent salt [**Figures 4 and 5(B)**]. Finally, the I_E/I_M ratio would stay constant at higher salt concentrations [**Figures 4 and 5(C)**]. This behavior is due to ionic bridging conformation limited by the number of SO_3^- groups in the polymer chain [**Figure 5(C)**].

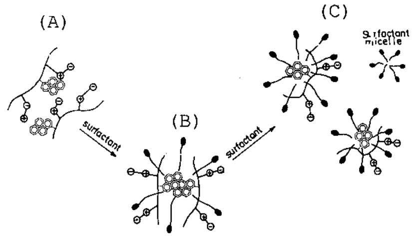


Figure 7. Proposed model of the interaction in the mixed poly(DMAPS/Py) and surfactant solution. (A) in water; (B) in low surfactant concentration; and (C) in high concentrations of surfactant.

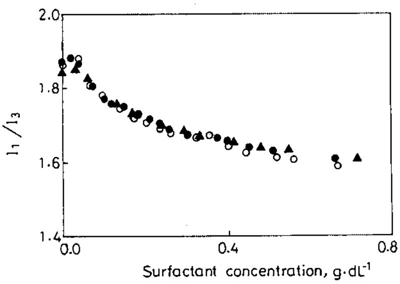


Figure 8. I_1/I_3 of poly(DMAPS/Py) in aqueous solution with different surfactant concentration. (A) (●): SDS; (B) (○): CTAB; and (C) (▲): Brij 35. Excitation wavelength: 330 nm. [poly(DMAPS/Py)]: 0.01 g/dL.

The interactions of cationic CATB, anionic SDS and neutral Brij 35 with water-soluble polymer have been studied in this work, showing that the addition of surfactants to aqueous solutions of polysulfobetaine can either induce or break the interpolymer aggregation. The nature of the association is dictated by surfactant concentration and charge. I_E/I_M increased with the first addition of surfactant **(Figure 6)**. When more surfactant concentrations were added, the I_E/I_M values decreased distinctly with an increased in the surfactant concentration **(Figure 6)**. As the concentration of the surfactant increases in the lower concentrations[**Figure 7(A)**], the interaction between the surfactants and the hydrophobic groups in the hydrophobically modified poly(DMAPS/Py) chains induced mixed micelles of inter- polymers and their surrounding surfactants [**Figure 7(B)**]. Micellar bridging occurs through hydrophobic association between pyrene labels with surfactant, and this micellar bridging enhances the formation of excimer[**Figure 7(B)**]. Therefore, high I_E/I_M were observed [**Figure 7(B)**]. With further addition of surfactant molecules, there was a decrease in the I_E/I_M value with increasing surfactant molecules, which interrupt the zwitterionic associations between ammonium groups and sulfonate groups within the polymer chains and break the inter-polymeric aggregate into intra-polymeric entanglement [**Figure 7(C)**]. That is, the micellar bridging caused by the surfactant was detected at a low surfactant concentration. The various amount of surfactant addition can induce different conformation of poly(DMAPS/Py) in aqueous solution, which is caused by zwitterionic interactions and hydrophobic associations between pyrene labels of polymer chains. The polymeric micelle is formed in water [**Figure 7(A)**] and the mixed micelle is formed in aqueous surfactant solution [**Figures 7(B) and 7(C)**]. While adding large concentrations of surfactant, the mixed micelle of inter- polymers and their surrounding surfactants was disrupted and changed to mixed micelle of intra- polymer and its surrounding surfactants [**Figure 7(C)**]. After a high surfactant concentration was reached, all the mixed micelle of inter- polymers and their surrounding surfactants changed to mixed micelles of intra- polymer and its surrounding surfactants [**Figure 7(C)**]. The I_E/I_M values will stay almost constant in aqueous surfactant solutions, as shown in **Figure 6**. It is well known that changes in I_1/I_3 reflect micelle or other similar aggregate formation. All curves plotted in **Figure 8** show a characteristic shape that I_1/I_3 value was a function of surfactant concentration. After the first addition of surfactants, the ratio is approximately constant and has a value typical for aqueous solutions without hydrophobic aggregations. At critical aggregate concentration (cac), I_1/I_3 starts to decrease because of probe solubilization in the micelle-like aggregates that gradually start to form along the polymer chain (**Figure 8**). Critical aggregate concentration (cac) values were determined as the first break in the curve. Only a limited number of such aggregates can be bound to one chain. Thus, above a certain detergent concentration, a saturation point is reached (>0.4 $g \cdot dL^{-1}$). Afterward, the ratio remains approximately constant at a value between

1.60 and 1.65 indicating constant polarity of the local environment sensed by pyrene. This value is usually found for pyrene media of micelle-like aggregations of surfactant in the presence of a polyelectrolyte. These results further prove the formation of mixed micelles of inter- polymers and their surrounding surfactants and the transformation between mixed micelle of inter- polymers and their surrounding surfactants and mixed micelle of intra-polymer and its surrounding surfactant.

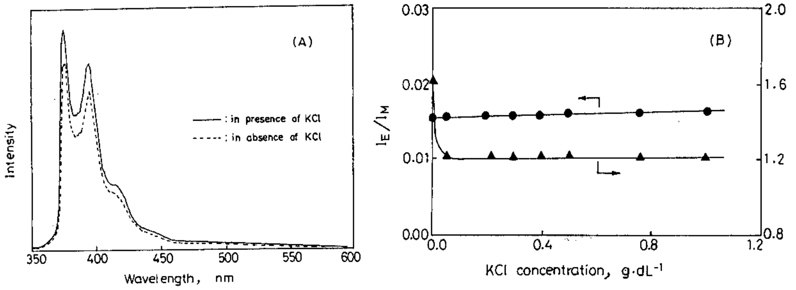


Figure 9. (A) Fluorescence spectra of poly(DMAPS/Py) in aqueous solution of neutral surfactant. (----): in absence of KCl and (—): in prescence of KCl. (B) I_E/I_M and I_1/I_3 of poly(DMAPS/Py) in neutral surfactant aqueous solution with addition of different KCl concentration. Excitation wavelength: 330nm. [poly(DMAPS/Py)]: 0.01 g/dL.

The intensity of excimer emission relative to that of the monomer emission (I_E/I_M) reflects intra- and inter- molecular interactions and microscopic conformation of polymer in solution. The ratio of the first to the third vibronic bands (I_1/I_3) in fluorescence spectra of pyrene depends on the polarity of microenvironment in media with pyrene, the I_1/I_3 ratio being lower in less polar media. The I_1/I_3 ratio of 1.89 for poly(DMAPS/Py) in pure water is higher than those reported for pyrene in aqueous solution [for example, the I_1/I_3 ratio for poly(2-acrylamido-2-methylpropanesulfonic acid / laurylmethacrylamide / 1-pyrenylmethylmethacrylamide) is 1.25].16) This implies that the pyrene residues in polymer are exposed to the aqueous phase, and those residues are confirmed within the interaction of R_4N^+ group and/or SO_3^- group.10,13,14) In H_2O, pyrene-labeled zwitterionic polysulfobetaine [poly(DMAPS/Py)] has extensive inter-molecular and intra-molecular association. The intra-molecular association results from interactions between the ammonium group (R_4N^+) and the sulfonate group (SO_3^-) within the poly(DMAPS/Py) chain.10,13,14) That is, the structure of betaine exhibits a dipole, typically an intra-molecular interaction is characterized by a dipole-dipole interaction along the same chain. Meanwhile, the intra-molecular and inter-molecular association results from interactions between the ammonium group (R_4N^+) and the sulfonate group ($SO3^-$) at the different poly(DMAPS/Py) chains. The association of the ammonium group (R_4N^+) and the sulfonate group (SO_3^-) would neutralize the zwitterionic condition of poly(DMAPS/Py) **[Figure 7(A)]**. As the degree of association increases, interaction between fluorescent hydrophobes (pyrenes) allows the formation of dimeric conformations that subsequently lead to excimer formation. Hence, poly(DMAPS/Py) shows a relatively remarkable excimer emission. When surfactant molecules are added into the poly(DMAPS/Py) aqueous solution, the pyrene labels would be buried in surfactant micelles, exhibiting less polarity of the local environment near pyrene **[Figure 7(B)]**. Particularly, when ionic surfactants (anionic SDS and cationic CTAB) are added to the aqueous poly(DMAPS/Py) solution, the ionic surfactant molecules and their counterions would shield the zwtterionic groups and the pyrene labels would be buried in the hydrophobic portions of the surfactant molecules. Then, the micellar bridging is caused and the mixed micelles of inter-polymer and their surrounding surfactants form in low surfactant concentration, resulting in an increase of I_E/I_M **[Figures 6 and 7(B)]**. When the mixed micelles of inter-polymer and their surrounding surfactants are formed, the I_1/I_3 values start to decrease [**Figures 7(B) and 8**]. As more surfactant is added, the surfactant molecules disrupt micellar bridging and mixed micelles of inter-polymer and their surrounding surfactants. The mixed micelles of inter-polymer and their surrounding surfactants become mixed micelles of intra-polymer and its surrounding surfactants [**Figure 7(C)**]. I_E/I_M ratios further decrease with the high concentrations of surfactant [**Figures 6 and 7(C)**], and the microenvironmental polarity of pyrene labels also decreases.

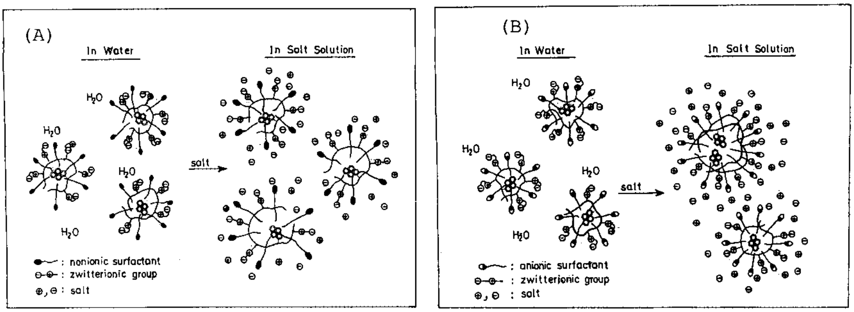


Figure 10. Proposed model of the interaction in the mixed poly(DMAPS/Py) and surfactant solution with KCl addition. (A) mixed poly(DMAPS/Py) and neutral surfactant solution;. (B) mixed poly(DMAPS/Py) and anionic surfactant solution

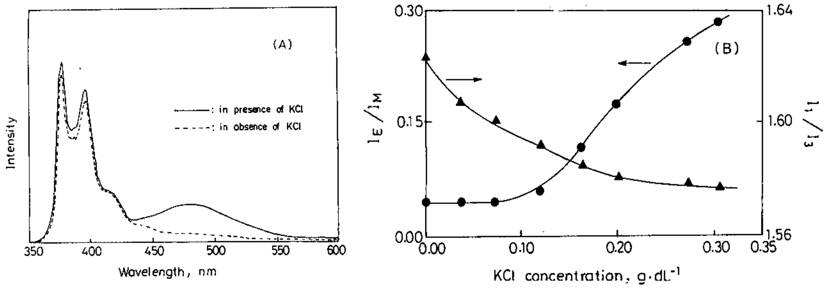


Figure 11. (A) Fluorescence spectra of poly(DMAPS/Py) in aqueous solution of anionic surfactant. (----): in absence of KCl and (—): in prescence of KCl. (B) I_E/I_M and I_1/I_3 of poly(DMAPS/Py) in anionic surfactant aqueous solution with addition of different KCl concentration. Excitation wavelength: 330 nm. [poly(DMAPS/Py)]: 0.01 g/dL.

Furthermore, when KCl salt was added into the mixed poly(DMAPS/Py) and neutral surfactant(Brij 35) solutions, the positive charge and negative charge within poly(DMAPS/Py) chains were shielded. However, the salt addition could not change the conformation of mixed micelle of intra- polymer and its surrounding surfactants. Thus, I_E/I_M and I_1/I_3 values were kept constant as shown in **Figures 9(A), 9(B) and 10(A)**. In mixed solutions of poly(DMAPS/Py) and an anionic surfactant (SDS), I_E/I_M results exhibited a maximum **(Figure 6)**. Micellar bridging was observed in the mixed solutions at low surfactant concentration (ca. 0.1 g·dL^{-1}). Also, as more surfactant was added (>0.1 g·dL^{-1}), the surfactant molecules would form mixed micelles of intra- polymer and its surrounding surfactants **[Figure 7(C)]**. I_E/I_M and I_1/I_3 values stayed constant. In addition, when a small amount of KCl was added to the mixed solution of poly(DMAPS/Py) and SDS, the ionic condition of polymer chain and surfactant was shielded. When a large amount of salt was added, all the ionic conditions of polymer chain and surfactant were shielded and the conformation formed at equilibrium was broken. The shielded mixed micelle of intra-polymer and its surrounding surfactants can join together and form mixed complex micelles of inter-polymers and their surrounding surfactants, and the mixed solution will be cloudy. The I_E/I_M values will increase distinctly and the I_1/I_3 values will decrease with increasing surfactant concentration**[Figures 11(A) and 11(B)]**. Also, when only KCl salt was added into saturated surfactant solution, similar phenomena were observed. The interaction in the mixed poly(DMAPS/Py) and surfactant solution with KCl addition was proposed. In mixed aqueous solution of poly(DMAPS/Py) and anionic surfactant, poly(DMAPS/Py) and surfactant contribute to the mixed micelle of intra- polymer and its surrounding surfactants **[Figure 7(B)]**. There is ionic repulsion among each mixed micelle of intra- polymer and its surrounding surfactants, resulting from interactions between the sulfonate groups (SO_3^-) at the end of anionic surfactant. That is, the conformation of mixed micelle of intra- polymer and its surrounding surfactants exhibits anionic corona**[Figure 10(B)]**. Meanwhile, the mixed micelle of intra- polymer and its surrounding surfactants was stablily present in aqueous solution **[Figure 10(B)]**. The I_E/I_M and I_1/I_3 were observed at constant values**[Figures 6 and 8]**. Furthermore, KCl salt was added into the mixed solution of poly(DMAPS/Py) and anionic surfactant **[Figure 10(B)]**, the ammonium group (R_4N^+) and the sulfonate groups (SO_3^-) within mixed micelle of intra- polymer and its surrounding surfactants could be shielded. As the repulsion of the sulfonate group (SO_3^-) was shielded, the mixed micelle of intra- polymer and its surrounding surfactants was in unstable aqueous solution **[Figure 10(B)]**. The mixed micelle of intra-polymer and its surrounding surfactants aggregated and formed mixed complex micelle of inter-polymers and their surrounding surfactants **[Figure 10(B)]**. The proposed model also illustrates the behaviors of the mixed solution of poly(DMAPS/Py) and anionic surfactant.

Conclusions

This study describes the effect of salt on the aqueous solution property of the poly(DMAPS/Py) in terms of fluorescence. I_E/I_M values decreased with an increase in the salt concentration. When surfactants are added into the poly(DMAPS/Py) aqueous solution, the pyrene labels were buried in surfactant micelles, exhibiting less polarity of the local environment near pyrene. Particularly, when ionic surfactants (anionic SDS and cationic CTAB) were added to the aqueous poly(DMAPS/Py) solution, the ionic surfactant molecules shielded the zwtterionic groups, and the pyrene labels were buried in the hydrophobic portions of the surfactant molecules. Then, the micellar bridging was caused and the inter-polymer micelles formed, resulting in an increase of I_E/I_M. When the mixed micelles of inter-polymers and their surrounding surfactants were formed, the I_1/I_3 values began to decrease. As more surfactant was added, the surfactant molecules disrupted micellar bridging and mixed micelles of inter-polymer and their surrounding surfactants. The mixed micelles of inter- polymers and their surrounding surfactants became mixed micelles of intra- polymer and its surrounding surfactants, and I_E/I_M ratios decreased with the concentrations of surfactant.

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