Interactions between Ionic Surfactants and Polysaccharides in Aqueous Solutions

Hongqian Bao,[†] Lin Li,*[,†] Leong Huat Gan,[‡] and Hongbin Zhang[§]

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Natural Sciences and Science Education, National Institute of Education, Nanyang Technological University, 1 Nanyang Walk, Singapore 637616, and Department of Polymer Science and Engineering, School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

Received August 29, 2008; Revised Manuscript Received October 8, 2008

ABSTRACT: Methylcellulose (MC), chitosan (CS), and κ-carrageenan (KC) are chosen as typical representatives of neutral and positively, and negatively charged polysaccharides, respectively. Sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) are chosen as anionic and cationic surfactants, respectively. From these polymers and surfactants, six combinations of polymer−surfactant are made: MC−SDS, MC−CTAB, CS−SDS, CS−CTAB, KC−SDS, and KC−CTAB. The polymer−surfactant interactions for the six pairs are systematically investigated by isothermal titration calorimetry (ITC). It was observed that MC−SDS exhibited strong hydrophobic interaction, as evidenced by the endothermic peak, followed by a weak ion−dipole interaction. KC−SDS did not show any ionic interaction, as expected, but exhibited weaker hydrophobic interaction than MC−SDS. Strong ionic interaction was found for CS−SDS, followed by hydrophobic interaction between some hydrophobic moieties of CS and SDS tails. Titration of CTAB with MC resulted in a pattern of polymer−surfactant interaction similar to that for the titration of CTAB with CS. KC showed strong interaction with CTAB by largely reducing the high endothermic enthalpy changes caused by the demicellization of CTAB. A general rule that determines the order (or priority) for a surfactant to bind to a polymer has been proposed based on our experimental results and discussion.

Introduction

Water-soluble polymer and ionic surfactant interactions are commercially important in a number of industrial applications (pharmaceutical formulations, food additives, cosmetic products, environment-friendly paints etc.). Considerable books and articles dealing with different aspects of their interactions and characteristic methods have been published.[1−6] The interactions between surfactants and polymers can be generally described by two critical concentrations. The first concentration, critical aggregation concentration (cac), corresponds to the surfactant concentration at which surfactant molecules start to bind to polymer molecules. So, cac represents the onset for the formation of polymer−surfactant aggregation complex. The second critical concentration, C_2, is commonly used to represent the surfactant concentration when the polymer becomes saturated with bound surfactant molecules. In addition, C_m is another critical concentration that represents the formation of free surfactant micelles in the polymer solution. For some systems free surfactant micelles start to form after the saturation concentration, and C_m is equal to C_2 under this condition. But for some other systems C_m is less than C_2, there is a competition between the formation of free surfactant micelles and polymer−surfactant aggregation complexes. The determinations of cac, C_m, and C_2 have been studied by Bloor and co-workers[7−9] by using both surfactant ion-selective electrodes and microcalorimetry.

The interactions between some uncharged polymers, such as poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(*N*-vinylpyrrolidone) (PVP), ethyl(hydroxyethyl) cellulose (EHEC), and triblock compolymers, and ionic surfactants in dilute aqueous solution have been extensively studied by isothermal titration calorimetry (ITC) in the literature.[10−14] Wang and Olofsson[11] derived cac and C_2 from the calorimetric titration curves, and they found that anionic surfactant sodium dodecyl sulfate (SDS) aggregated strongly with polymers of low hydrophobicity (PEO, for instance) while some cationic surfactants [alkyltrimethylammonium bromide (RTABr)] were different. Dai et al.[12] observed the order of binding in the triblock copolymer (PPO−PEO−PPO) and SDS system according to the hydrophobic degree of different segments.

Methylcellulose (MC) is a hydrophobically modified nonionic water-soluble polysaccharide, which has been widely used in the food and pharmaceutical industries. A MC aqueous solution is able to gel upon heating, due to the hydrophobic association of MC chains.[15] Li and co-workers[16,17] recently reported the surfactant's effects on the gelation of MC using micro-differential scanning calorimetry (DSC). When above the critical micelle concentration (cmc), both CTAB and SDS show a salt-in effect on MC, which shifts the sol−gel transition of MC to higher temperature. However, the effects of SDS and CTAB on MC are different. SDS has a weaker salt-in effect on MC than CTAB does, because the cmc of SDS is about 9 times that of CTAB at room temperature. Application of ITC to the study of interactions between MC and surfactants has not been found in the literature.

In the last two decades, interactions between polyelectrolytes (especially biomacromolecules such as polysaccharides) and oppositely charged surfactants have attracted a great deal of interest due to their applications in the biological industry.[18−20] Chitosan (CS) is a cationic polysaccharide. Many applications of CS deal with the interactions of CS with anionic molecules such as anionic phosphates, lipids, or proteins.[21−23] The influences of pH, salt, and temperature on interactions between CS and SDS have been studied by Thongngam and Mc-

* Corresponding author: tel (+65) 6790-6285; fax (+65) 6791-1859; e-mail mlli@ntu.edu.sg.
[†] School of Mechanical and Aerospace Engineering, Nanyang Technological University.
[‡] Natural Sciences and Science Education, National Institute of Education, Nanyang Technological University.
[§] Shanghai Jiao Tong University.

10.1021/ma801957v CCC: $40.75
Published on Web 11/06/2008

Clements[24,25] using ITC. The strong electrostatic binding between CS and SDS was observed at pH = 3.0, at which CS was fully protonated. The amount of SDS bound to CS at saturation was weakly affected by the presence of NaCl and temperature variation.[25] Carrageenans (CARs) are a family of water-soluble and linear sulfated polysaccharides extracted from red seaweeds. In the family of carrageenan, there are three main members: κ, ι, and λ. As the first member, κ-carrageenan (KC) has one sulfate group within every disaccharide repeating unit ideally. Filipović-Vinceković et al.[20,26] have investigated the interactions between dodecylammonium chloride (DDAC) and CARs by surface tension, conductometry, light microscopy, light scattering, etc. They found that the effect of the CAR concentration on the cac and cmc of surfactant was very weak. The increase in the charge density of CAR (from κ to ι and λ CARs, which have more sulfate groups per disaccharide unit) increased cac and the cac/cmc ratio and shifted the precipitation toward higher concentration.[26] However, ITC studies on interactions between cationic surfactants and CARs have not been found in the literature.

Isothermal titration calorimetry (ITC) is a powerful tool for studying thermodynamic interactions between a polymer and a surfactant in an aqueous solution. In this work, methylcellulose (MC), chitosan (CS), and κ-carrageenan (KC) are chosen as the representatives of nonionic, cationic, and anionic polysaccharides respectively. Their interactions with sodium dodecyl sulfate (SDS) and with cetyltrimethylammonium bromide (CTAB) (serving as anionic and cationic surfactants, respectively) are systematically studied by ITC. Except for the ITC studies on interactions between CS and SDS, which can be found in the literature,[24,25] this is the first report in which the polymer−surfactant pairs MC−SDS, MC−CTAB, CS−CTAB, KC−SDS, and KC−CTAB are studied by means of ITC. A comprehensive understanding of the characteristic molecular interactions within these six polymer−surfactant systems will be given.

Experimental Section

Materials. A cellulose derivative, methylcellulose (MC, trade name SM4000), was kindly provided by Shinetsu Chemical Co. Ltd., Japan. The polymer had an average degree of substitution (DS) of 1.8 and a weight-average molecular weight of 310 000 as determined by light scattering. The material was used as received without further purification. Medium molecular weight (MMW) chitosan (CS) with a nominal degree of deacetylation, 75∼85%, was purchased from Sigma−Aldrich and purified according to the method reported by Gan et al.[27] κ-Carrageenan (KC) was also obtained from Sigma and directly dissolved in hot water (about 50 °C) to prepare stock solutions (0.25 wt %). Sodium dodecyl sulfate (SDS) was obtained from BDH Laboratory Supplies and cetyltrimethylammonium bromide (CTAB) was supplied from Sigma, both of which were used as received. Other reagents, such as acetic acid and sodium hydroxide, are of analytical grade, and deionized water (Milli-Q filter unit, Millipore, resistivity is 18.2 $\mu\Omega\cdot$cm) was used throughout the experimental process.

Isothermal Titration Calorimetric Experiments. The isothermal microcalorimetric experiments were carried out on an isothermal titration calorimeter (ITC) (Microcal). The microcalorimeter consists of a reference cell and a sample cell of 1.35 mL, with both cells insulated by an adiabatic shield. In this study, the titration was carried out by stepwise injection of surfactant solutions from a 250 μL injection syringe into the sample cell filled with either water (or buffer) or dilute polysaccharide solutions. The concentrations of all the polymer solutions as titrate were fixed at 0.1 wt % for comparative results. In addition, the effect of polymer concentration was studied for some selected polymer−surfactant pairs (MC−CTAB, KC−SDS, and KC−CTAB) where polymer concentrations of 0.05 and 0.25 wt % were used. The syringe is tailor-made such that the tip acts as a blade-type stirrer to ensure an optimum mixing efficiency at 400 rpm. Most titrations were performed at a constant temperature of 25.0 ± 0.1 °C. The low concentrations (≤ 0.25 wt %) of the polymer solutions and the moderate temperatures applied were also to provide a relatively low viscosity at any point of titration, which did not affect the mechanical stirring of the microcalorimeter. By use of the interactive software, an automatic injection schedule was made by setting the number of injections, volume of each injection, and time between injections. The time interval between coterminous injections was set to 240 s. The heat evolved or absorbed by each injection in the course of titration was directly measured by the microcalorimeter.

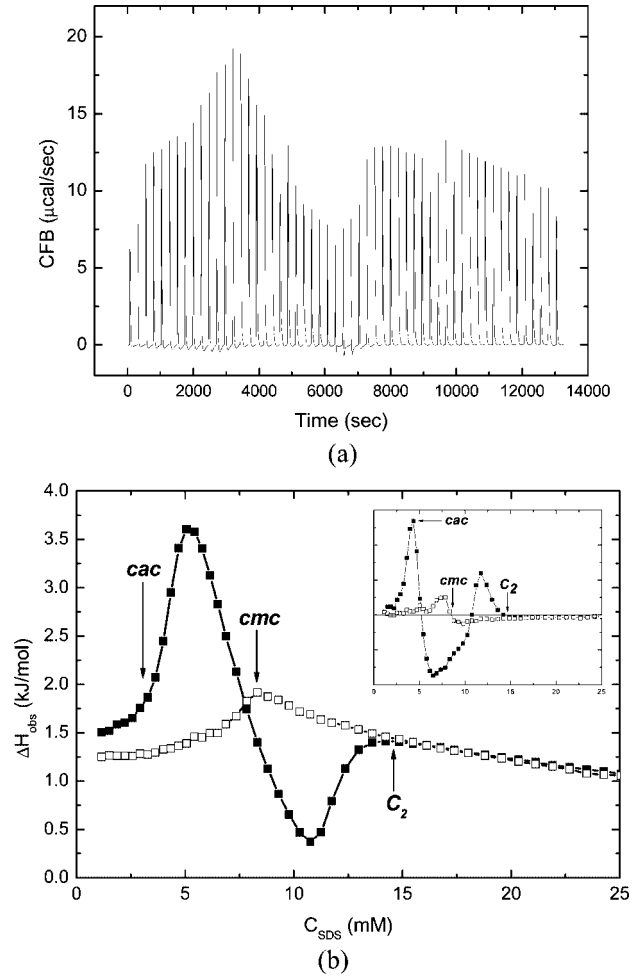

Figure 1. Calorimetric titration of 200 mM SDS into 0.1 wt % MC at 25 °C. (a) Thermogram showing cell feedback (CFB) versus time. (b) Differential enthalpy curves versus concentration of SDS (■); (inset) difference plots of the calorimetric curves. (□) Dilution of SDS (200 mM) in water at the corresponding temperature.

Results and Discussion

1. Interaction between MC and SDS. The calorimetric titration curve (■) for the addition of 200 mM SDS solution to a 0.1 wt % MC solution at 25 °C is shown, together with the thermogram of cell feedback (CFB), in Figure 1. The corresponding curve for the dilution of SDS in water (□) is included also. The SDS concentration (200 mM) is about 24 times the cmc (8.3 mM[1,28]) of SDS at 25 °C, so that the 200 mM SDS solution is a micellar solution. When the micellar solution of SDS is titrated into the sample cell filled with deionized water, the micelles of titrated SDS start dissociating to produce monomers until the concentration of SDS in the sample cell reaches its cmc. The cmc (about 8.3 mM) of SDS is shown as the surfactant concentration for the maximum of the dilution curve or the slope of the differential curve becomes zero in the inset of Figure 1b. When the SDS concentration exceeds the

cmc, the micelles will only be diluted. Thus, the thermodynamic properties of the demicellization of SDS can be obtained from the ITC curve.

ΔG_{mic} and ΔS_{mic} can be calculated from[12]

$$\Delta G_{mic} = (1 + K)RT \ln (cmc) \quad (1)$$

$$\Delta G_{mic} = \Delta H_{mic} - T\Delta S_{mic} \quad (2)$$

where K is the micellar change fraction and equals 0.85 for SDS.[29,30] At the point of cmc, ΔG_{mic} is approximately 2.0 kJ/mol. Thus, we get $\Delta G_{mic} = -22.0$ kJ/mol and $\Delta S_{mic} = 80.5$ J/mol·K, which are consistent with values reported in the literature.[29,30]

The titration curve for SDS into MC deviates from the dilution curve at the first injection, and the binding enthalpy starts to increase with increasing SDS concentration and decreases after reaching the maximum. As a result, a sharp endothermic peak appears. The critical aggregation concentration (cac) is shown as the inflection point in the leading edge of the endothermic peak according to the definition of Wang and Olofsson.[10] C_2, the concentration where the titration curve in the polymer solution joins the dilution curve, is recognized where the slope of the differential curve becomes zero. The calorimetric curve at 25 °C for addition of 200 mM SDS into 0.1 wt % MC solution gives cac = 4.3 mM and C_2 =14.2 mM. The amount of surfactant bound to the polymer was nearly 9.9 mM, calculated from the concentration range between cac and C_2.

From a thermodynamic point of view, the enthalpy change at cac can be expressed as[31]

$$\Delta H = \Delta H \text{ (dilution of surfactant micelles and monomers)} + \Delta H \text{ (demicellization of surfactant micelles)} + \Delta H \text{ (binding of surfactant monomers to polymer chains)} \quad (3)$$

Since the enthalpy changes of dilution and demicellization of SDS are experimentally observed to be small at 25 °C,[13] the measured enthalpy change (denoted as ΔH_{obs}) is mainly attributed to the enthalpy change of the formation of polymer−SDS complexes, ΔH_{agg}. The Gibbs energy ΔH_{agg} can also be derived from

$$\Delta G_{agg} = (1 + K)RT \ln (cac) \quad (4)$$

Since ΔH_{agg} is positive, the contribution to the Gibbs energy is dictated by $T\Delta S_{agg}$ as $\Delta G_{agg} = \Delta H_{agg} - T\Delta S_{agg}$. The endothermic peak corresponding to the cooperative binding describes the formation of SDS micelles on MC chains. When the cac is reached, the hydrophobic units of MC undergo a dehydration process for being solubilized by SDS micelles from water. Dehydration and formation of MC−SDS complexes are both entropy-driven and enthalpy-unfavorable because a large amount of heat, as represented by the sharp endothermic peak, is needed to disrupt the ordered water cages around the hydrophobic moieties of the polymer and SDS.

When the SDS concentration exceeds 5 mM, ΔH_{obs} decreases rapidly and intersects with the dilution curve at $C_{SDS} = 7.8$ mM, which is very close to the cmc of SDS in water. During the process, the number of SDS monomers per micelle increases and the growing electrostatic repulsion between the SDS head groups impedes the further binding of SDS to the polymer−SDS complex. The exothermic contribution to ΔH_{obs} should originate from the rehydration of MC segments that are expelled from the cores of the mixed micelles. This mechanism was first proposed by Wang and Olofsson[10,11] for the EHEC−SDS system and subsequently promoted to the PEO−SDS system. Close to C_2, the polymer chains intermingle in the SDS headgroups region via ion−dipole association, which screens the contact between hydrophobic groups of surfactant and water, thus give a favorable surface energy contribution. At C_2, the MC has been saturated with SDS and further addition of SDS tends to only dilute the free micelles.

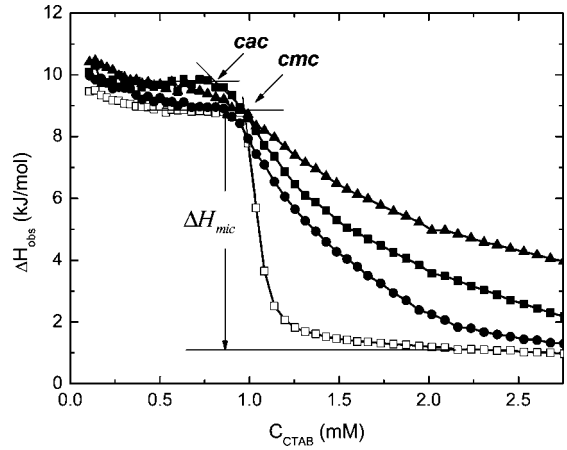

Figure 2. Calorimetric titration curves for titration of 20 mM CTAB into MC solutions of different concentrations: (●) 0.05, (■) 0.1, and (▲) 0.25 wt % at 25 °C. (□) Dilution of concentrated CTAB (20 mM) in water at the same temperature.

2. Interaction between MC and CTAB. Calorimetric titration curves (solid symbols) for the addition of 20 mM CTAB into 0.05, 0.1 and 0.25 wt % MC solutions at 25 °C are shown in Figure 2, where the corresponding dilution curve of CTAB into water is presented for comparison. It is interesting to note that the initial dilution of CTAB into water shows a large enthalpy change (~9.6 kJ/mol) while the enthalpy change for the dilution of SDS into water is very small (~1.3 kJ/mol). Here, the comparison between CTAB and SDS is made under a reasonable condition that SDS and CTAB are diluted from their micellar solutions of 200 and 20 mM, respectively, which are 24 and about 22 times their individual cmc in water at 25 °C. The enthalpy of dilution for surfactant micelles is generally considered to be negligible as compared to the enthalpy of demicellization. Thus, the ΔH_{obs} plateau at CTAB concentrations <0.9 mM is mainly attributed to the enthalpy of demicellization of CTAB into water. ΔH_{obs} decreases from 0.9 mM and then quickly reaches the second plateau at high concentrations of CTAB. The second plateau indicates that the concentration of CTAB in titrate has been higher than its cmc and the titrant (20 mM CTAB solution) is only diluted and does not undergo demicellization anymore. Therefore, the second plateau can be used as a measure of the dilution enthalpy, ΔH_{dil}. The transition from the first plateau to the second one is related to the completion of CTAB demicellization. Thus, the inflection point (at the end of the first plateau) is the concentration of CTAB in the titrate, at which the CTAB micelles stop to demicellize. Therefore, the inflection point is the same as the cmc of CTAB. As indicated in Figure 2, the position of cmc is estimated to be around 0.94 mM, which is in good agreement with values reported in the literature.[1,10]

Titration of CTAB into MC with different concentrations (0.05, 0.1, and 0.25 wt %) results in similar plateaus of ΔH_{obs} at low concentrations of CTAB. The ΔH_{obs} plateau increases in height with increasing MC concentration, indicating that the demicellization enthalpy of CTAB has been increased by the presence of MC in the titrate. This is based on an assumption that CTAB does not bind to MC chains when its concentration is below the cac. The more MC in the titrate, the higher the first plateau. By analogy with the notation used in other polymer−surfactant systems,[10,29] we regard the inflection point in each curve as the cac, the concentration at which polymer−surfactant aggregation occurs. The cac, as indicated in Figure 2, decreases as the MC concentration increases: cac = 0.86, 0.76, and 0.62 mM for 0.05, 0.1, and 0.25 wt % MC, respectively. The depression of cac by increasing MC concentration is a similar phenomenon that can be found in many nonionic polymer−ionic

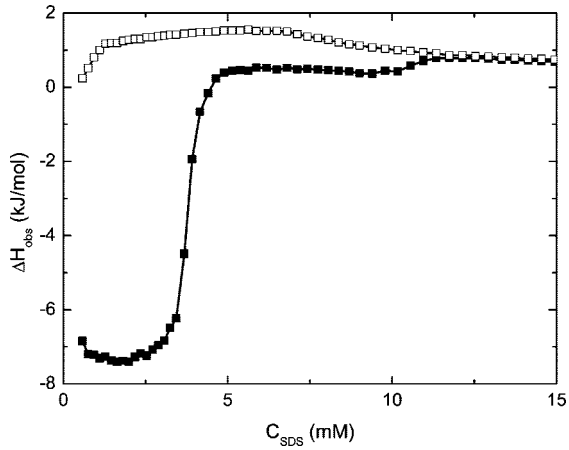

Figure 3. Calorimetric titration curve. (■) Addition of 100 mM SDS to 0.1 wt % CS solutions in 100 mM acetate buffer, pH 3.0, at 25 °C. (□) Dilution of SDS (100 mM) into the corresponding buffer solution.

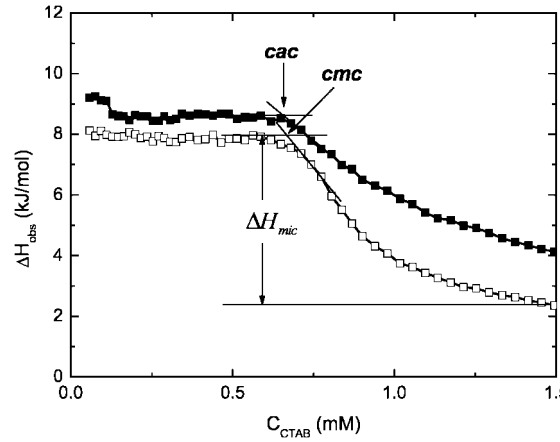

Figure 4. Calorimetric titration curve. (■) Titration of 10 mM CTAB into 0.1 wt % CS solution of pH 3.0 at 25 °C. (□) Dilution of concentrated CTAB (10 mM) into pH 3.0 buffer solution at the same temperature.

surfactant systems such as PPO−SDS,[11] dextran−CTAC,[32] and even hydrophobically modified polyelectrolyte DMRX−CTAC.[33]

After each cac, ΔH_{obs} gradually decreases with CTAB titration. For the titration of CTAB with the lowest concentration (0.05 wt %) of MC, the titration curve approaches the dilution curve at high concentrations of CTAB, meaning that the binding of CTAB to MC has been nearly saturated. In the concentration range from cac to saturation, it is believed that the demicellization of CTAB coexists with the binding of CTAB to MC. The decrease in ΔH_{obs} is because the amount of CTAB demicellization decreases with the titration. As MC is present in the titrate and CTAB binds to MC continuously, the binding saturation occurs only when all MC chains have been maximally bound by CTAB molecules.

The effect of MC concentration on the titration behavior can be understood easily. Before the cac, the ΔH_{obs} plateau increases with increasing MC concentration, which is attributed to the increased hydrophobicity of water by MC. After the cac, the ΔH_{obs} curve is higher at a higher concentration of MC. At a lower concentration of MC, the binding saturation could be achieved by adding a smaller amount of CTAB. When the concentration of MC is higher, the amount of CTAB required for the binding saturation is larger. Thus, at a given CTAB concentration, the binding degree (defined as the number of CTAB molecules bound per chain of MC) decreases with increasing MC concentration. At the same time, the number of CTAB micelles that could demicellize increases with increasing MC concentration. As a result, a higher ΔH_{obs} is shown at a higher concentration of MC. The saturation concentration C_2 for 0.05 wt % MC should be close to 2.75 mM CTAB, while C_2 for 0.1 and 0.25 wt % MC should be approximately 2 and 5 times that for 0.05 wt % MC, respectively.

3. Interaction between CS and SDS. Thongngam and McClements[24,25] systematically studied the interactions of SDS and CS using isothermal titration calorimetry. In the present work, we also carried out similar ITC experiments on this system and regarded it as a representative system for the interactions between cationic polyelectrolyte and anionic surfactant. In order to perform a comparable study, we choose room temperature (25 °C) and pH 3.0 to examine the interaction of CS with SDS. A 100 mM SDS solution was isothermally titrated at 25 °C into either a buffer solution or a CS-containing buffer solution at pH 3.0. The ITC results are shown in Figure 3.

With titration of SDS into the buffer solution at pH 3.0, a slow and endothermic increase in ΔH_{obs} is observed until about C_{SDS} = 6.5 mM. Then a mild decrease in ΔH_{obs} occurs from 6.5 mM and ΔH_{obs} tends to level off at high concentrations of SDS. The peak point around 6.5 mM is approximately regarded as the cmc of the surfactant in the pH 3.0 buffer solution, and it is in close agreement with the value reported in the literature.[25] At pH 3.0, CS is protonated to become a cationic polyelectrolyte that attracts anionic SDS electrostatically. This kind of ionic interaction is much stronger than hydrophobic association or ion−dipole attraction. Therefore, when SDS is titrated into CS at pH 3.0, a distinct exothermic valley is obtained in the concentration range from 0 to 5 mM, followed by an endothermic climb until about 11.5 mM, at which the titration curve merges with the dilution one. The merging point, 11.5 mM, is defined as the saturation concentration C_2. The broad endothermic plateau between the exothermic valley and C_2, which is slightly positive in value, is considered to be due to some weak hydrophobic interaction between CS and SDS.

When SDS is titrated into a CS solution, the formation of either soluble or insoluble complexes between oppositely charged ions is an important concern. Thongngam and McClements[25] used turbidity measurements to study the formation of CS−SDS complexes, which was caused by the strong electrostatic attraction between CS (at pH 3.0, the initial concentration of CS was 0.1 wt %) and SDS. In the presence of NaCl, turbidity was found to reach a maximum at SDS = 6.7 mM, indicating the formation of CS−SDS complexes or aggregates. When those complexes are large in size, precipitation may occur. However, in an ITC experiment, the injection syringe-driven stirring ensures homogeneous mixing of SDS with CS at any time of titration. On the other hand, since turbidity did not decrease significantly beyond the maximum turbidity, the redissolution of those CS−SDS complexes at high concentrations of SDS still remained unknown.[25]

4. Interaction between CS and CTAB. Figure 4 shows ITC curves for the titration of 10 mM CTAB into a 0.1 wt % CS solution and a buffer solution, respectively, at pH 3.0 and 25 °C. Quite different from what we have observed in the oppositely charged polymer−surfactant system (for example, Figure 3), the enthalpy pattern observed in Figure 4 is similar to the interaction between MC and CTAB (Figure 2), which is a system of uncharged polymer−ionic surfactant.

As expected, the cmc of CTAB in the buffer solution decreased to 0.65 from 0.93 mM, which is attributed to the screening effect from the small amount of salt counterions in the buffer, since the electrostatic repulsion between surfactant headgroups normally opposes micellization.[10] Incorporation of

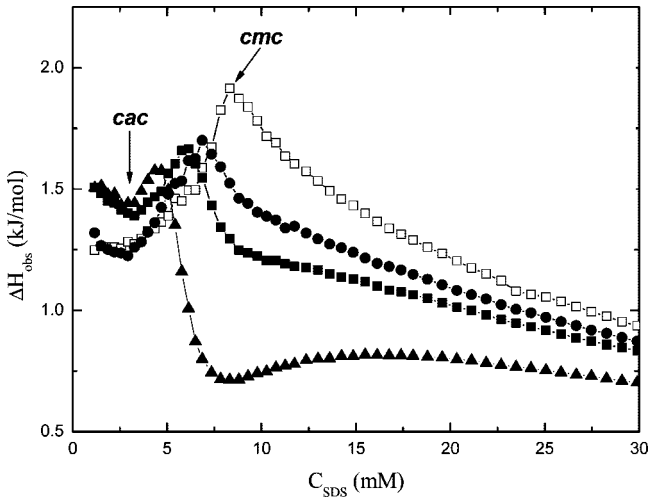

Figure 5. Calorimetric titration curves for addition of 200 mM SDS to KC solutions of different concentrations: (●) 0.05, (■) 0.1, and (▲) 0.25 wt % at 25 °C. (□) Dilution of SDS (200 mM) in water at the corresponding temperature.

positively charged CS into the buffer solution slightly shifts the titration curve upward. The cac is reflected as the inflection point of the enthalpic titration curve, which is 0.62 mM, slightly smaller than the cmc of CTAB. Compared with the above-discussed MC−CTAB system at the same 0.1 wt % polymer concentration, CS−CTAB experiences a smaller cac. This difference should be attributed to the lower hydrophobicity of CS than MC. Furthermore, the positively charged CS may prevent CTAB monomers from aggregating by electrostatic repulsion, thus retarding the decrease in cac.

Bai et al.[32] proposed two simultaneous processes during the aggregation of surfactant in hydrophobically modified polyelectrolytes with the same charge as the surfactant: a noncooperative inclusion of surfactant molecules in the hydrophobic microdomains of polymer, which can be described as cic (critical incorporation concentration), and a cooperative self-aggregation of the bound surfactant, described by cac. The inflection point determined by ITC, which we call cac, is probably a combination of the two processes mentioned above. According to Bai et al.,[32] the cac values of all the *N*-(2-hydroxypropyl)-*N*,*N*-dimethyl-*N*-alkylammonium chloride-grafting dextran (DMRX)−CTAC/CTAB systems are lower than the cmc values of the corresponding free surfactants due to the presence of the polyelectrolyte backbone and pendant groups. They found that the higher the hydrophobicity of the polymer, the lower the cac for the same hydrophobe concentration.

5. Interaction between KC and SDS. The interactions between a cationic polyelectrolyte and a cationic surfactant have been discussed in section 4. The negatively charged counterparts are presented in this section. Calorimetric curves for titrating 200 mM SDS into 0.05, 0.1, and 0.25 wt % KC solutions at 25 °C are shown in Figure 5. The dilution curve (□) of SDS is also given. The observed enthalpy curves exhibit the similar pattern as other polymer−surfactant systems with the same charges: alginate−SDS[33,34] and DMRX (D40Oct30)−DTAC.[32] In the initial stage of the titration, ΔH_{obs} deviates from the dilution curve, depending on polymer concentration. This indicates that binding of SDS to KC takes place at low concentrations of SDS despite the electrostatic repulsion exists. The cac is difficult to define, but it seems to be weakly dependent on polymer concentration: decreasing with increasing polymer concentration, which is in accordance with the results from D40Oct30−DTAC.[32] The concentration, C_m, at which surfactant micelles start to form is referred to as the critical micelle concentration (cmc) in the presence of a polymer. As

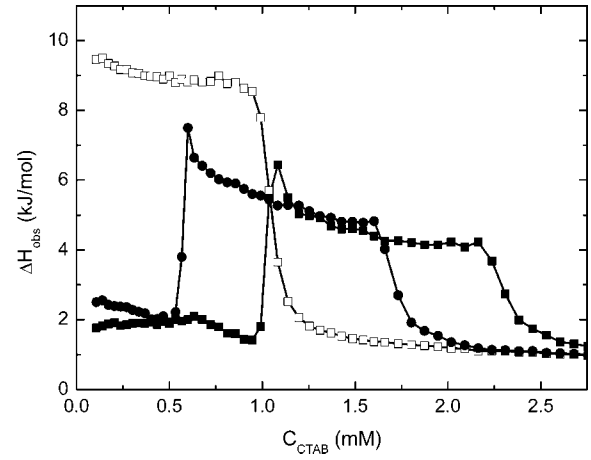

Figure 6. Calorimetric titration curves for titration of 20 mM CTAB into (●) 0.05 and (■) 0.1 wt % KC solutions at 25 °C. (□) Dilution of CTAB (20 mM) in water at the corresponding temperature.

is well-known, polyelectrolytes have a similar effect on the cmc of ionic surfactant as a simple salt does, but their effect is weaker than that of a salt.[35] In this case, the increase of polyelectrolyte concentration enhances the strength of counterions (K^+ and Ca^{2+}) in the solutions, which in turn leads to a gradual decrease in C_m (not shown in Figure 5). Moreover, the higher hydrophobicity of the titrate solution at a higher polymer concentration tends to promote micellization of the surfactant, leading to a smaller C_m.

At the beginning, the SDS micelles disassociate into free monomers. As both KC and SDS are anionic, ionic binding of SDS to KC is impossible. Thus, SDS can bind only to the hydrophobic groups or units of KC, which is an endothermic binding process where SDS tails bind to KC. Once the hydrophobic groups or units of KC are fully saturated by the SDS molecules, the free micelles appear at C_m. Beyond C_m, the overall enthalpy changes become smaller at a higher polymer concentration, indicating that the dilution of SDS to a polymer solution needs less heat than that for the dilution to water.

6. Interaction between KC and CTAB. As mentioned previously, a mixture of an ionic surfactant and an oppositely charged polyelectrolyte exhibits strong association dominated by electrostatic attraction between the ionized groups on the polyelectrolyte and the charged headgroups of the surfactant. The calorimetric curves for titrating 20 mM CTAB into 0.05 and 0.1 wt % KC solutions at 25 °C is shown in Figure 6, together with the corresponding CTAB dilution curve. Electrostatic binding via Columbic interaction occurs from the first point of titration and is represented as a flat and broad exothermic plateau relative to the dilution curve of CTAB. For convenience, we call this the "lower plateau". The small positive ΔH_{obs} values (around 2 kJ/mol) of the lower plateau could comprise two thermodynamically countervailing processes: demicellization of CTAB, which is highly endothermic ($\Delta H_{demic} = -8.2$ kJ/mol),[10] and the Columbic interaction between CTAB and KC, which is highly exothermic. When $\Delta H_{demic} \geq \Delta H_{ele}$, where ΔH_{ele} is the enthalpy changes caused by electrostatic interaction between CTAB and KC, ΔH_{obs} will be above the horizon. A similar pattern of the calorimetric titration curve can be observed in the chitosan−sodium taurocholate (NaTC) interaction, which is another oppositely charged colloidal system.[36] Since ΔH_{mic} of SDS at 25 °C is very small as compared to the electrostatic binding of SDS to CS, the exothermic valley below the horizon is observed in Figure 3 for CS−DS interactions. For KC−CTAB interactions, the positive (i.e., endothermic) ΔH_{obs} means that the electrostatic interaction between KC and CTAB could not overwhelm the

enthalpy changes of demicellization (ΔH_{demic}) because ΔH_{demic} of CTAB is quite large.

The effect of polymer concentration on the initial ΔH_{obs} is obvious: the lower plateau is longer for the higher concentration of KC. It is interesting to note that the length of the lower plateau at 0.05 wt % KC is approximately half that at 0.1 wt % KC. Since the end of the lower plateau is considered as the finishing point of the electrostatic binding of CTAB to KC, more chains of KC in the solution need more CTAB molecules to bind electrostatically to result in a longer plateau.

The lower plateau is followed by a steep increase at $C_{CTAB} = 0.5$ and 1 mM for 0.05 and 0.1 wt % KC respectively. At 0.1 wt % KC, after reaching a sharp peak, the enthalpy curve levels off from about 1.1 mM to form a pronounced endothermic plateau until about 2.2 mM. The endothermic plateau is attributed to the hydrophobic binding of CTAB to the polymer. In this range, the dissociation of CTAB micelles could take place to produce CTAB monomers that bind to the polymer. The hydrophobic binding of CTAB to KC takes place gradually and slows down slightly with increasing CTAB concentration. When the hydrophobic binding of CTAB to KC is nearly saturated, the enthalpy curve decreases dramatically and merges gradually with the dilution curve at high concentrations of CTAB.

Obviously, the endothermic plateau represents the whole process of hydrophobic binding of CTAB to KC until saturation. The plateau height is approximately independent of the polymer concentration. The polymer chains in the 0.05 wt % solution are fully saturated by the bound CTAB molecules at about $C_2 = 2.1$ mM, whereas those in the 0.1 wt % solution need more CTAB molecules to reach the saturation. Thus, C_2 for 0.1 wt % KC is expected to be about 4.2 mM.

It is well accepted that, in the presence of a polymer, polymer-induced micellization or demicellization may occur. When 20 mM CTAB is titrated into a KC solution, the demicellization of CTAB micelles is accelerated by the strong electrostatic attraction of KC. Once KC is electrostatically saturated by CTAB at the isopotential point (i.e., the end of the lower plateau), the additional surfactant micelles are diluted into the aqueous solution and then interact with the hydrophobic groups or units of KC. After the isopotential point, the further titration does not give the high ΔH_{obs} as the dilution does, implying that the additional CTAB micelles do not dissociate fully before reaching its cmc. It may be reasonably considered that in the presence of KC the CTAB micelles undergo only partial demicellization to produce surfactant monomers for hydrophobic binding to KC. The partial demicellization of CTAB and the hydrophobic binding of CTAB to KC result in the endothermic plateau of ΔH_{obs}. However, the polymer-induced cmc of CTAB is not present as a clear transition position on the calorimetric curve.

Similarly to the system of CS−SDS, the strong electrostatic attraction between KC and CTAB might lead to the formation of insoluble complexes. On the other hand, the insoluble complexes might be dissolved again by further adding CTAB. These concerns have not been elucidated in the present work, but they should be verified through future work such as light scattering studies.

7. A General Rule for Polymer−Surfactant Interactions. When a micellar surfactant solution (i.e., $C \gg$ cmc) is isothermally titrated into a dilute polymer aqueous solution, as already described in eq 3, the thermodynamic process may generally include one, two, or all three of these events: (i) dilution of surfactant micelles and monomers, (ii) demicellization of surfactant micelles, and (iii) binding of surfactant monomers or micelles to polymer chains, depending on the type of polymer−surfactant interactions and the stage of titration. Events i and ii are generally similar for all types of polymer−surfactant pairs. However, binding properties for a surfactant to a polymer, or in other words polymer−surfactant interactions, are greatly affected by the type of surfactant and polymer.

Polymer−surfactant interactions are categorized into three types: hydrophobic interactions (van der Waals forces), ion−dipole interactions, and ionic interactions. If three types of interactions are possible at the same time, a general rule to determine the order (or priority) of surfactant binding to polymer would be ionic interaction (i.e., electrostatic attraction) > hydrophobic interaction > ion−dipole interaction. There are typically three cases to be taken into account. Case 1 is when an ionic surfactant is titrated into a nonionic polymer solution; only hydrophobic and ion−dipole interactions may be present. Case 2 is when an ionic surfactant is titrated into a solution of an ionic polymer with the same charge as the surfactant; the thermodynamic behavior will be similar to case 1. Case 3 is when an ionic surfactant is titrated into a solution of an ionic polymer with the opposite charge as the surfactant; a strong polymer−surfactant interaction will be shown due to the strong electrostatic interaction between surfactant and polymer.

In this study, three types of polymers (MC, CS, and KC) and two types of surfactants (SDS and CTAB) are chosen to make six polymer−surfactant pairs, which typically represent the above-mentioned three cases of polymer−surfactant interactions. Nonionic surfactants are not used in this study as they cannot show all types of interaction with three types of polysaccharides. ITC results representing the typical polymer−surfactant interactions of the six pairs studied in this work are summarized in Figure 7. Calorimetric curves for titration of SDS into MC, CS, and KC are shown in Figure 7a, while those for titration of CTAB into MC, CS, and KC are given in Figure 7b.

In Figure 7a, MC−SDS exhibits strong hydrophobic interaction, as evidenced by the endothermic peak, followed by a weak ion−dipole interaction. KC−SDS does not show any ionic interaction as expected, but exhibits the weak hydrophobic interaction as compared with MC−SDS. Strong ionic interaction is found for CS−SDS, as evidenced by a deep valley of exotherm, followed by the hydrophobic interaction between some hydrophobic moieties of CS and SDS tails. Finally, at high concentrations of SDS, any kind of polymer is fully saturated to result in a similar ITC curve.

In Figure 7b, the titration of CTAB into MC gives a similar pattern of polymer−surfactant interaction as that for the titration into CS; this is expected because no ionic interactions are possible in these two pairs of polymer−surfactant. In addition, the stronger hydrophobic interactions between MC and CTAB lead to the higher endothermic plateau than that for CS−CTAB. KC shows strong interaction with CTAB by largely reducing the high endothermic enthalpy changes caused by the demicellization of CTAB. After the isopotential point of KC is reached, the hydrophobic interaction with CTAB becomes possible.

Conclusions

Molecular interactions between three polysaccharides (MC, CS, and KC) and two ionic surfactants (SDS and CTAB) have been studied by ITC. MC−SDS exhibited strong hydrophobic interaction, as evidenced by the endothermic peak, followed by a weak ion−dipole interaction. KC−SDS did not show any ionic interaction, as expected, but exhibited weaker hydrophobic interaction than MC−SDS. Strong ionic interaction was found for CS−SDS, followed by hydrophobic interaction between some hydrophobic moieties of CS and SDS tails. Titration of CTAB into MC resulted in a similar pattern of polymer−surfactant interaction to that for titration of CTAB into CS. KC showed strong interaction with CTAB

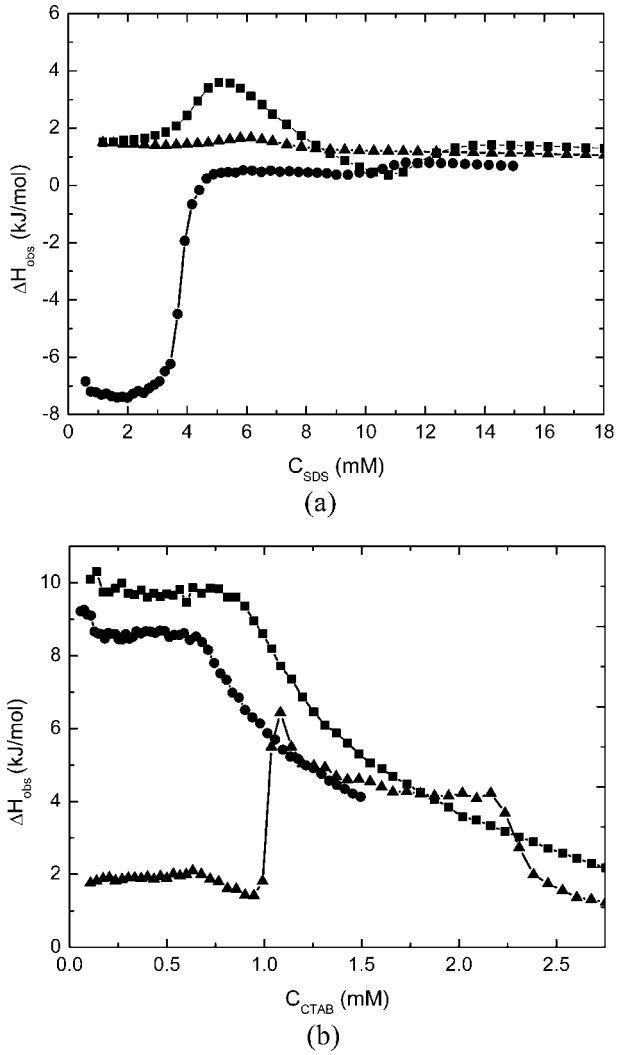

Figure 7. Calorimetric titration curves: (a) titration of SDS into (■) MC, (●) CS, and (▲) KC; (b) addition of CTAB to (■) MC, (●) CS, and (▲) KC. The titration temperature was 25 °C, and the initial polymer concentrations were 0.1 wt %.

by largely reducing the high endothermic enthalpy changes caused by the demicellization of CTAB. When three types of interactions are possible simultaneously, a general rule determining the order (or priority) for a surfactant to bind to a polymer has been verified to be ionic interaction (i.e., electrostatic interaction) > hydrophobic interaction > ion−dipole interaction. In addition, the ionic binding of an ionic surfactant to an ionic polymer is achieved through the surfactant ionic heads that bind to ionic groups of polymer chains, while the hydrophobic binding is completed through the surfactant tails that bind to hydrophobic moieties of polymer chains.

Supporting Information Available: Figure showing titration of SDS into MC, CS, and KC at 25 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Jönsson, B.; Lindman, B.; Holmberg, K.; Kronberg, B. *Surfactants and Polymers in Aqueous Solution*; John Wiley & Sons:Chichester, U.K., 1998.
(2) Kwak, J. C. T. *Polymer-Surfactant Systems, Surfactant Science Series 77*;Marcel Dekker:New York, 1998.
(3) Chu, D. Y.; Thomas, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 6270–6276.
(4) Winnik, M. A.; Bystryak, S. M.; Chassenieux, C.; Strashko, V.; Macdonald, P. M.; Siddiqui, J *Langmuir* **2000**, *16*, 4495–4510.
(5) Wallin, T.; Linse, P. *Langmuir* **1996**, *12*, 305–314.
(6) Sokolov, E. L.; Yeh, F.; Khokhlov, A.; Chu, B. *Langmuir* **1996**, *12*, 6229–6234.
(7) Ghoreishi, S. M.; Fox, G. A.; Bloor, D. M.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* **1999**, *15*, 5474–5479.
(8) Bloor, D. M.; Wan-Yunus, W. M. Z.; Wan-Badhi, W. A.; Li, Y.; Holzwarth, J. F.; Wyn-Jones, E *Langmuir* **1995**, *11*, 3395–3400.
(9) Li, Y.; Ghoreishi, S. M.; Warr, J.; Bloor, D. M.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* **1999**, *15*, 6326–6332.
(10) Wang, G.; Olofsson, G. *J. Phys. Chem.* **1995**, *99*, 5588–5596.
(11) Wang, G.; Olofsson, G. *J. Phys. Chem. B* **1998**, *102*, 9276–9283.
(12) Dai, S.; Tam, K. C.; Li, L. *Macromolecules* **2001**, *34*, 7049–7055.
(13) Dai, S.; Tam, K. C. *J. Phys. Chem. B* **2001**, *105*, 10759–10763.
(14) Dai, S.; Tam, K. C. *Langmuir* **2004**, *20*, 2177–2183.
(15) Li, L.; Shan, H.; Yue, C. Y.; Lam, Y. C.; Tam, K. C.; Hu, X. *Langmuir* **2002**, *18*, 7291–7298.
(16) Wang, Q.; Li, L.; Liu, E.; Xu, Y.; Liu, J. *Polymer* **2006**, *47*, 1372–1378.
(17) Li, L.; Liu, E.; Lim, C. H. *J. Phys. Chem. B* **2007**, *111*, 6410–6416.
(18) Caram-Lelham, N.; Sundelöf, L.-O. *Biopolymers* **1996**, *39*, 387–393.
(19) Zhou, S.; Chu, B. *Adv. Mater.* **2000**, *12*, 545–556.
(20) Tomašić, V.; Tomašić, A.; Filipović-Vinceković, N. *J. Colloid Interface Sci.* **2002**, *256*, 462–471.
(21) Grenha, A.; Seijo, B.; Serra, C.; Remunan-Lopez, C. *Biomacromolecules* **2007**, *8*, 2072–2079.
(22) Sonvico, F.; Cagnani, A.; Rossi, A.; Motta, S.; Di Bari, M. T.; Cavatorta, F.; Alonso, M. J.; Deriu, A.; Colombo, P. *Int. J. Pharm.* **2006**, *324*, 67–73.
(23) Zheng, Y.; Yang, W.; Wang, C.; Hu, J.; Fu, S.; Dong, L.; Wu, L.; Shen, X. *Eur. J. Pharmaceut. Biopharmaceut.* **2007**, *67*, 621–631.
(24) Thongngam, M.; McClements, D. J. *J. Agric. Food Chem.* **2004**, *52*, 987–991.
(25) Thongngam, M.; McClements, D. J. *Langmuir* **2005**, *21*, 79–86.
(26) Vinceković, M.; Bujan, M.; Šmit, I.; Filipović-Vinceković, N. *Colloids Surf., A* **2005**, *255*, 181–191.
(27) Gan, Q.; Wang, T.; Cochrane, C.; McCarron, P. *Colloids Surf., B* **2005**, *44*, 65–73.
(28) Johnson, I.; Olofsson, G.; Jönsoon, B. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 3331–3344.
(29) Wang, Y.; Han, B.; Yan, H.; Kwak, J. C. T. *Langmuir* **1997**, *13*, 3119–3123.
(30) Seng, W. P.; Tam, K. C.; Jenkins, R. D.; Bassett, D. R. *Macromolecules* **2000**, *33*, 1727–1733.
(31) Meagher, R. J.; Hatton, T. A.; Bose, A. *Langmuir* **1998**, *14*, 4081–4087.
(32) Bai, G.; Catita, J. A. M.; Nichifor, M.; Bastos, M. *J. Phys. Chem. B* **2007**, *111*, 11453–11462.
(33) Bu, H.; Kjøiksen, A.-L.; Elgsaeter, A.; Nyström, B. *Colloids Surf., A* **2006**, *278*, 166–174.
(34) Yang, J.; Zhao, J.; Fang, Y. *Carbohydr. Res.* **2008**, *343*, 719–725.
(35) Binana-Limbele, W.; Zana, R. *Colloids Surf.* **1986**, *21*, 483–494.
(36) Thongngam, M.; McClements, D. J. *Food Hydrocolloids* **2005**, *19*, 813–819.

MA801957V