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ARTICLE

Interaction of a Food-Grade Cationic Surfactant (Lauric Arginate) with Food-Grade Biopolymers (Pectin, Carrageenan, Xanthan, Alginate, Dextran, and Chitosan)

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Lauric arginate (LAE) is a food-grade cationic surfactant that is a highly potent antimicrobial active against a wide range of food pathogens and spoilage organisms. In compositionally complex environments, the antimicrobial activity of cationic LAE is likely to be impacted by its interactions with other charged components. The purpose of this study was to characterize the interactions between cationic LAE and various food grade biopolymers with different charge characteristics: anionic (pectin, alginate, carrageenan, xanthan), neutral (dextran), and cationic (chitosan). Isothermal titration calorimetry (ITC) and turbidity measurements were used to characterize surfactant−biopolymer interactions and the solubility of any aggregates formed. ITC and turbidity measurements suggested that no complex formation occurred between the cationic LAE and the cationic or neutral biopolymers, although the critical micelle concentration (cmc) of the surfactant was changed because of excluded volume effects. On the other hand, ITC measurements indicated a strong binding interaction between cationic LAE and anionic biopolymers. The amount of surfactant bound and the solubility of the aggregates formed depended strongly on biopolymer type. The results of this study have important implications for the application of LAE in compositionally complex systems.

KEYWORDS: Isothermal titration calorimetry; polysaccharides; biopolymers; lauric arginate; binding; complexation

INTRODUCTION

More and more food products are being produced on a large industrial scale and distributed over wide geographic areas, which has led to considerable challenges in maintaining their quality and safety throughout their shelf life. Effective control of bacterial growth in foods is a major concern in order to reduce incidences of spoilage and food-borne diseases. Lauric arginate (N^{α}-lauroyl-L-arginine ethyl ester monohydrochloride, LAE) is a cationic surfactant, derived from lauric acid, L-arginine, and ethanol, which has been shown to be a highly efficacious antimicrobial that has a broad spectrum of activity against a wide range of food pathogens and spoilage organisms (*1*−*3*). It has been approved as generally recognized as safe (GRAS) within the United States for certain food applications (*1*,*4*). The high antimicrobial activity of LAE has been attributed to its action on the cytoplasmic membranes of microorganisms, where it alters their metabolic processes without causing cellular lysis (*2*). In addition, LAE has a low oil−water equilibrium partition coefficient ($K_{OW} < 0.1$), which means it tends to concentrate in the aqueous phase of products, where most bacterial action occurs (*1*). Ingested LAE is hydrolyzed within the human gastrointestinal tract by chemical and metabolic pathways, which quickly break the molecule into its natural components: lauric acid and L-arginine (*5*).

The relatively low toxicity and high antimicrobial activity of LAE make it a particularly valuable means of controlling or preventing microbial growth in foods and other products. Nevertheless, its widespread utilization within the food and beverage industry may be limited because of its potential to interact with various other components within the compositionally complex matrix found in these products. LAE is a cationic surfactant that can interact strongly with either anionic or hydrophobic groups on other molecules, which may have important consequences for its practical application. Its interactions with other components may alter its solubility in aqueous solutions and therefore affect the appearance and stability of final products (*6*). For example, in mildly acidic conditions LAE exists in aqueous solutions as small micelles that do not scatter light strongly and therefore lead to a transparent system, but if it forms complexes with other molecules, the resulting aggregates may be large enough to scatter light and sediment (*6*). In addition, the antimicrobial activity of LAE may be adversely affected if it interacts with other components within a complex system, since this will change its ability to approach and interact with bacterial cell membranes (*4*, *7*). Finally, LAE is known to bind to anionic biopolymers naturally present within the mouth (e.g., mucins), which can lead to a perceived bitterness or astringency.

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An improved understanding of the interactions of LAE with other components in foods is therefore important in order to maintain its beneficial attributes (e.g., antimicrobial activity) or to reduce its potentially detrimental attributes (e.g., perceived bitterness, precipitation). In this study, we examined the interactions of LAE with various kinds of food-grade polysaccharides. Polysaccharides are widely used in the food industry as functional ingredients to modify texture, improve stability, or maintain water holding capacity (*8*). A number of polysaccharides with different charge characteristics were selected for this study to better understand the origin and nature of the interactions: anionic (pectin, alginate, carrageenan, and xanthan), neutral (dextran), cationic (chitosan). We hypothesized that each polysaccharide would interact differently with LAE based on differences in its charge characteristics. In a previous study, we used isothermal titration calorimetry (ITC) and turbidity measurements to characterize the interactions of LAE with anionic pectin (*6*). These measurements showed that LAE bound to pectin and formed complexes that could be either soluble (transparent) or insoluble (turbid) depending on solution composition. A better understanding of the interactions between cationic LAE and polysaccharide molecules in aqueous solutions will facilitate the rational design of lauric arginate antimicrobial systems with improved functionality in foods and other applications.

MATERIALS AND METHODS

Materials. The cationic surfactant LAE ($C_{20}H_{41}N_4O_3Cl$, MW = 421.0 g mol^{-1}), available commercially under the trade name Mirenat-CF (10.5% w/v LAE in 89.5% w/v propylene glycol solvent) was provided by Vedeqsa Grupo LAMIRSA (Terrassa, Barcelona, Spain). The polysaccharide ingredients used in this study were obtained from various sources. High methoxyl pectin (HMP) with a degree of esterification (DE) of approximately 70% (Pectin 1400) was provided by TIC Gums (Belcamp, MD). Low methoxyl pectin (LM) with a degree of esterification of approximately 30% and a molecular weight of 180 kDa was provided by CP Kelco (Atlanta, GA, USA). Iota-carrageenan (Viscarin SD 389) with 32% of ester sulfate was provided by FMC Biopolymer (Drammen, Norway). Alginate (Protanal LF20/40) with a molecular weight of 190.6 kDa was provided by FMC Biopolymer (Drammen, Norway). Xanthan (prehydrated and pretested Ticaxan Xanthan) was provided by TIC Gums (Belcamp, MD). Dextran from *Leuconostoc mesenteroides* with a molecular weight of 167 kDa was provided by Sigma Aldrich (St Louis, MO). Chitosan with a degree of deacetylation of 92.5% was provided by Primex (Siglufjordur, Iceland). Distilled and deionized water was used for the preparation of all solutions. Ideally, it would be useful to know the molecular weight, linear charge density, conformation, and flexibility of each of the polysaccharides used in this study. In future studies, it would be useful to use polysaccharide samples where all of this information was available.

Solution Preparation. Surfactant solution was prepared by dispersing LAE (Mirenat-CF) into doubly distilled water to a final concentration of 1.8% w/v LAE (15.34% propylene glycol). The pH of this solution was then adjusted to pH 3.5 using either HCl or NaOH. Polysaccharide solutions (0.1 wt %) were prepared by dispersing powdered biopolymer into aqueous propylene glycol solution (15.34% w/v) and stirring for at least 60 min at room temperature before use to ensure complete dispersion and dissolution. The pH of all solutions was then adjusted to pH 3.5. The propylene glycol content of the surfactant and polysaccharide solutions was kept the same to avoid heat of dilution effects in the isothermal titration calorimeter.

Isothermal Titration Calorimetry (ITC). An isothermal titration calorimeter (VP-ITC, Microcal Inc., Northampton, MA) was used to measure enthalpies of mixing at 25 °C. Fifty-nine aliquots of 5 μL of surfactant solution (1.8 w/v % LAE, 15.34% w/v, pH 3.5) were injected sequentially into a 1480 μL titration cell initially containing either buffer solution or 0.1 wt % polysaccharide in buffer solution (15.34% w/v propylene glycol, pH 3.5). Each injection lasted 20 s, with an interval of 240 s between successive injections. The solution in the titration cell was stirred at a speed of 315 rpm throughout the experiments. All solutions were degassed prior to the measurements being carried out. ITC experiments were carried out on freshly prepared duplicate samples.

Turbidity Measurements. Turbidity measurements were designed to follow the same dilution protocol as the ITC measurements. Aliquots of surfactant solution (0−1500 μL, 1.8 w/v % LAE, 15.34% w/v propylene glycol, pH 3.5) were injected into test tubes initially containing 7.5 mL of either buffer solution or 0.1 wt % biopolymer in buffer solution (15.34% w/v propylene glycol, pH 3.5). The resulting solutions were then mixed thoroughly and stored overnight prior to analysis. The optical turbidity (at 600 nm) of biopolymer, surfactant, and biopolymer−surfactant solutions was measured using a UV−visible spectrophotometer (Spectrosonic 21D, Milton Roy, Rochester, NY) at ambient temperature. The samples were contained within 1 cm path length optical cells, and buffer solution was used as a control. Turbidity measurements were carried out on freshly prepared duplicate samples, and the mean and standard deviation were calculated from these values.

RESULTS AND DISCUSSION

Influence of Sign of Polysaccharide Charge. Initially, we examined the influence of the sign of the polysaccharide charge on the characteristics of LAE−polysaccharide interactions. Cationic surfactant (LAE) was titrated into solutions containing cationic (chitosan), neutral (dextran), or anionic (carrageenan) polysaccharides, and the resulting changes in enthalpy, turbidity, and appearance were measured. Heat flow versus time profiles resulting from sequential injections of 5 μL aliquots of surfactant solution (1.8%, w/v LAE) into a 1480 μL titration cell containing either buffer solution or polysaccharide in buffer solution were measured (**Figure 1**). The nature of the resulting curves was strongly dependent on the electrical properties of the polysaccharide molecules.

In the absence of polysaccharide, relatively large endothermic peaks were initially observed when the surfactant solution was injected into the reaction cell (**Figure 1a**). These enthalpy changes can be attributed to micelle dissociation because the surfactant concentration in the injector was initially well above the critical micelle concentration (cmc), while that in the reaction cell was well below the cmc (*9*). Hence, the injector initially contained mainly surfactant micelles with some surfactant monomers, which dissociated upon injection into the reaction cell. The endothermic nature of these peaks ($\Delta H > 0$) indicates that demicellization led to an increase in the overall entropy of the system at this temperature, since micelle dissociation is thermodynamically favorable below the cmc ($\Delta G < 0$); therefore, $T\Delta S > \Delta H$. This entropy increase can be attributed to changes in the structural organization of water molecules around hydrophobic groups, the increase in entropy due to release of surfactant monomers from micelles, and the release of counterions associated with the surfactant headgroups when micelles break down to monomers (*9*). After a certain number of injections, there was an appreciable decrease in peak height because the surfactant concentration in the reaction cell exceeded the cmc, and so the micelles titrated into the reaction cell no longer dissociated and exposed their nonpolar tails to water. Above the cmc the enthalpy change is therefore only the result of micelle dilution effects (*9*). The dependence of the enthalpy change per injection on the surfactant concentration in the reaction cell was calculated by the instrument from heat flow versus time profiles (**Figure 2**). As described previously (*6*), the cmc of the surfactant was determined from the inflection point in the ΔH versus surfactant concentration curves as 0.19 ± 0.01 wt %, which is equivalent to 4.5 ± 0.2 mM LAE. This is in reasonable agreement with previous studies using a similar system, where a value of 0.21 ± 0.01 wt % was reported (*6*). The slight difference between the cmc of LAE

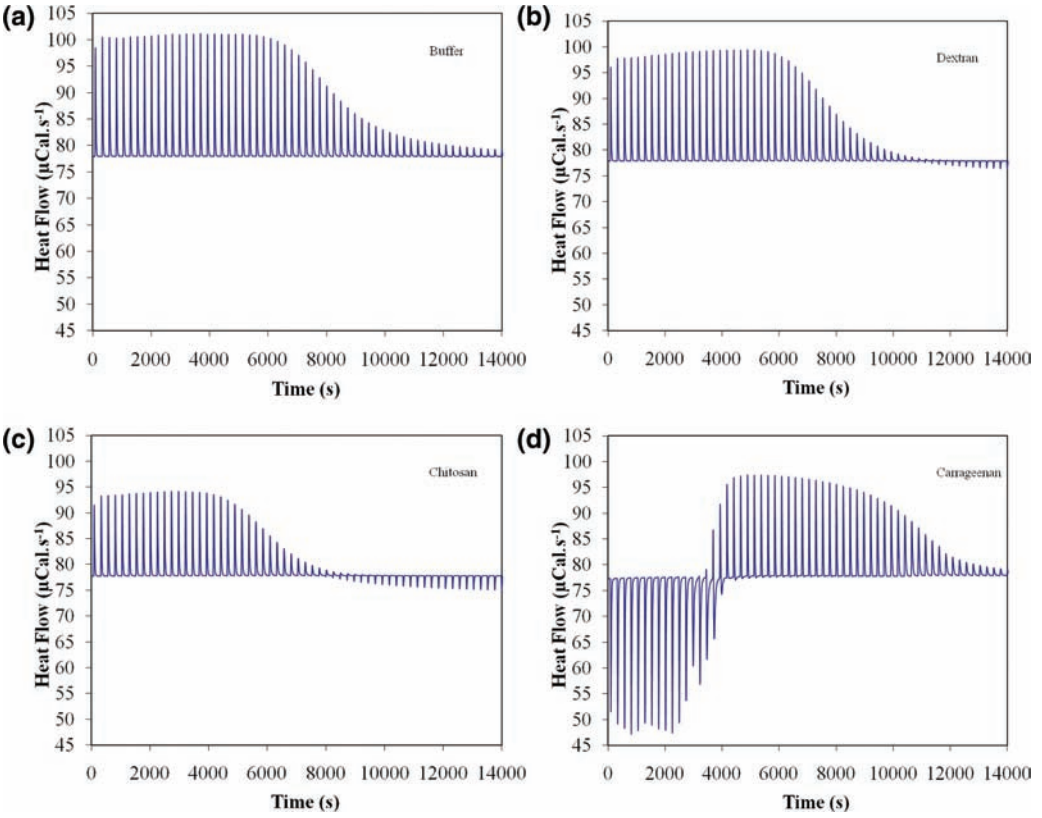

Figure 1. Heat flow versus time profiles resulting from injection of 5 μL aliquots of 1.8% w/v LAE into a 1480 μL titration cell containing different aqueous solutions at pH 3.5 and 25.0 °C: (**a**) buffer; (**b**) 0.1% dextran; (**c**) 0.1% chitosan; (**d**) 0.1% carrageenan.

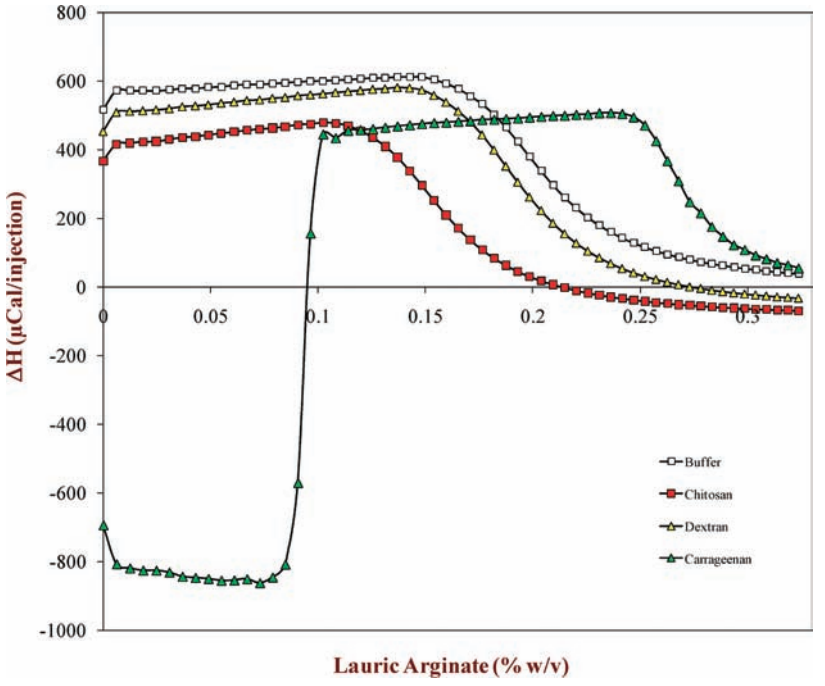

Figure 2. Dependence of enthalpy change per injection on the LAE concentration in the reaction cell when LAE was injected into a reaction cell containing different aqueous solutions at pH 3.5 and 25.0 °C: buffer; 0.1% dextran; 0.1% chitosan; 0.1% carrageenan.

reported in this study and that found in the earlier study may be due to differences in instrument performance, ingredient quality, sample preparation procedure, or mathematical analysis protocol. All the solutions containing only LAE in buffer were transparent, indicating that aggregates large enough to scatter light were not formed.

The presence of 0.1 wt % dextran in the reaction cell caused only a slight modification of the enthalpy curves (**Figures 1b** and **2**), compared to the control sample without polysaccharide in the reaction cell (**Figures 1a** and **2**). The enthalpy change associated with micelle dissociation was similar in the absence or presence of dextran, as demonstrated by the fact that the ΔH

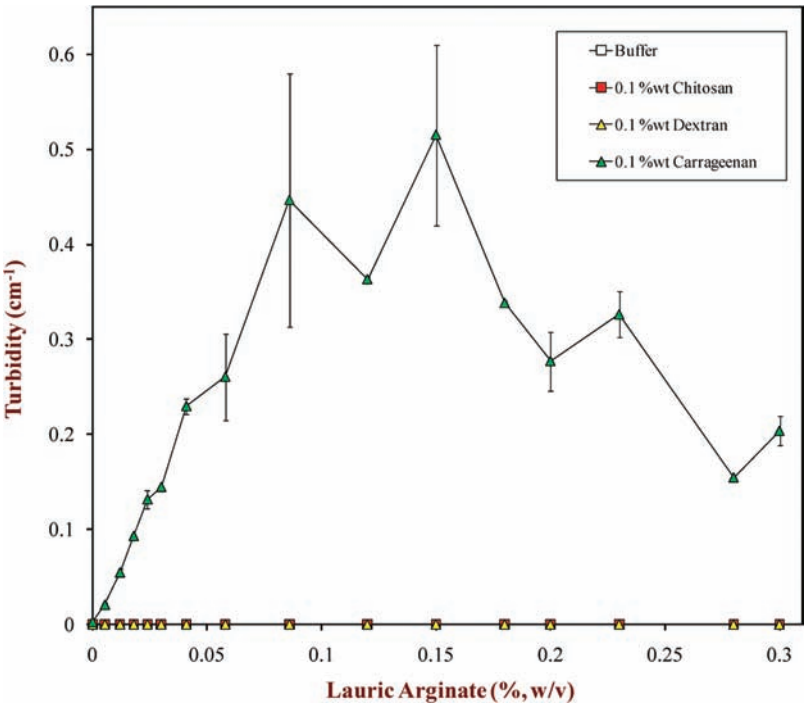

Figure 3. Dependence of sample turbidity on LAE concentration when LAE was injected into a reaction cell containing different aqueous solutions at pH 3.5 and 25.0 °C: buffer; 0.1% dextran; 0.1% chitosan; 0.1% carrageenan.

measured at low LAE levels was similar for the two systems (**Figure 2**). The presence of dextran caused little change in the critical micelle concentration of the LAE determined from the inflection point (cmc = 0.18 ± 0.01 wt %), suggesting that there was little interaction between this neutral polysaccharide and the cationic LAE. The dextran−LAE solutions remained optically transparent at all LAE concentrations (**Figure 3**), indicating that no complexes large enough to scatter light were formed.

The presence of 0.1 wt % cationic chitosan in the reaction cell caused an appreciable change in the enthalpy titration curves (**Figures 1c** and **2**), compared to the control sample without polysaccharide (**Figures 1a** and **2**). In general, the overall shape of the enthalpy versus LAE concentration profile was similar to the control, but the enthalpy changes shifted downward in the presence of chitosan. The enthalpy changes at low LAE concentrations became less endothermic, while those at high LAE concentrations became more exothermic (**Figure 2**). The presence of chitosan also caused an appreciable decrease in the effective critical micelle concentration of the LAE (cmc* = 0.14 ± 0.01 wt %) compared to the control. A possible explanation of this phenomenon is an excluded volume effect. There would be a relatively strong electrostatic repulsion between the cationic chitosan molecules and the cationic LAE molecules, which would limit the volume of solution available to the LAE molecules. This would be equivalent to increasing the net concentration of LAE molecules within the remaining aqueous solution. It is therefore possible to estimate the magnitude of the excluded volume (Φ_{exc}) in the reaction cell from the difference in the cmc measurements: Φ_{exc} = (cmc − cmc*)/cmc, where cmc and cmc* are the measured critical micelle concentrations in the absence and presence of polysaccharide. We calculated that the excluded volume in the presence of 0.1 wt % chitosan was about 26%. This value is much higher than the weight percent of chitosan because of the range of the electrostatic interactions. The dextran and chitosan solutions also remained optically clear at all LAE concentrations (**Figure 3**), indicating that no large complexes were formed.

The presence of 0.1 wt % carrageenan in the reaction cell also caused an appreciable change in the enthalpy titration curves (**Figures 1d** and **2**), compared to the control (**Figures 1a** and **2**), indicating that there was some form of interaction between the cationic surfactant and anionic biopolymer. As described previously (*6*), it is convenient to divide the enthalpy versus surfactant concentration profile into a number of different regions for the oppositely charged surfactant−polysaccharide systems depending on the nature of the interactions taking place:

Region I: 0−0.1 wt % LAE. In this region, the enthalpy change was highly exothermic in the presence of carrageenan but endothermic in its absence (**Figure 2**). This indicated that there was a highly *exothermic* interaction between the cationic LAE and the anionic carrageenan. We postulate that the LAE molecules titrated into the reaction cell bound strongly to the carrageenan molecules. It is likely that the positive headgroups of the LAE molecules bound to negative carboxylic acid groups on the carrageenan molecules through electrostatic attraction. The ITC data do not allow us to establish whether LAE micelles dissociated into monomers and then the monomers bound to the carrageenan or whether the LAE micelles bound directly to the carrageenan. We postulate that the carrageenan molecules had become saturated with LAE at the end of region I, which suggests that there was about 0.1 wt % LAE bound per 0.1 wt % carrageenan at saturation.

Region II: 0.1−0.25 wt % LAE. In this region, the enthalpy change was fairly similar (highly endothermic) in the presence and absence of carrageenan, indicating that there was little direct interaction between the polysaccharide and surfactant. The carrageenan molecules had become saturated with LAE at the end of region 1. Hence, any additional LAE micelles titrated into the reaction cell dissociated into *monomers* because the free surfactant concentration in the aqueous phase was below the cmc, thereby leading to a highly endothermic enthalpy change. In this case, the effective cmc of the LAE in the presence of carrageenan was greater than in the absence of polysaccharide (cmc* = 0.25 wt %). The actual cmc of the LAE in the aqueous

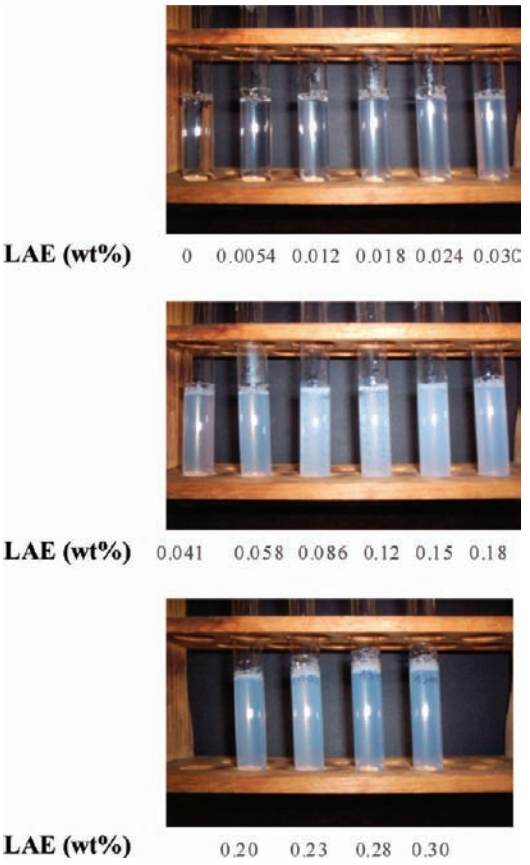

Figure 4. Visual appearance of aqueous solutions containing 0.1% carrageenan and different levels of LAE.

phase of this system should therefore be equal to cmc* (~0.25 wt %) minus the amount of LAE bound to the carrageenan molecules at saturation (~0.1 wt %), which leads to a cmc value of ~0.15% LAE. This value is in fairly good agreement with the value of 0.19% determined for the cmc in buffer solution. The reason that it is lower may be due to the presence of counterions that screen the electrostatic interactions or to excluded volume effects as discussed earlier.

Region III: >0.25 wt % LAE. In this region, the enthalpy change became progressively less endothermic with increasing surfactant concentration, which followed a similar trend as that observed in the absence of carrageenan but at higher surfactant concentrations. We postulate that the concentration of free surfactant in the continuous phase had increased above the cmc so that any additional LAE micelles titrated into the reaction cell remained as micelles. The relatively small enthalpy changes observed at higher surfactant concentrations can be attributed to enthalpy of dilution effects, i.e., alterations in the distance (and therefore molecular interactions) between the micelles and other components within the reaction cell.

The turbidity of the carrageenan−LAE solutions increased with increasing LAE concentrations from around 0 to 0.15 wt %, indicating the formation of complexes that were large enough to scatter light (**Figure 3**). At higher LAE concentrations, the turbidity decreased somewhat, which suggested that there was some reduction in the number and/or size of the electrostatic carrageenan−LAE complexes formed. Visible observation of the carrageenan−LAE solutions confirmed that there was a change in the structure of the complexes formed in the solutions with increasing LAE concentration (**Figure 4**). Initially, the solutions became increasingly turbid as the LAE concentration was increased but remained homogeneous in appearance.

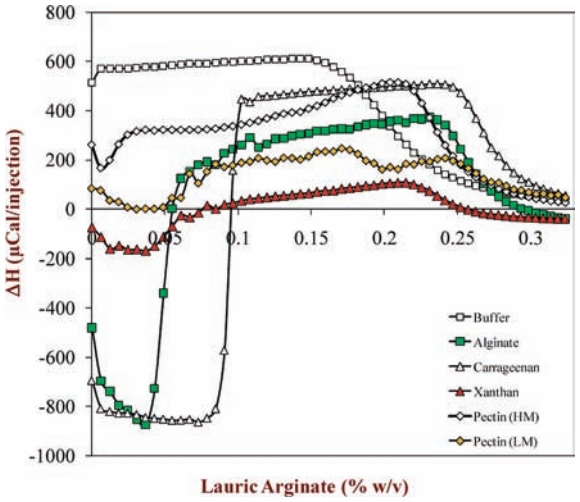

Figure 5. Dependence of enthalpy change per injection on the LAE concentration in the reaction cell when LAE was injected into a reaction cell containing different aqueous solutions at pH 3.5 and 25.0 °C: buffer or 0.1% polysaccharide solutions.

At intermediate LAE concentrations (0.086 and 0.12 wt %) large aggregates could be observed in the solutions by the naked eye and by optical microscopy. This effect may have been due to charge neutralization of the complexes and bridging of the anionic carrageenan molecules by cationic LAE monomers or micelles. However, at higher LAE concentrations (≥0.15 wt %), the solutions again became homogeneously cloudy and were stable to gravitational separation, suggesting that the complexes formed were large enough to scatter light but too small to rapidly sediment. These results suggest that the carrageenan molecules may have become saturated with LAE, which would have increased the net charge and electrostatic repulsion between the complexes as well as decreased the number of free anionic groups on the polysaccharide backbone available for formation of electrostatic bridges.

These measurements clearly indicate that there is a distinct difference in the behavior of different kinds of polysaccharides with LAE. Cationic polysaccharides reduce the effective cmc of the cationic surfactant by reducing the available solution volume through electrostatic repulsive interactions (thereby increasing the effective surfactant concentration), whereas anionic polysaccharides increase the effective cmc by surfactant binding through electrostatic attractive interactions. Neutral polysaccharides appear to have little impact on the behavior of LAE in solution.

Influence of Anionic Polysaccharide Type. In this series of experiments, we compared the interactions of LAE with various kinds of anionic polysaccharides typically used in foods: carrageenan, pectin, xanthan, and alginate. These polysaccharides were chosen because they have different molecular structures and charge characteristics as outlined in Materials and Methods. The enthalpy change versus LAE concentration profiles for the different anionic polysaccharides are shown in **Figure 5**. There were appreciable differences in the enthalpy profiles for the various kinds of anionic polysaccharides, indicating that the nature of the surfactant−polysaccharide interactions was different.

Alginate and Carrageenan. The general shape of the enthalpy versus LAE concentration profiles were fairly similar for alginate and carrageenan (**Figure 5**), which are both linear anionic polysaccharides with relatively high linear charge densities (*10*). Alginate molecules have one carboxyl group per monosaccharide unit along their polysaccharide chains, whereas carrageenan molecules have one sulfate group per monosaccharide unit (*8*).

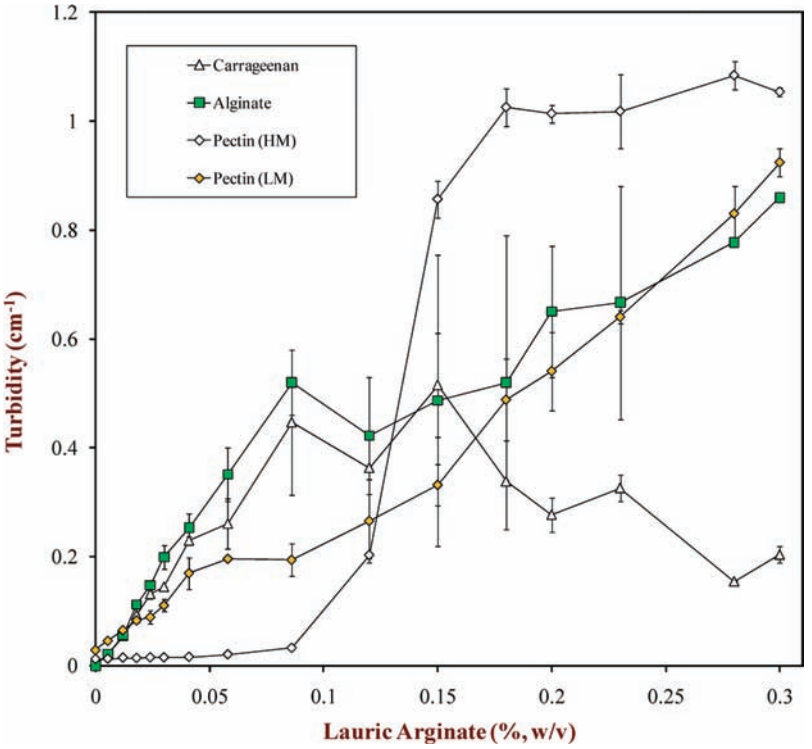

Figure 6. Dependence of sample turbidity on LAE concentration when LAE was injected into a reaction cell containing different aqueous solutions at pH 3.5 and 25.0 °C: buffer or 0.1% polysaccharide solutions.

The enthalpy change was highly exothermic at low LAE concentrations, indicating strong surfactant binding until saturation is reached (region I), then became highly endothermic at intermediate LAE concentrations indicating dissociation of nonbound micelles as they were titrated into the reaction cell (region II), and then became less endothermic indicating that the LAE concentration in the aqueous phase exceeded the cmc so that micelle dissociation no longer occurred (region III). The width of region I was appreciably greater for carrageenan (0−0.1 wt % LAE) than for alginate (0−0.07 wt % LAE), which suggests that carrageenan was able to bind more surfactant molecules before it became saturated. If it is assumed that the average molecular weight of a monosaccharide subunit is 162 g mol^{-1} and the molecular weight of LAE is 421 g mol^{-1} (*6*), then the binding capacities of carrageenan and alginate expressed on a molar basis were about 0.38 and 0.27 LAE per monosaccharide, respectively. For both alginate and carrageenan there was initially a progressive increase in the solution turbidity with increasing LAE concentration (**Figure 6**), indicating the formation of insoluble complexes that were large enough to scatter light. In general, the appearance of LAE−alginate solutions (**Figure 7**) followed a similar trend as LAE−carrageenan solutions, being homogeneous and cloudy at low LAE concentrations (< 0.03 wt %), forming large aggregates that sediment at intermediate LAE concentrations (0.03 − 0.23 wt %), and being homogeneous and cloudy again at high LAE concentrations (≥0.28 wt %) (full data not shown). These results suggest that relatively stable colloidal dispersions of LAE−carrageenan and LAE−alginate can be formed at either low or high LAE concentrations, which may have important implications for their practical utilization within foods.

High and Low Methoxyl Pectin. The enthalpy−LAE profiles of the two types of pectin were appreciably different from that of the alginate and carrageenan (**Figure 5**). At low LAE concentrations, the enthalpy change was less endothermic in the presence of pectin than in its absence, suggesting that there was still an exothermic interaction between the cationic LAE and the anionic pectin molecules. However, the interaction seemed considerably weaker (less exothermic) than that measured for alginate and carrageenan. This may have been because pectin has a lower charge density and also because pectins are branched molecules (*10*). At intermediate LAE concentrations, the enthalpy change was highly endothermic for the two pectin samples, indicating dissociation of nonbound micelles titrated into the reaction cell (region II), and then became less endothermic indicating that the LAE concentration in the aqueous phase exceeded the cmc (region III). There were appreciable differences between the low methoxyl (LM) and high methoxyl (HM) pectin samples. At low LAE concentrations, the difference in enthalpy change in the absence and presence of polysaccharide was much larger for the LM−pectin than for the HM−pectin sample, which can be attributed to the fact that the former has a higher number of negatively charged carboxyl groups available for the positively charged surfactant head groups to interact with.

The turbidity of the LM−pectin samples increased progressively with increasing LAE concentration, indicating that relatively large insoluble complexes were formed as soon as the surfactant was added to the system (**Figure 6**). Visual observation of the LM−pectin samples (**Figure 7**) indicated that relatively large aggregates were formed that tended to move upward ("cream") at relatively low LAE concentrations (< 0.23 wt %) but move downward ("sediment") at higher LAE concentrations after 24 h of storage (full data not shown). This suggests that the surfactant−polysaccharide complexes formed were less dense than water at low LAE concentrations but denser than water at high LAE concentrations. The complexes could be dispersed by shaking the test tubes, but they rapidly separated into two phases again after a few hours of storage, indicating that they were not very stable to aggregation and gravitational separation. The HM−pectin samples remained optically clear from 0 to 0.09 wt % LAE, but then their turbidity increased steeply from 0.09 to 0.18 wt % LAE before leveling off at higher LAE concentrations

Figure 7. Visual appearance of aqueous solutions containing 0.1% polysaccharide and different levels of LAE.

(**Figure 6**). This suggests that LAE may have formed soluble complexes with HM−pectin at low concentrations but formed insoluble complexes at higher concentrations. At low LAE concentrations, there may have been a sufficiently strong electrostatic or steric repulsion between the HM−pectin/LAE complexes to prevent extensive aggregation. However, once a critical LAE concentration was exceeded, the complexes may have aggregated through either charge neutralization or bridging effects. After 24 h of storage, the HM−pectin/LAE solutions appeared transparent from 0 to 0.09 wt % LAE, were homogeneous and cloudy at 0.12 wt % LAE, but formed a thin (< 10% of sample height) turbid gel-like layer at the bottom of the test tubes at higher LAE concentrations (**Figure 7**). When the tubes were shaken, they formed a cloudy homogeneous suspension, which settled out again after 24 h of storage.

Xanthan. The general shape of the enthalpy versus LAE concentration profile of the xanthan was similar to those of the other samples (**Figure 5**), with a trough at low LAE concentrations (region I), a broad peak at intermediate LAE concentrations (region II), and a reduction in the magnitude of this peak at high LAE concentrations (region III). However, the magnitudes of the peaks and troughs were much smaller than those recorded for the other polysaccharides. This suggests that the nature of the interactions of LAE with xanthan was also different. Indeed, visual observation of the xanthan/LAE samples indicated that

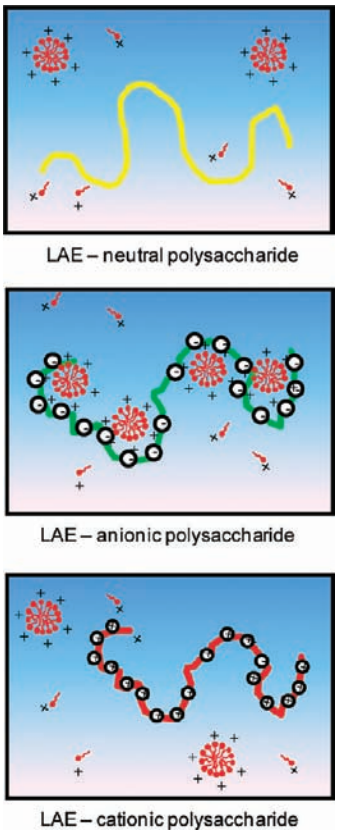

Figure 8. Schematic representation of the surfactant−polymer complexes formed between cationic LAE and anionic, neutral, or cationic polysaccharides.

large whitish gel-like aggregates were formed in the samples at all LAE concentrations (**Figure 7**). Xanthan is a fairly rigid anionic polysaccharide, and consequently it may not be able to wrap around the cationic surfactant micelles, which would mean that extensive complex association might occur through a bridging mechanism as indicated in recent studies with other cationic micelles (*11*).

Characteristics and Importance of Surfactant−Polysaccharide Interactions. Over the past few decades, there have been extensive studies of the interactions of surfactants with polymers in aqueous solutions, which have been reviewed in detail elsewhere (*12*−*15*). These studies have identified some of the most important characteristics of surfactant−polymer complexes: the number of surfactant monomers bound per polymer chain; the strength of surfactant−polymer interactions; the nature of the interactions (e.g., electrostatic, hydrophobic, hydrogen bonding, and/or van der Waals); the structural organization of the surfactant molecules along the polymer chain (e.g., monomers versus clusters); the change in polymer conformation and interactions after surfactant binding; and the physicochemical properties of the complexes formed (e.g., rheology, stability, and optical properties). Surfactant−polymer complexes with different physicochemical and functional characteristics can be formed depending on polymer type, surfactant type, polymer and surfactant concentrations, temperature, ionic strength, pH, and order of addition.

Our study has shown that isothermal titration calorimetry (ITC) can provide valuable information about interactions between a food-grade cationic surfactant (LAE) and various food-grade polysaccharides. The technique was able to quantify enthalpy changes associated with the dissociation of micelles in biopolymer free solutions and with the binding of surfactant to polysaccharide in solutions containing biopolymer. The enthalpy

versus surfactant profiles highlighted that different phenomena occurred in the surfactant−biopolymer solutions depending on polysaccharide charge. The cmc of cationic LAE is reduced in the presence of cationic polysaccharides because of excluded volume effects but is increased in the presence of anionic polysaccharides because of surfactant binding. Turbidity measurements and visual observations indicated that either soluble or insoluble surfactant−polysaccharide complexes could be formed depending on polysaccharide type and concentration. HM−pectin was able to form soluble complexes with LAE at relatively low concentrations, whereas carrageenan and alginate were able to form relatively stable colloidal dispersions at high LAE concentrations. Binding of LAE to anionic polysaccharides was attributed to electrostatic attraction between the cationic surfactant and the anionic charge groups on the polysaccharide backbone.

In summary, this study has shown that there are appreciable differences between the binding and aggregation behavior of LAE with food-grade polysaccharides depending on polysaccharide type (**Figure 8**). The interaction of cationic LAE with polysaccharides may have important implications for the application of lauric arginate as a functional ingredient in food and other industrial applications. For example, complexation interactions may impact the ability of LAE to act as an antimicrobial agent or they may impact its sensory attributes (i.e., ability to cause astringency). Further studies are therefore needed to quantify the influence of LAE−polysaccharide interactions on the antimicrobial and sensory attributes of LAE. In addition, further studies should also be carried out to provide more detailed information about how the composition, structure, and physicochemical properties of LAE−polysaccharide complexes depend on polysaccharide molecular characteristics. This will require the application of a wide range of thermodynamic, physicochemical, and structural techniques to well-characterized polysaccharide and surfactant systems (*15*).

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