Evidence of complexation between poly(acrylic acid) and sodium dodecyl sulfate

C. Maltesh and P. Somasundaran

Langmuir Center for Colloids & Interfaces, Columbia University, New York, NY 10027, USA

(Received 18 May 1992; accepted 21 August 1992)

Abstract

Interactions between poly(acrylic acid) (PAA) and sodium dodecyl sulfate (SDS) in aqueous solution were studied using fluorescence spectroscopy. Pyrene labeled PAA was used to study changes in conformation of the polymer on its association with SDS. Externally added pyrene was used to study the aggregation behavior of the surfactant in the absence and presence of PAA. Effects of polymer concentration and pH were determined. It was observed that PAA and SDS interact, under acidic pH conditions, when the PAA concentration is low. Under conditions where the PAA is ionized, there are no interactions between PAA and SDS, but if the polymer concentration is high then an increase in ionic strength due to the dissociation of a large number of carboxylic acid groups results in aggregation of the surfactant, even at concentrations much lower than its critical micelle concentration in the absence of any polymer.

Keywords: Complexation; poly(acrylic acid); sodium dodecyl sulfate.

Introduction

Polymers and surfactants are used together in several industrial and commercial applications. As a result, interactions between water-soluble polymers and charged surfactants have been studied in the literature with the aim of determining the mechanism of interaction as well as to characterize the resultant aggregate formed [1]. Most of the studies have concentrated on non-ionic polymers and anionic surfactants or polyelectrolytes and oppositely charged surfactants. All the work done in this area, so far, is being accumulated to provide an exhaustive reference [2]. The polymers commonly used in consumer products such as detergents are carboxylates and polyethers while the major surfactant component is anionic in nature. Yet there are very few investigations into the interactions between carboxylates such as poly(acrylic acid) (PAA) and anionic surfactants such as sodium dodecyl sulfate (SDS). Binana-Limbele and Zana [3] studied interactions between SDS and sodium poly(acrylate) (NaPAA) using fluorescence and conductivity measurements. They concluded that there was no direct interaction between SDS and NaPAA but the latter acts as a salt, decreasing the critical micelle concentration of SDS through electrostatic effects. Using viscometric measurements Lipooulos et al. [4] concluded that there were no interactions between NaPAA and SDS. But in an earlier study, Eliassaf [5] observed that at low values of pH the reduced viscosity of PAA increased as the SDS concentration was increased. Also it has been observed that the flotation of hematite fines using SDS can be enhanced using small amounts of PAA [6]. In an attempt to elucidate the exact nature of interactions between PAA and SDS a fluorescence spectroscopic investigation was undertaken. Effects of
polymer concentration and pH were also determined.

Materials and methods

Pyrene labeled PAA (PyPAA) was synthesized at the National Chemical Laboratory, Pune, India, according to the method of Turro and Arora [7] and the details of the synthesis are given elsewhere [8]. The molecular weight of PyPAA, as determined by intrinsic viscosity measurements, was 45000. The pyrene content estimated from UV absorption spectra was 1.35 wt.%. In addition, PAA of weight average molecular weight 50000 purchased from Polysciences, Inc., was used as received.

SDS of purity greater than 99% was purchased from ICN Pharmaceuticals and used as received. Pyrene from Aldrich Chemicals was recrystallized from ethanol. Fisher Scientific reagent grade hydrochloric acid and sodium hydroxide were used for pH adjustments. All samples were prepared at an ionic strength of 0.01 M NaCl. Stock solutions of polymer and surfactant were first prepared and subsequently diluted with 0.01 M NaCl to achieve the desired concentrations. All solutions were prepared by weight.

Fluorescence spectra were recorded on a Photon Technology LS-100 spectrophotometer. The excitation wavelength was 335 nm. For polymer conformation studies using PyPAA, the intensities of monomer emission at 376 nm and that of excimer emission around 480 nm were recorded. For micro-polarity measurements, using externally added pyrene, fluorescence intensities at 373 nm (first peak) and 383 nm (third peak) were recorded. The sample cells were of 10 mm path length and a correction was applied to remove lamp flickering artifacts. An excitation slit width of 1 nm and emission slit widths of 0.4 nm were used.

Results and discussion

PAA behaves as a random coil in dilute solutions in the presence of simple electrolytes. The randomly distributed pendant pyrene groups on the polymer chain, at low concentrations, do not affect significantly its dissolution characteristics [9]. Pyrene groups are constantly in motion due to the high mobility of the polymer segments to which they are covalently attached. The distance between the pyrene groups on the polymer chain is determined by its conformation and the mobility of the segments. An excited pyrene group interacts with a ground state pyrene group to form an excimer when they approach each other within 4–5 Å. The formation of an excimer will depend upon the conformation of the polymer and hence, the extent of intramolecular excimer formation (given by the ratio of excimer to monomer intensities or \(I_e/I_m\)) provides a measure of the statistical conformation of the labeled polymer chain. It can therefore be referred to as the coiling index. A large value of the \(I_e/I_m\) ratio suggests polymer chain contraction, whereas a small value of \(I_e/I_m\) suggests polymer expansion and/or segmental rigidity. Excimers can also be formed when pyrene molecules on two different polymer chains interact. This intermolecular excimer will contribute to the overall excimer formation but will not be a true indicator of polymer conformation. To determine the contribution of intermolecular excimers, the \(I_e/I_m\) ratio was determined as a function of the PyPAA concentration. It was observed that there was no change in the value of \(I_e/I_m\) up to a concentration of 100 ppm which means that all excimers formed in the present tests were intramolecular and a true indicator of polymer conformation. In the present study, the concentration of PyPAA never exceeded 18 ppm.

The ratio of the intensities of the third and first peaks \((I_3/I_1)\) of the pyrene emission spectrum is sensitive to the polarity of the medium in which the pyrene resides [10]. The value of this ratio is approximately 0.6 in polar solvents like water but rises to greater than or equal to 1 in non-polar solvents and surfactant micelles. This feature has been exploited for studying surfactant aggregation in solution as well as at the solid–liquid interface [11]. Since this ratio can be used to
characterize the polarity of an unknown medium, it will be referred to here as the polarity parameter. The final value of the $I_3/I_1$ ratio reported is an average of the various environments experienced by the pyrene molecule, i.e. pyrene in water, pyrene in hydrophobic aggregates, etc.

Aggregation of SDS was studied in the absence and presence of PAA using externally added pyrene. The concentration of pyrene was maintained at its maximum solubility limit in water ($\approx 5 \cdot 10^{-7}$ kmol m$^{-3}$). Changes in the polarity parameter of externally added pyrene as a function of SDS concentration are reported in Fig. 1. In the absence of PAA, at low SDS concentrations, the polarity of the medium reported by pyrene is that of water ($I_3/I_1 \approx 0.6$). Above a certain SDS concentration the value of the polarity parameter rises to about 1 and remains constant thereafter. This concentration is the critical micelle concentration (CMC) of SDS in 0.01 M NaCl. In the presence of 18 ppm PAA the aggregation characteristics of SDS are altered slightly as indicated by the increase in the pyrene polarity parameter value at a lower SDS concentration than in the absence of PAA. This suggests that there are interactions between PAA and SDS; but if the PAA acts to lower the CMC of SDS as reported earlier [3] then the response of pyrene would be similar to that observed here. There is no increase in the ionic strength of the solution due to the presence of 18 ppm PAA since 0.01 M NaCl is used as a background electrolyte and it is highly unlikely that PAA at this dilute concentration could lower the CMC of SDS to such an extent. To clarify whether the observed behavior was the result of direct interaction between PAA and SDS or if PAA was acting merely to lower the CMC of SDS, the aggregation behavior of SDS was studied in the presence of 18 000 ppm PAA. At 18 000 ppm PAA, the interactions are different from those detected at 18 ppm PAA. Aggregation of SDS is shifted to higher surfactant concentrations in the presence of larger amounts of the polymer. If PAA was acting to lower the CMC of SDS, the presence of a larger amount of PAA would lower the CMC to a greater extent than smaller amounts. As is seen from Fig. 1, the presence of more PAA does not result in a greater decrease of the CMC and this could suggest that PAA and SDS do interact physically and that PAA does not act merely to lower the CMC of the surfactant.

To interpret this interesting behavior of SDS at high PAA concentrations, the effect of PAA concentration on its interactions with SDS were studied. The results given in Fig. 2 show that the PAA concentration does have a significant role in its interactions with SDS. At the lower SDS concentration, as the PAA concentration is initially increased, interactions between PAA and SDS become stronger until they reach a stable level between 18 and 500 ppm PAA. Above this polymer concentration, there will be fewer surfactant molecules to aggregate on individual polymer chains. At the higher SDS concentration, as more and more PAA is present, the value of the polarity parameter decreases steadily. This could be due to a decrease in the number of surfactant aggregates present on the polymers. This result agrees with that in Fig. 1.

Changes in the coiling index of PyPAA were determined as a function of PAA concentration. To avoid formation of intermolecular excimers, the
concentration of PyPAA was kept constant (18 ppm) and the amount of unlabeled PAA was varied. The results are given in Fig. 3 for the case of PAA alone as well as in the presence of a fixed amount of SDS. In the absence of SDS, the conformation of PAA remains constant until around 10000 ppm. Above 10000 ppm, the coiling index increases sharply. This decrease in coil dimensions could be due to an increase in the ionic strength of the solution due to the high PAA concentration rather than any interaction between the PAA chains. In the presence of a fixed amount of SDS, the coiling index is lower at low polymer concentrations. Binding of the surfactant to the polymer results in an expanded polyacrylic chain. This could be due to the repulsion among the bound surfactant molecules. As the PAA concentration is increased, a change in conformation from the PAA–SDS system to that of PAA alone is detected above 20 ppm and at high concentrations (above 10000 ppm) the conformation of PAA is the same in the absence and presence of SDS. At high polymer concentrations, there may not be enough surfactant molecules to form aggregates on the polymer and hence the behavior detected is that of polymer alone. The conductivity of the solution was unaffected up to a PAA concentration of 10000 ppm and increased sharply only beyond this concentration.

Changes in the polarity parameter of pyrene were determined in the presence of fixed amounts of SDS and PAA as a function of pH. Two polymer concentrations and two surfactant concentrations were chosen and the results are shown in Fig. 4. The SDS concentrations chosen were $4 \times 10^{-4}$ kmol m$^{-3}$ where interactions commence between PAA and SDS as inferred from Fig. 1 and

![Fig. 3. Changes in excimer formation of PyPAA on its interaction with SDS.](image)

![Fig. 4. Effect of pH on interactions between PAA and SDS as detected by changes in pyrene monomer fluorescence. Two concentrations of PAA and SDS were used.](image)
At pH 6.6 in the presence of large and small amounts of PAA. At this pH the PAA is dissociated and there should be no interactions between the PAA and SDS since both will bear similar charges. At a polymer concentration of 18,000 ppm, SDS aggregates at concentrations much lower than that in the absence of PAA (Fig. 5). However, at the lower polymer concentration used there is very little effect of PAA on the aggregation behavior of SDS. This lends support to the proposed mechanism that under conditions when the PAA is ionized there are no interactions between PAA and SDS and the ionic strength of the solution resulting from the dissociation of the carboxylic acid groups is the factor affecting the micellization of the surfactant.

Summary

Interactions between PAA and SDS were studied under a variety of conditions of polymer concentration and pH using fluorescence spectroscopy. These interactions are found to depend significantly on the PAA concentration. It was also

![Fig. 5. Changes in pyrene monomer fluorescence in the presence of PAA and SDS at high values of pH.](image)
observed that there is interaction between the polymer and the surfactant at low PAA concentrations and acidic pH conditions. Under conditions when the PAA is ionized, there are no interactions between the polymer and SDS. When the polymer concentration is high, an increase in the ionic strength of the solution resulting from the dissociation of the –COOH groups alters the micellar properties of SDS. This study provides evidence for possible physical interactions between PAA and SDS and suggests that PAA does not merely act to lower the CMC of SDS akin to simple electrolytes.

Acknowledgments

Financial support from the National Science Foundation, Unilever Research U.S. Inc., and the NALCO Chemical Company are gratefully acknowledged.

References

7 N.J. Turro and K.S. Arora, Polymer, 27 (1986) 783.