

Calorimetric studies of the interaction between sodium alginate and sodium dodecyl sulfate in dilute solutions at different pH values

Jisheng Yang,^{a,b,*} Jianyu Zhao^a and Yun Fang^{b,*}

^a*School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China*

^b*School of Chemical and Material Engineering, Southern Yangtze University, Wuxi 214122, China*

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Abstract—Interactions between the polyelectrolyte sodium alginate (NaAlg) and the anionic surfactant sodium dodecyl sulfate (SDS) have been investigated by microcalorimetric techniques. The polymer–surfactant interactions were observed between NaAlg and SDS at different pH values in dilute solution. The thermodynamic parameters for their interaction process are evaluated from the results of the observed dilution enthalpy curves. As the pH value of the solution decreases from 7 to 6, NaAlg polymers have an obvious effect on the cmc of SDS as a simple salt, which indicates no association between SDS and NaAlg owing to electrostatic repulsion. With the progressive decrease of pH value from 5 to 3, the hydrophobic segments in the alginate chains are increasing and the hydrophilic segments decreasing, and the aggregation between SDS and alginate due to hydrophobic interactions is observed.

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1. Introduction

In the last two decades much interest has been focused on interactions between polyelectrolytes and surfactants because of their widespread application in a variety of fields.¹ Polyelectrolyte–surfactant systems often have physicochemical characteristics that differ from nonionic polymer–surfactant systems.^{2–6} Considerable studies have dealt with interactions between polyelectrolytes and oppositely charged surfactants.^{7–9} The strong association between polyelectrolytes and oppositely charged surfactants is driven by electrostatic attraction and hydrophobic interactions. Polyelectrolytes interact with oppositely charged surfactant micelles so strongly that in many cases irreversible macroscopic phase separation occurs.¹⁰ At the same time, much effort has been expended to explore the interactions between polyelectrolytes and like-charged surfactants.^{11–15} In the reported studies, much interest has been focused on

the interactions between hydrophobically modified polyelectrolytes and surfactants.^{10,12,16–19} The mechanism and strength of the interactions depend on the characteristics of the surfactants and polyelectrolytes, that is, the structure of the surfactant's hydrophobic part, as well as the charge density, degree of substitution, chain conformation, hydrophobicity, and molecular weight of the polyelectrolyte chains.

Alginate is both a biopolymer and a polyelectrolyte that are considered to be biocompatible, non-toxic, non-immunogenic and biodegradable. It can be characterized as an anionic copolymer comprised of mannuronic acid (M block) and guluronic acid (G block) units arranged in an irregular blockwise pattern of varying proportions of GG, MG, and MM blocks.²⁰ The mannuronic acid forms β -(1→4) linkages, so that M-block segments show linear and flexible conformation; the guluronic acid, differently, gives rise to α -(1→4) linkages, which serves to introduce a steric hindrance around the carboxyl groups. For this reason the G-block segments provide folded and rigid structural conformations that are responsible for a pronounced

* Corresponding authors. Tel.: +86 514 87975568 (J.Y.); e-mail addresses: jsyang@yzu.edu.cn; yunfang@126.com

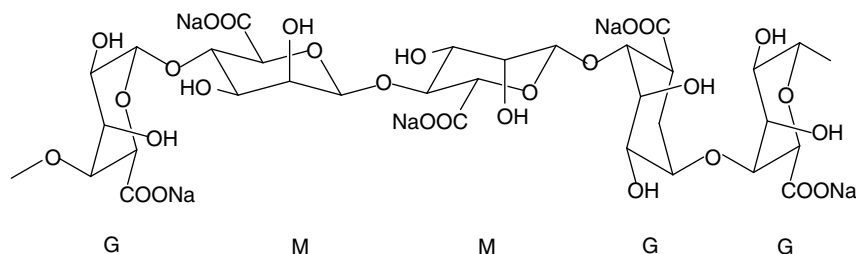


Figure 1. Molecular structure of sodium alginate.

stiffness of the molecular chains. In Figure 1 the M and G blocks of the alginic acid salts with their representative sequence are reported.

The microstructural features of sodium alginate are biocompatible unbranched binary copolymers that have been widely used as a type of desired biomaterials in many fields such as cell immobilization,²¹ tissue engineering,²² drug delivery,²³ controlled release,²⁴ immobilization of micro-organisms,²⁵ as well as in food applications.²⁶ The mixtures of alginate and surfactants often have special physicochemical properties, which lead to their widespread applications in a variety of industrial fields. Therefore, the study of the interaction between polymers and surfactants in aqueous solutions is of fundamental importance, as well as of significance for practical applications.

By using rheology, turbidity, and small-angle neutron scattering (SANS) measurements, Bu et al.²⁷ showed the interaction of alginate and hydrophobically modified (HM)-alginate solutions with different surfactants. The turbidity and SANS results indicated that the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) and Gemini induce the formation of large inhomogeneous structures in the alginate solutions, whereas their effects on the structure of HM-alginate were less marked. The addition of the nonionic surfactant Brij 35 led to altered solvent conditions for both alginate and HM-alginate solutions. Compared to the changes induced by the cationic and the nonionic surfactants, the effect of SDS on the structure of the solutions were less marked. Rheological measurements generally showed small viscosity changes upon addition of the surfactants to unmodified alginate. The HM-alginate system showed a different behavior, with a marked viscosity enhancement upon addition of ionic surfactants. Ren et al.²⁸ have demonstrated the effects of chemical composition and sequence of alginate on aggregation with positively charged surfactants. The interaction and aggregation were investigated using fluorescence emission of pyrene probes and dynamic light scattering to reveal effects of the polyelectrolyte composition and surfactant structure.

In addition to the above measurements, calorimetry is one of the most sensitive techniques used in the investigation of the enthalpy change of the interaction between

molecules in solution. Such data can provide detailed information about the binding process of surfactants in the absence and presence of a polymer.²⁹ In this work we desire to study on the interactions between a natural polymer sodium alginate (NaAlg) and an anionic surfactant sodium dodecyl sulfate (SDS) by microcalorimetric techniques. Alginates have $-\text{COO}^-$ and $-\text{COOH}$ groups along the chain conferring different charge densities depending on the pH. The hydrophilic and hydrophobic units along a molecule chain can be altered by the protonation and deprotonation of carboxyl groups in the backbone chain. As such, the alginate is a polyelectrolyte, depending on the pH. Owing to hydrophobic interaction at lower pH, the aggregation between NaAlg and SDS can be demonstrated. The aim of this work is to provide increased insights into the microscopic interactions between NaAlg and SDS at different pH values in dilute solution. The thermodynamic parameters for the interaction process are evaluated from the results of the observed dilution enthalpy curves.

2. Experimental

2.1. Materials

NaAlg, purchased from Sinopharm Chemical Reagent Co., Ltd, was refined twice by dissolving it in distilled water, filtering, precipitation with ethanol, and finally drying the material in vacuum at 60 °C. The viscous-average molecular weight of sodium alginate used was 430 kDa, determined by viscometric methods.³⁰ The alginate was analyzed by ^1H NMR spectroscopy at 70 °C using a Bruker AVANCE 600 (600 MHz) spectrometer.^{31,32} The molar fraction of guluronic acid residues (F_G) was determined by NMR spectroscopy to be $F_G = 0.85$, $F_M = 0.15$. Analytical grade hydrochloric acid, sodium hydroxide, and sodium phosphate were obtained from Sinopharm Chemical Reagent Co., Ltd. Anionic surfactant sodium dodecyl sulfate, of >99% purity, was obtained from Aldrich Chemical Co. These materials were used as received without further purification. Doubly distilled water was used for the preparation of all solutions.

2.2. Solution preparation

A stock buffer solution was prepared by dispersing 5 mM phosphate buffer in doubly distilled water. A biopolymer solution was prepared by dissolving 1.0 wt % NaAlg in the stock buffer solution, stirring for at least 4 h to ensure complete dispersion, and then storing overnight at room temperature. By mixing biopolymer solutions with the stock buffer solutions, adjusting to the desired pH (3–7) using HCl or NaOH, dilute NaAlg solutions were obtained. A stock of 0.1 M SDS was prepared in 5 mM phosphate stock buffer solution. The pH of each of the solutions was adjusted to the appropriate value prior to mixing. It should be noted that there would be a slight difference in the ionic strength of solutions at different pH values due to the different amounts of acid or base they contained.

2.3. Isothermal titration calorimetry (ITC)

An isothermal titration calorimeter (VP-ITC, Microcal Inc., Northampton, MA) was used to measure the enthalpy changes resulting from SDS–NaAlg interactions. Aliquots of 5 μ L of concentrated SDS were injected sequentially into a 1.438-mL titration cell initially containing either 5 mM phosphate buffer solution or 0.1 wt % NaAlg in 5 mM phosphate buffer. Doubly distilled water was added to the reference cell. The temperature of the solution in the titration cell was 25.0 ± 0.1 °C. The syringe is tailor-made such that the tip acts as a blade-type stirrer to ensure continuous mixing efficiency at 307 rpm. Using interactive software, an injection schedule was automatically carried out after setting up the number of injections, the volume of each injection, and the time between each injection. The duration of each injection was 10 s, and the time delay (to allow equilibration) between successive injections was 240 s. Raw data were obtained as a plot of heating rate (μ cal/s) against time (min). These raw data were then integrated to obtain a plot of observed enthalpy change per mole of injected SDS (ΔH_{obs} , kJ/mol) against SDS concentration (mM). All experiments were repeated twice, and the reproducibility was within $\pm 3\%$.

3. Results and discussion

Figure 2 shows the calorimetric titration curves for isothermal titration of 0.1 M micellar SDS into phosphate buffer solution and 0.1 wt % NaAlg phosphate buffer solutions (pH 7 and pH 3), respectively. These calorimetric titration curves contain a raw heat signal, that is, expressed as the electrical power, cell feedback (CFB), required to maintain a constant temperature difference between the sample and reference cells.

From Figure 2a, the CFB for titration of 0.1 M SDS in the absence of NaAlg polymer exhibits an increasing endothermic signal until a maximum at the eighth injection, and thereafter, the positive signal decreases. In the presence of NaAlg polymer (pH 7), the initial portion of the calorimetric titration curves (see Fig. 2b) follows that of Figure 2a. At around the fourth injection, the CFB curve reaches a maximum, which then decreases drastically through to the ninth injection, and thereafter, the CFB decreases slightly. From Figure 2c, in the presence of NaAlg polymer (pH 3), the CFB curve exhibits a smaller maximum at around the third injection. The positive signal changes negative signal at around the seventh injection.

Integration of the CFB signal with respect to time at the i th injection normalized to the concentration of SDS injected yielded the observed enthalpy change (ΔH_{obs}) between the $(i - 1)^{\text{th}}$ and i^{th} injections. Figures 3a and 4a show the differential enthalpic curves for titration of 0.1 M SDS into NaAlg with varying pH values, where the ΔH_{obs} for each injection is plotted against the concentration of SDS. The titration curve of 0.1 M SDS in buffer solution (pH 3–7), which remains almost unchanged, is included in both figures. As expected, the titration process for SDS is endothermic, and the maximum of the calorimetric curve corresponds to the critical micelle concentration (cmc). Since the SDS concentration in the injectant solution is well above the cmc at the initial stage (below cmc) of the titration process, the SDS micelles de-micellize into monomers after they are titrated into the sample solution, which is accompanied by an endothermic heat effect. Thereafter, the monomer solution has been further diluted. Above cmc, the added micelles are only diluted.³³ The enthalpic curve (see Fig. 3a) representing the SDS–NaAlg system exhibits the same values, at lower SDS concentrations, as that of pure SDS, and the maximum of these curves are located at the same position.

The difference between the titration curve of SDS and the differential enthalpic curves with NaAlg polymers (see Fig. 4a) is ascribed to SDS–NaAlg association. The curves of NaAlg polymers follow the de-micellization portion of the dilution curve where no polymer–surfactant association is observed. These curves then begin to deviate from the titration curve of SDS at a critical concentration that corresponds to the onset for binding of SDS onto NaAlg, which is commonly referred to as the critical aggregation concentration (cac). The ΔH_{obs} becomes less endothermic due to progressive binding of SDS monomers onto NaAlg. This reduction in ΔH_{obs} continues until a second critical concentration after the cmc, denoted as C_m . This is the concentration where free micelles start to form. The critical concentrations, such as cmc, cac, and C_m , described above can be clearly identified from the plots

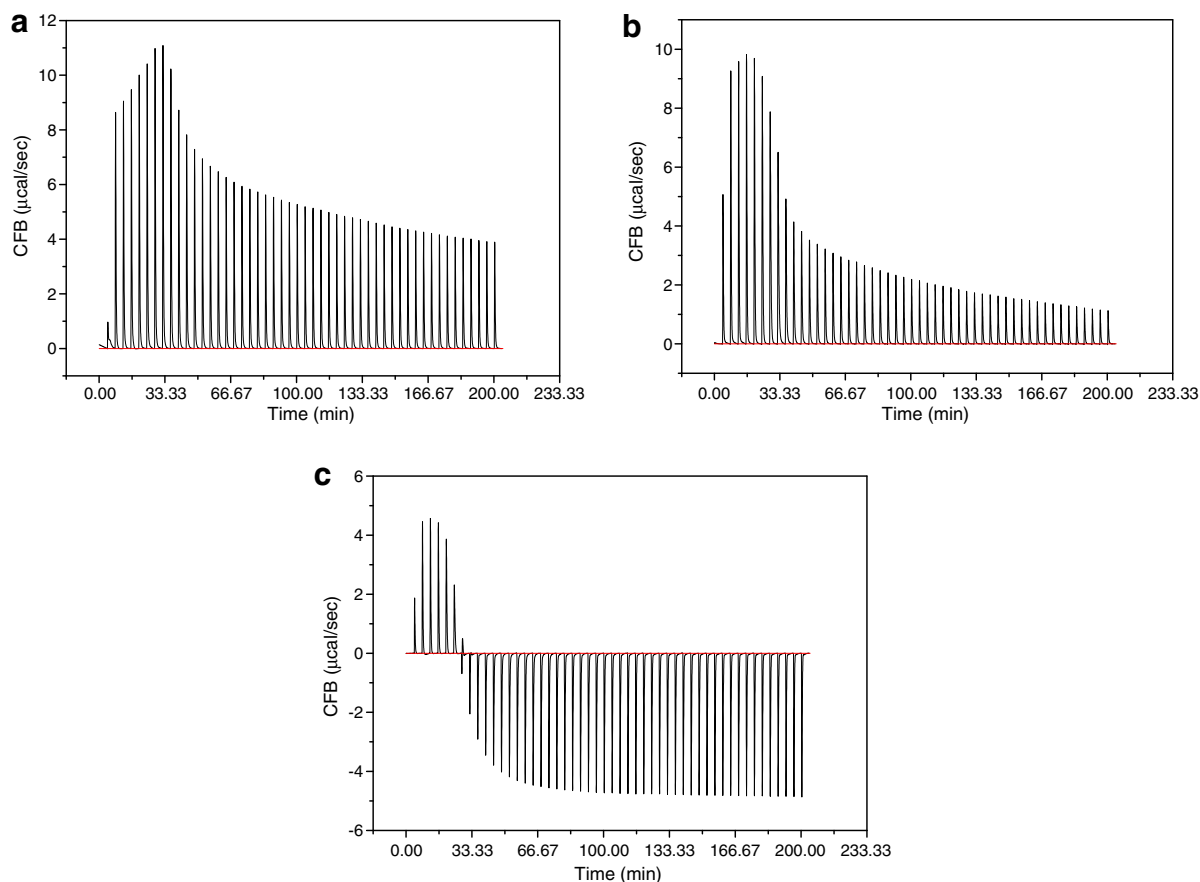


Figure 2. Thermograms showing cell feedback (CFB) versus time for calorimetric titration of 100 mM SDS into (a) 5 mM phosphate buffer solution and (b) 0.1 wt % NaAlg solution (pH 7) and (c) 0.1 wt % NaAlg solution (pH 3) at 25 °C.

of the difference curves of titration of SDS into buffer solution and NaAlg polymers as shown in Figures 3b and 4b.

The difference curve contains the incremental enthalpy changes ($\Delta H_{\text{obs}[i]} - \Delta H_{\text{obs}[i-1]}$) plotted against the change in surfactant concentration (ΔC_{SDS}), where i refers to the i^{th} injection. The cac is defined by Wang and Olofsson³³ as the onset point where the differential enthalpic curve for their polymer deviates from the dilution curve. This is identified as the first peak in the difference curve. In the presence of NaAlg polymer (pH 3–5) the deviation of the curve shifts to a less endothermic enthalpy change, and the cac corresponds to the first peak (see Fig. 4a). This is identified by the point where the slope of the difference curve is equal to zero. The values of cmc and cac for the titration of SDS into buffer solution and NaAlg polymers are tabulated in Tables 1 and 2.

Bu et al.¹³ have investigated interactions between alginate (unmodified and hydrophobically modified) and surfactants of different types (including also SDS) by microcalorimetry, rheology and turbidimetry. Significant polymer–surfactant interactions were observed between hydrophobically modified alginate and SDS,

whereas for mixtures of unmodified alginate and SDS, only a weak synergism was detected. By using fluorescence measurement, Neumann and co-workers⁹ showed that the interaction of polyelectrolyte alginate and surfactant of the same charge (SDS) seems to present only very weak interactions. However, electrolytes have a significant effect on the cmc of the ionic surfactant.³⁵ An increase in the concentration of electrolytes leads to a reduction in cmc. Polyelectrolytes were reported³⁶ to have the same type of effect on the cmc of the ionic surfactant as simple salts, only that the effect is weaker than that of a simple salts. NaAlg is an anionic polyelectrolyte, and the increased concentration of counterions in the SDS–NaAlg solution induces a lower cmc of SDS. Since both the polymer and the surfactant are negatively charged, no association between SDS and alginate is expected,³⁵ but screening of the electrostatic interactions of the polymer may occur at higher SDS concentrations. Just as Table 1 shows the values of cmc for the titration of SDS into water, buffer solution, and NaAlg solution are 8.1 mM, 4.4 mM, and 3.8 mM, respectively.

With the progressive decrease of pH, the number of dissociated carboxylic groups in alginate chains decreases, which makes alginate lose its hydrophilicity

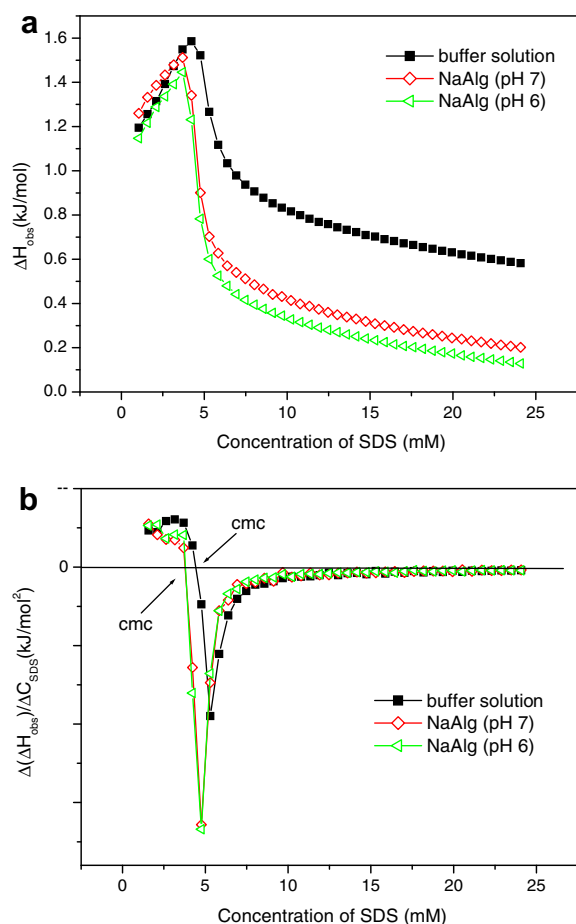


Figure 3. (a) Differential enthalpic curves for titration of 100 mM SDS into buffer solution or 0.1 wt % NaAlg polymers with varying pH values: 7 and 6 plotted against concentration of SDS at 25 °C. (b) Difference curves of the differential enthalpic curves in (a) indicating the positions of cmc.

to some extent. When some dissociated carboxylic groups in alginate chains are gradually protonated, the hydrophobic segments appear in alginate chains. Cao et al.³⁷ showed that the alginate molecules can form hydrophilic–hydrophobic aggregates in aqueous solution depending on the pH of the medium. They postulated this pH dependence of ‘aggregation’ as a signature for self-assembly caused by the partial protonation of dissociated carboxyl groups in the alginate main chain. Here, in Figure 4, as the pH value decreases from 5 to 3, the hydrophobic segments in the alginate chains increase, and the hydrophilic segments decrease. The position of the endothermic peak shifts to lower concentration as shown in Figure 4a. The cac obtained from its difference curves depicted in Figure 4b decreases from 3.7 mM to 2.7 mM. The depression of cac is mainly due to enhanced hydrophobic interactions between the NaAlg polymer hydrophobes and the hydrophobic portion of the SDS molecules.

The peak height of the endothermic enthalpic curves is known to be related to polymer hydrophobicity.^{15,29,33}

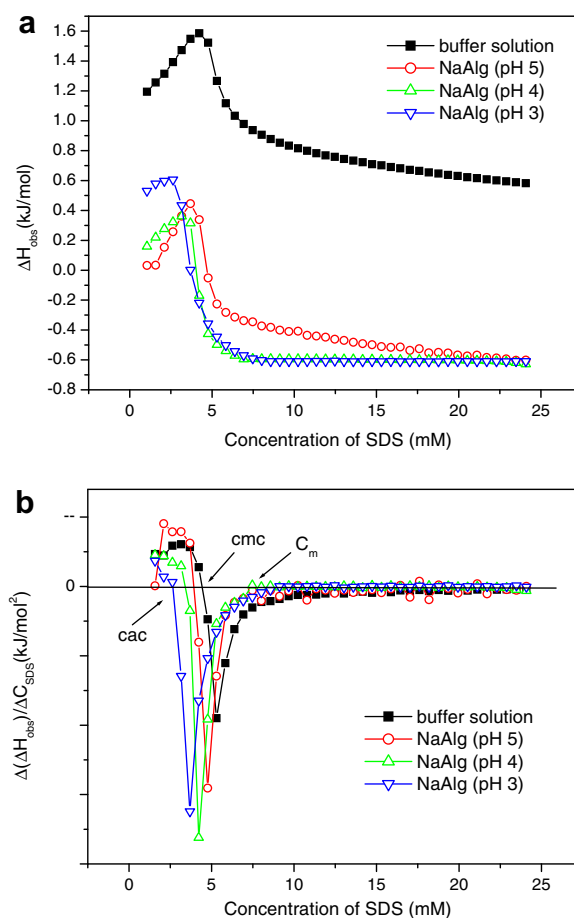


Figure 4. (a) Differential enthalpic curves for titration of 100 mM SDS into buffer solution or 0.1 wt % NaAlg polymers with varying pH values: 5, 4, and 3 plotted against concentration of SDS at 25 °C. (b) Difference curves of the differential enthalpic curves in (a) indicating the positions of cmc, cac, and C_m .

By varying the degree of protonation of carboxylate groups in sodium alginate chains, one is able to control the nature of the hydrophobic junctions by changing, not only the hydrophobicity, but also the accessibility of the hydrophobes in the NaAlg polymer.³⁸ From Figure 4a and Table 2, as the pH value decreases from 5 to 4, the peaks of the endothermic curves and the enthalpy change of SDS aggregation (ΔH_{agg}) in the presence of NaAlg polymers are close to each other under these conditions, which means that the hydrophobicity of NaAlg polymers is close to each other, too. However, when the pH value is about 3, the value of ΔH_{agg} rises obviously. This is because the pK_a values of G and M have been determined to be 3.65 and 3.38,³⁷ respectively, which suggests a high degree of protonation of the carboxylic acid for the alginate sample at pH 3.

Using the thermodynamic equations derived from the charged phase separation and mass-action models, the Gibbs free energy change of micellization (ΔG_{mic}) in the absence or presence of NaAlg polymer (pH 7, 6)

Table 1. Critical micelle concentration and thermodynamic parameters for micellization of SDS in 5 mM phosphate buffer solution and 0.1 wt % NaAlg solution (pH 7, 6) at 25 °C

| Solution | cmc (mM) | ΔG_{mic} (kJ/mol) | ΔH_{mic} (kJ/mol) | $T\Delta S_{\text{mic}}$ (kJ/mol) |
|-----------------------|------------------|----------------------------------|----------------------------------|-----------------------------------|
| 5 mM phosphate | 4.4 | −24.9 | −1.58 | 23.3 |
| 0.1 wt % NaAlg (pH 7) | 3.8 | −25.6 | −1.51 | 24.1 |
| 0.1 wt % NaAlg (pH 6) | 3.8 | −25.6 | −1.44 | 24.2 |
| Water | 8.1 ^a | | | |

^a Values obtained from literature.³⁴**Table 2.** Critical aggregation concentration and thermodynamic parameters for aggregation of SDS in the presence of 0.1 wt % NaAlg solution (pH 5, 4, 3) at 25 °C

| Solution | cac (mM) | ΔG_{agg} (kJ/mol) | ΔH_{agg} (kJ/mol) | $T\Delta S_{\text{agg}}$ (kJ/mol) | ΔG_{ps} (kJ/mol) |
|-----------------------|----------|----------------------------------|----------------------------------|-----------------------------------|---------------------------------|
| 0.1 wt % NaAlg (pH 5) | 3.7 | −25.7 | −0.45 | 25.2 | −0.1 |
| 0.1 wt % NaAlg (pH 4) | 3.4 | −26.1 | −0.36 | 25.7 | −0.5 |
| 0.1 wt % NaAlg (pH 3) | 2.7 | −27.1 | −0.61 | 26.5 | −1.5 |

and Gibbs free energy change of aggregation (ΔG_{agg}) in the presence of NaAlg polymers (pH 5, 4, 3) are determined from the following equations:²⁹

$$\Delta G_{\text{mic}} = (1 + K) \text{rt} \ln [\text{cmc}] \quad (1)$$

$$\Delta G_{\text{agg}} = (1 + K) \text{rt} \ln [\text{cac}] \quad (2)$$

A factor of $(1 + K)$ is needed to calculate the free energy of micellization and aggregation of ionic SDS, where K is the micellar charge fraction with a value of 0.85.³⁹ The enthalpy change and free energy change are then used to calculate the entropy change of micellization (ΔS_{mic}) and the entropy change of aggregation in the presence of polymer (ΔS_{agg}). All these parameters are summarized in Tables 1 and 2. The values of enthalpy change obtained calorimetrically are very much smaller than the term $T\Delta S$. The results suggest that both of the aggregation processes for SDS in the absence and presence of NaAlg polymers are entropy driven. The micellization behavior of surfactant and formation of polymer–surfactant mixed micellar junctions are analogous to each other; therefore, the dominant driving force behind these processes is similarly governed by a positive entropy gain. In the presence of NaAlg polymers with pH values of 5, 4 and 3, respectively, ΔS_{agg} of SDS is more positive than ΔS_{mic} , signifying that the entropic contributions to the NaAlg–SDS interaction tend toward a more disordered environment.

According to the literature,³⁴ the free energy to drive 1 mol of surfactant-free micelle into polymer-bound micelle could be derived from the relationship

$$\Delta G_{\text{ps}} = \Delta G_{\text{agg}} - \Delta G_{\text{mic}} \quad (3)$$

This value can be used to define the binding strength of a surfactant onto a polymer. The result shows that ΔG_{ps} is dependent on the pH value of solution (see Table 2). The more negative ΔG_{ps} at −1.5 kJ/mol for pH 3 clearly indicates that the interaction between SDS and

NaAlg at pH 3 is much stronger compared to that at pH 4 or 5. Avaltroni et al.⁴⁰ investigated the influence of the pH on the conformation of alginic acid and the formation of aggregates. In the pH range of 8–4, a slight decrease in the gyration radius (R_g) and the molecular persistence lengths (L_p) was observed as the pH approached the pK_a of the molecule. Protonation of the alginic acid is expected to decrease the intramolecular electrostatic repulsion, resulting in a small reduction in molecular rigidity and size that is reflected by the decrease in L_p and R_g . As the molecule is protonated further below pH 4, the increase in size is interpreted as a limited aggregation (40% increase in average size) due to the reduction in intermolecular repulsion (greatly overwhelming any size decrease due to the reduction in intramolecular repulsion). As our experiments demonstrate, in this zone, the junctions in the NaAlg–SDS cluster require a lower concentration to initiate surfactant binding and are stronger than those above pH 4.

4. Conclusion

The results show that the interacting behaviors between SDS and NaAlg polymers are dependent on the pH of the solution. When the pH of the solution decreases from 7 to 6, NaAlg polymers have the same type of effect on the cmc of SDS as a simple salt. In this process, no association between SDS and alginate is expected, owing to electrostatic repulsion. However, as the pH value of solution further decreases from 5 to 3, the aggregation between SDS and alginate is shown owing to hydrophobic interactions. At pH 3, the junctions in the NaAlg–SDS cluster require a lower concentration to initiate surfactant binding and are stronger than at pH 4 or 5 as revealed by the reduction in cac and ΔG_{ps} . The cluster of NaAlg–SDS also shows higher ΔS_{agg} at pH 3 than at pH 4 or 5.

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