Maltodextrin−Anionic Surfactant Interactions: Isothermal Titration Calorimetry and Surface Tension Study

A. Wangsakan, P. Chinachoti, and D. J. McClements*

Biopolymers and Colloids Research Group, Department of Food Science, University of Massachusetts, Amherst, Massachusetts 01003

Interactions between maltodextrin (DE = 10) and an anionic surfactant (sodium dodecyl sulfate, SDS) were studied in a buffer solution (pH 7.0, 10 mM NaCl, 20 mM Trizma, 30.0 °C) using isothermal titration calorimetry (ITC), surface tension, differential scanning calorimetry (DSC), and turbidity techniques. ITC measurements indicated that the binding of SDS to maltodextrin was exothermic and that, on average, one SDS monomer bound per 24 glucose units of maltodextrin at saturation. Surface tension measurements indicated that there was a critical surfactant concentration (∼0.05 mM SDS) below which surfactant and maltodextrin did not interact and that the amount of surfactant bound to the maltodextrin above this concentration increased with increasing maltodextrin concentration. Turbidity measurements indicated that the solutions remained transparent at all maltodextrin (0−1 wt %) and SDS (0−20 mM) concentrations studied, which suggested that phase separation did not occur. DSC measurements indicated that no phase transitions occurred between 10 and 110 °C for maltodextrin solutions (0.5 wt %) in the presence or absence of surfactant. A phase diagram was developed to describe the interactions between SDS and maltodextrin.

Keywords: *Isothermal titration calorimetry; maltodextrin; surfactant; binding*

INTRODUCTION

Interactions between biopolymers and surface-active lipids are important in many industrial and natural processes. Surfactants alter the conformation and self-association of biopolymers in aqueous solutions, which leads to changes in the appearance, stability, and rheology of the solution (*1*−*9*). Biopolymer−surfactant interactions at droplet surfaces alter the physicochemical properties of oil-in-water emulsions stabilized by biopolymers (*10*−*15*). The binding of amphiphilic bile acids to water-soluble dietary fibers in the small intestine has been proposed to be one of the major mechanisms by which fibers reduce cholesterol and colon cancer (*16*−*20*). The quality of many food products may also be influenced by interactions of biopolymers with other types of small amphiphilic molecule, such as flavors, antioxidants, pro-oxidants, and preservatives (*21*−*27*).

Amphiphilic molecules may interact with biopolymers in a variety of different ways. When amphiphilic molecules are mixed with a solution of polymer molecules, they may exist in either a free or a bound form (*28*−*30*). In either of these forms, the amphiphilic molecules may be present as individual molecules or as molecular clusters (e.g., micelles). The partitioning of amphiphilic molecules between different locations depends on the concentrations and molecular characteristics of the polymer and amphiphile as well as on prevailing environmental conditions such as temperature, pressure, and solvent composition (*1*, *8*). A variety of physicochemical mechanisms may either favor or oppose binding, including electrostatic interactions, hydrophobic interactions, hydrogen bonding, and configurational entropy (*31*−*33*). The relative importance of these mechanisms depends on the precise nature of the polymer−amphiphile system and usually has to be established experimentally. When one or more amphiphilic molecules bind to a biopolymer molecule, they may induce a conformational change in the biopolymer or change the degree of self-association of the biopolymer molecule with its neighbors (*34*). Changes in the conformation or aggregation of biopolymer molecules may lead to an appreciable change in their functional attributes, e.g., surface activity, thickening, or gelation (*35*).

The objective of our study was to improve the current understanding of interactions between starch and surface-active lipids. Starch is one of the most widely used functional biopolymers in food products (*36*). Natural starch is usually composed of a mixture of amylose and amylopectin, which are α-polyglucans that have different molecular structures and functional properties (*37*). It is well-established that amylose, the linear component of starch, can form helical inclusion complexes with a variety of compounds, e.g., iodine (*38*, *39*), alcohols (*40*), free fatty acids (*41*, *42*), glyceryl monostearate (*43*, *44*), long-chain aliphatic compounds (*45*), and lysolecithin (*46*). The formation of these complexes has been shown to retard the firming and retrogradation of starch (*47*), to reduce the stickiness of starch, to improve the freeze−thaw stability of starch (*48*), to prevent leaching of amylose during gelatinization, to inhibit the swelling of starch granules heated in water, and to reduce the water-binding capacity of starch (*49*). In addition, in vitro and in vivo studies have shown that the formation of amylose−lipid complexes increases the resistance of starch to enzymatic digestion (*50*−*53*). An improved understanding of the origin and nature of the interactions between starch and surface-active lipids would

* To whom correspondence should be addressed.

10.1021/jf0103471 CCC: $20.00
Published on Web 09/14/2001

lead to the design of foods with improved nutritional, physicochemical, and sensory properties.

In this study, we used a maltodextrin−anionic surfactant (SDS) system to model the interactions between starch and amphiphilic lipids. This system was chosen because the maltodextrin and surfactant were both water-soluble and had well-defined physicochemical properties. Maltodextrins are digestive byproducts of starch that contain linear amylose and branched amylopectin degradation products (*54*). They are commonly used as functional ingredients in foods because of their ability to form gels, retain water, modify texture, and encapsulate lipids (*54*−*56*). Previous studies have shown that linear chains within maltodextrin and starch molecules form helical structures upon interacting with hydrophobic tails of amphiphilic lipid molecules (*57*). These polysaccharide−lipid complexes have different molecular and physiochemical properties than the polysaccharide alone. Consequently, an improved understanding of the nature of the interactions between polysaccharides and amphiphilic lipids could lead to the development of functional ingredients with enhanced or unique properties. It should be noted that a wide variety of different types of amphiphilic lipids are present in food products, e.g., ionic surfactants, nonionic surfactants, and phospholipids. The anionic surfactant (SDS) used in this study may therefore not accurately model the behavior of many of these lipids, and additional work needs to be carried out using other types of amphiphilic lipids.

MATERIALS AND METHODS

Materials. Maltodextrin DE 10 (Maltrin M 100, lot M9933231) was obtained from Grain Processing Corporation (Muscatin, IA). Sodium dodecyl sulfate (SDS, L-4509, lot 107H0006) and Trizma base (T-1503, lot 29H5442) were purchased from Sigma Chemical Co. (St. Louis, MO). Sodium chloride (lot 7581KXRE) was purchased from Mallinckrodt Baker, Inc. (Paris, KY). Hydrochloric acid solution (HCl, lot 971558) was purchased from Fisher Chemical (Fair Lawn, NJ). Deionized and distilled water was used for the preparation of all solutions.

Solution Preparation. A stock buffer solution (pH 7.0, 10 mM NaCl, 20 mM Trizma) was prepared by dispersing Trizma base and sodium chloride into water and then adjusting the pH with hydrochloric acid solution. (It should be noted that we initially tried potassium phosphate monobasic (KH_2PO_4) as a buffer, but this caused precipitation of SDS, and so we used Trizma instead). Maltodextrin solutions were prepared by dispersing powdered maltodextrin (0.25%, 0.5%, 0.75%, and 1.0% w/v) into stock buffer solution and stirring for 60 min at room temperature before use. Surfactant solutions were prepared by dispersing powdered SDS into stock buffer solution and stirring for 60 min at room temperature before use.

Isothermal Titration Calorimetry. An isothermal titration calorimeter (VP-ITC, Microcal Inc., Northampton, MA) was used to measure enthalpies of mixing at 30.0 °C. The 10-μL aliquots of 35 mM SDS solution were injected sequentially into a 1480-μL reaction cell initially containing either buffer solution or maltodextrin solution. Each injection lasted 20 s, and there was an interval of 300 s between successive injections. The solution in the reaction cell was stirred at a speed of 315 revertants min^{-1} throughout the experiments. All solutions were degassed prior to the measurements being carried out.

Surface Tension Measurements. A digital tensiometer with a Wilhelmy plate (K10ST, Krüss, Charlotte, NC) was used to measure the surface tension of aqueous surfactant solutions in the presence or absence of maltodextrin in a temperature-controlled measurement cell (30.0 ± 0.5 °C). Surfactant solutions were prepared and then stored in a 30 °C water bath overnight. These solutions were then stirred to ensure that they were homogeneous and placed in the tensiometer measurement cell for 20 min before measurements were performed. Three measurements were made on each sample, and the final result was reported as the mean. The standard deviation of the measurements was always better than 0.5 mN m^{-1}.

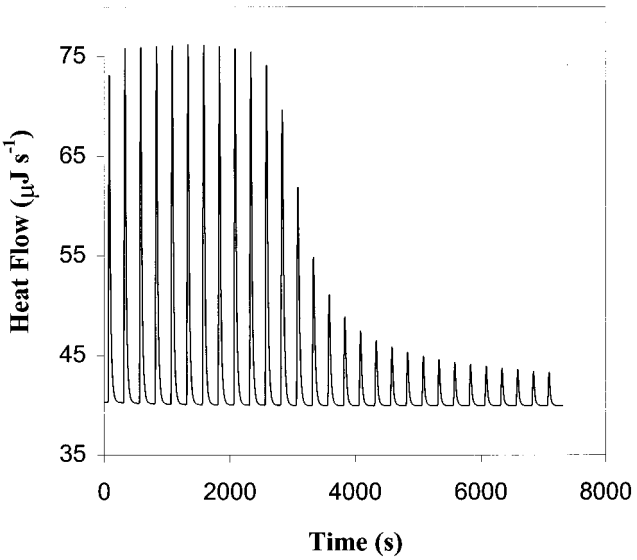

Figure 1. Heat flow vs time profiles resulting from injection of 10-μL aliquots of 35 mM SDS into a 1480-μL reaction cell containing buffer solution at 30.0 °C.

Turbidity Titrations. The 100-μL aliquots of 35 mM SDS solution were injected at 3-min intervals into a glass vial initially containing 14.5 mL of either buffer solution or 1% w/v maltodextrin solution. Solutions were stirred continuously throughout the experiment using a magnetic stirrer. The turbidity at 600 nm (Spectronic 21D, Milton Roy, Rochester, NY) of the maltodextrin solutions was measured at the end of each 3-min period.

Differential Scanning Calorimetry. An ultrasensitive differential scanning calorimetry (VP-DSC, Microcal Inc., Northampton, MA) was used to measure enthalpy changes resulting from heating aqueous solutions of maltodextrin and SDS. The solution to be analyzed was placed in the measurement cell, and buffer solution was placed in the reference cell. The heat flow required to keep a zero temperature difference between the two cells was then recorded as the cells were heated from 10 to 110 °C at 1.5 °C/min. A background scan was carried out using distilled water in both the sample and measurement cells, which was subtracted from the measurements made on the samples.

RESULTS AND DISCUSSIONS

Characterization of SDS Micellization in Buffer Solutions. Initially, ITC and tensiometer experiments were carried out to establish the critical micelle concentration (CMC) of the SDS in the buffer solutions used in this study. A heat flow versus time profile resulting from sequential injections of 10-μL aliquots of surfactant solution (35 mM SDS, pH 7.0, 10 mM NaCl, 20 mM Trizma) into a 1480-μL reaction cell initially containing stock buffer solution (pH 7.0, 10 mM NaCl, 20 mM Trizma) is shown in Figure 1. The surfactant concentration in the injector was well above the CMC, so that the injector initially contained primarily micelles. Initially, a series of large endothermic peaks was observed when the surfactant solution was injected into the reaction cell. These enthalpy changes are the result of micelle dissociation because the surfactant concentration in the reaction cell remained below the CMC for

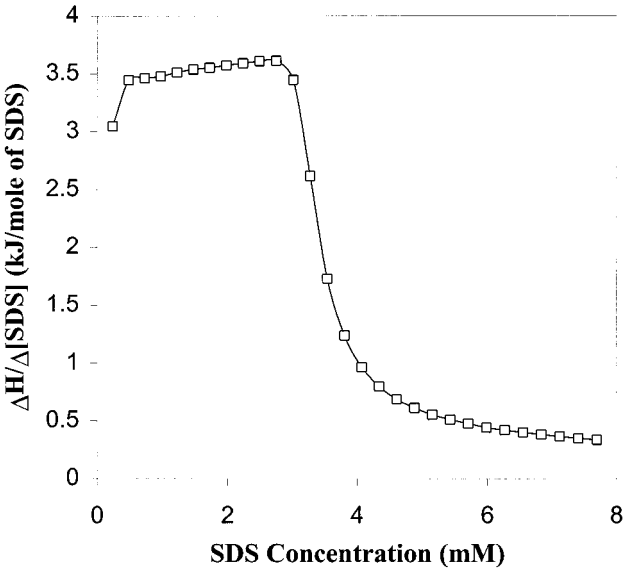

Figure 2. Dependence of enthalpy change per mole of surfactant on the surfactant concentration in the reaction cell for SDS injected into buffer solution at 30.0 °C.

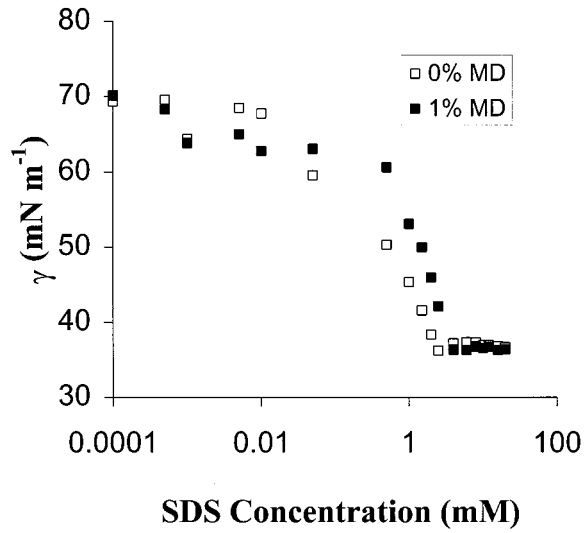

Figure 3. Dependence of surface tension on SDS concentration for aqueous solutions containing 0 and 1% (w/v) maltodextrin at 30.0 °C.

the first few injections (*58*). 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 injected into the reaction cell no longer dissociated. Above the CMC, the enthalpy change is therefore only the result of micelle dilution effects (*58*). The dependence of the enthalpy change per mole of surfactant ($\Delta H/\Delta$[SDS]) injected into the reaction cell on the surfactant concentration in the reaction cell was calculated by integration of the heat flow versus time profiles (Figure 2). The CMC of the SDS was determined from the inflection point in the $\Delta H/\Delta$[SDS] versus surfactant concentration curve as 3.4 ± 0.1 mM.

The CMC of the SDS in the stock buffer solution was also determined by tensiometry. The surface tension (γ) of aqueous buffer solutions containing different SDS concentrations was measured (Figure 3). At low surfactant concentrations (<0.01 mM), the surface tension was similar to that of pure water (~70 mN m^{-1}). As the surfactant concentration was increased, there was a

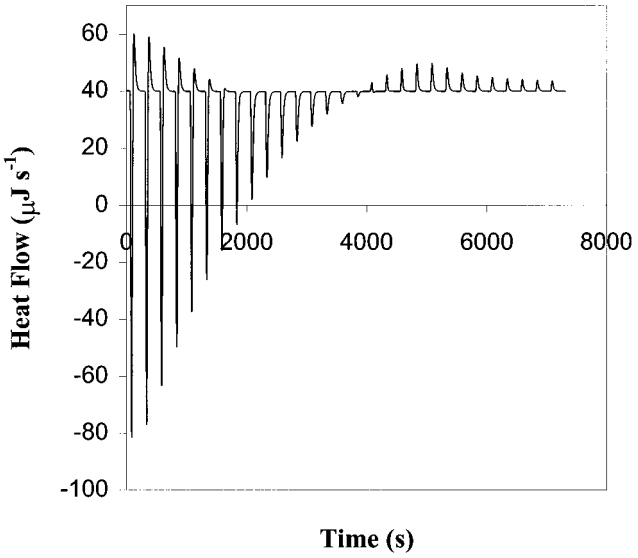

Figure 4. Heat flow vs time profiles resulting from injection of 10-μL aliquots of 35 mM SDS into a 1480-μL reaction cell containing 1% (w/v) maltodextrin solution at 30.0 °C.

sharp decline in the surface tension, indicating adsorption of SDS to the air−water interface. At high surfactant concentrations (>3 mM), the surface tension remained approximately constant as the SDS concentration was increased (~37 mN m^{-1}), which indicated that the surface had become saturated with surfactant. The CMC was defined as the intersection point of linear plots of γ versus log(SDS) extrapolated from (i) the region where the surface was saturated with surfactant and (ii) the region where there was the steepest decrease in surface tension with surfactant concentration. This procedure gave a CMC of 2.2 ± 0.1 mM for SDS (Figure 3), which was slightly lower than the value determined by the ITC technique. It is well-recognized that different analytical methods give slightly different values for the CMC of surfactants because of differences in their sensitivity to monomers and micelles (*59*). It should also be noted that there was a slight minimum in the γ versus log(SDS) curve around the CMC (Figure 3), which is indicative of some surface-active impurities within the SDS. The difference in CMCs determined by the two techniques could therefore also be partly due to the presence of impurities in the SDS. The CMCs determined in this study are in good agreement with those determined by other workers under comparable experimental conditions. For example, the CMC of SDS at room temperature decreases from 8.1 mM at 0 mM NaCl to 1.4 mM at 100 mM NaCl (*59*).

Characterization of SDS−Maltodextrin Interactions. In the absence of maltodextrin, the enthalpy change resulting from the injection of SDS into buffer solution was endothermic below the CMC because of micelle dissociation but decreased appreciably above the CMC because of micelle dilution effects (Figures 1 and 2). In the presence of maltodextrin, there was initially a large exothermic contribution to the enthalpy change at low surfactant concentrations (Figures 4 and 5), which suggested that the SDS interacted with the maltodextrin. The exothermic enthalpy changes associated with these interactions could have been due to binding of SDS to maltodextrin or due to changes in the conformation of the maltodextrin (e.g., a coil-to-helix transition). However, it is not possible to identify the physical origin of the enthalpy changes from ITC

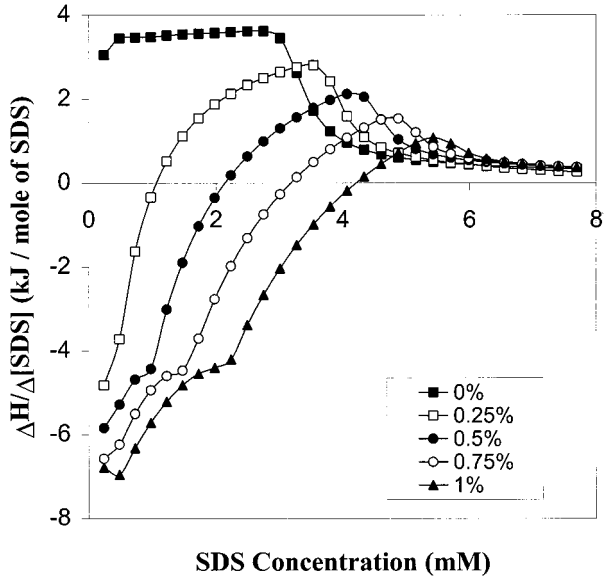

Figure 5. Dependence of enthalpy change per mole of surfactant on the surfactant concentration in the reaction cell for SDS injected into maltodextrin solutions at 30.0 °C.

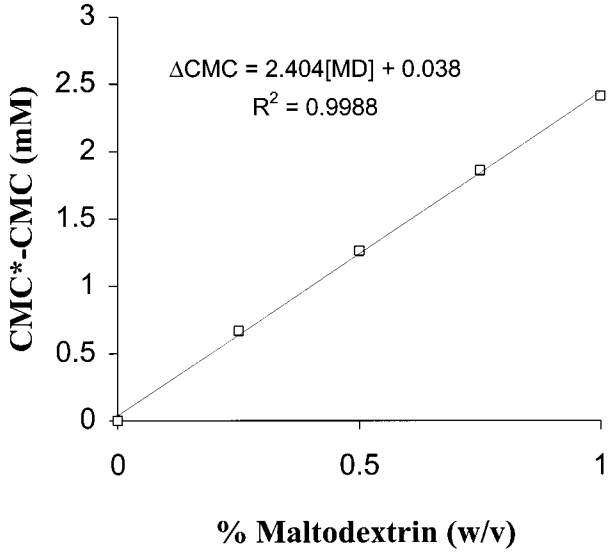

Figure 6. Increase in apparent critical micelle concentration of SDS in maltodextrin−surfactant solutions containing different maltodextrin concentrations at 30.0 °C.

measurements alone. Surface tension measurements were used to provide some information about binding of SDS molecules to maltodextrin (see below). It would also have been useful to monitor changes in the conformation of the maltodextrin molecules (e.g., using optical rotation measurements), but we did not have the appropriate instrumentation available for this study.

The enthalpy change upon injection of SDS into the reaction cell was highly dependent on the initial concentration of maltodextrin present (Figure 5). Nevertheless, the enthalpy change versus surfactant concentration profiles followed a fairly similar pattern for all maltodextrin concentrations. At low SDS concentrations, the enthalpy change was highly exothermic. As the SDS concentration was increased, the enthalpy change increased until it eventually reached an endothermic maximum. At still higher SDS concentrations, the enthalpy change became increasingly less endothermic and eventually tended toward the value observed for injection of SDS into the reaction cell above the CMC in the absence of maltodextrin. The observed changes in the enthalpy profiles can be explained in terms of the interaction of surfactant molecules to the maltodextrin. At low surfactant concentrations, there was an exothermic reaction due to binding of SDS molecules to the maltodextrin. As the surfactant concentration increased, the number of available binding sites on the maltodextrin decreased; hence, the exothermic contribution to the enthalpy change associated with binding was decreased. Eventually, all of the binding sites on the maltodextrin became saturated; therefore, any further SDS micelles injected into the reaction cell dissociated into monomers, leading to an endothermic reaction. When the concentration of free SDS monomers in the aqueous phase increased above the CMC, micelle dissociation no longer occurred, and the enthalpy change was only due to micelle dilution effects. Consequently, the enthalpy changes at high surfactant concentrations are similar to those observed for the injection of SDS into the reaction cell above the CMC in the absence of maltodextrin.

An apparent critical micelle concentration (CMC*) for each of the maltodextrin−SDS solutions was determined from the inflection point in the $\Delta H/\Delta$[SDS] versus [SDS] curves that occurred after the endothermic peak (Figure 5). The difference between the CMC of the surfactant in the presence and absence of maltodextrin (ΔCMC = CMC* − CMC) should be equal to the amount of surfactant that binds to the maltodextrin at saturation, which is normally expressed by the symbol T_2 (*28*, *29*). There was a linear increase in ΔCMC with maltodextrin concentration (Figure 6), which is consistent with the behavior of other types of natural and synthetic polymer (*28*, *29*). The slope of the linear plot of ΔCMC versus maltodextrin concentration was used to calculate that on average there was one SDS molecule bound per 24 glucose units in the maltodextrin at saturation (assuming a molecular weight of 171 g/glucose unit). This is close to the value of one SDS molecule bound per 29 glucose units in amylose found by previous workers (*57*). The maltodextrin used in this study had an average degree of polymerization of 10 glucose units, so there was an average of one SDS molecule bound per two maltodextrin molecules. This suggests that not all of the maltodextrin molecules were capable of binding surfactant molecules. Previous studies suggest that the binding of amphiphilic lipids to glucose polymers results in the formation of a complex in which the hydrophobic tail of the lipid is surrounded by a helix of glucose monomers (*57*, *60*). Commercial maltodextrins are highly polydisperse, i.e., they contain a mixture of carbohydrate molecules of widely differing chain length. It is therefore possible that some of the shorter maltodextrin molecules in our study were not long enough to form stable helices around the tail of the SDS molecules. The hydrocarbon tail of a SDS molecule is approximately 1.7 nm long (*61*). Previous studies indicate that linear alcohols and fatty acids form helices with six D-glucosyl residues per turn (*62*), which have an average length of about 0.8 nm per turn (*63*). The alkyl chains of SDS molecules have been shown to fit into helices of about 12−16 glucose units, corresponding to a length of about 1.6−2.0 nm. It is therefore possible that only those maltodextrin molecules in the solution that have a degree of polymerization around 12 or higher may have sufficient glucose units to completely surround the hydrocarbon tail of SDS and form stable helices.

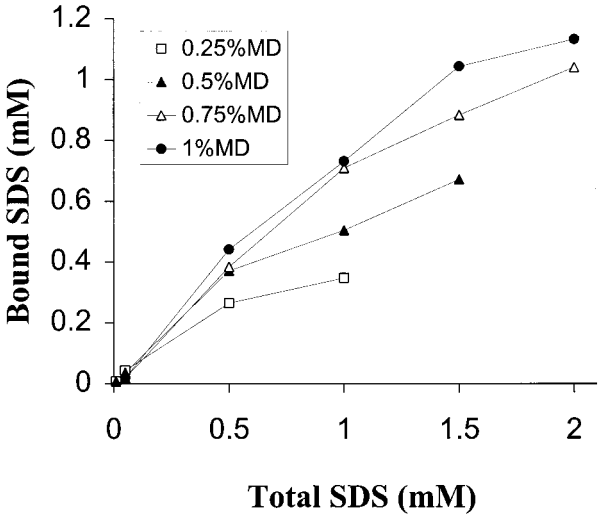

Figure 7. Binding isotherms determined using tensiometer for maltodextrin–surfactant solutions containing different maltodextrin concentrations at 30.0 °C.

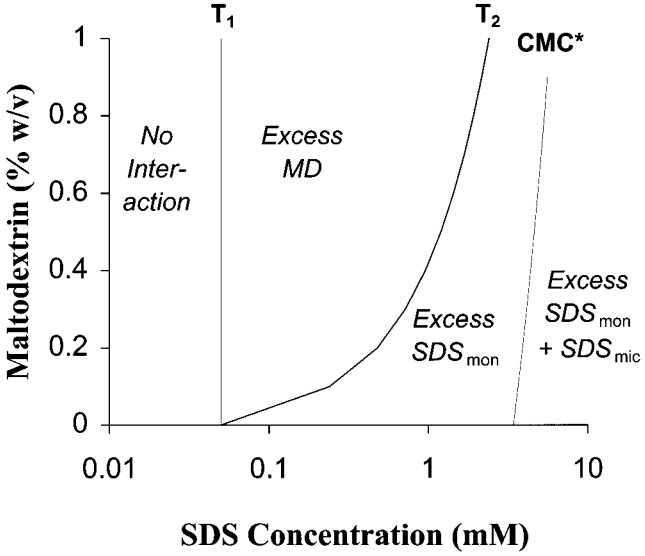

Figure 8. Phase diagram for maltodextrin–SDS solution at 30.0 °C, constructed from surface tension and ITC measurements. SDS_{mon} is the concentration of the surfactant monomers, and SDS_{mic} is the concentration of the surfactant micelles.

Surface tension measurements were used to provide information about the binding of SDS to maltodextrin. The free SDS concentration ($[SDS]_{free}$) in the aqueous phase of a maltodextrin–surfactant solution was estimated by measuring the surface tension of the solution. The value of $[SDS]_{free}$ was then determined from a plot of surface tension versus surfactant concentration in the absence of maltodextrin (Figure 3). This approach assumes that the change in surface tension at the air–water interface is due solely to the adsorption of SDS. If the maltodextrin–SDS complex were surface active, then it would also reduce the surface tension (*57*). In fact, we found that there was a slow decrease in the interfacial tension of maltodextrin–SDS solutions over time (0–24 h), suggesting that the complex did slowly adsorb to the interface. For this reason, we always made measurements 20 min after placing a fresh sample into the tensiometer so that the measured change in surface tension was dominated by the rapidly adsorbing SDS monomers rather than by the slowly adsorbing maltodextrin–SDS complexes. The tensiometer technique was also restricted in the range of free surfactant concentrations that it could determine because the surface tension was fairly insensitive to SDS concentration at low (<0.05 mM) and high (>2 mM) surfactant concentrations (Figure 3). For this reason, free SDS concentrations were only calculated for solutions that had surface tensions greater than 45 mN m^{-1} and less than 65 mN m^{-1}.

The influence of maltodextrin on the surface tension versus surfactant concentration profile for a 1% (w/v) maltodextrin solution is shown in Figure 3. The change in the amount of bound surfactant with increasing SDS concentration for solutions containing different maltodextrin concentration is shown in Figure 7. The surface tensions of the surfactant solutions in the presence and absence of maltodextrin were fairly similar up to SDS concentrations of ~0.05 mM, indicating that there was no significant binding of surfactant to the maltodextrin. This lower critical binding concentration, usually referred to as T_1, was fairly independent of maltodextrin concentration, in agreement with the behavior of other types of polymers (*28*, *29*). At surfactant concentrations greater than T_1, the degree of SDS binding increased with maltodextrin concentration (Figure 7). The binding of surfactant to the maltodextrin in this region is demonstrated by the rightwards shift in the surface tension versus SDS concentration curve (Figure 3). It was not possible to determine the surfactant concentration where the maltodextrin became saturated with SDS using tensiometer measurements because the surface tension was fairly insensitive to surfactant concentration around and above the CMC.

By combining data from the surface tension and ITC techniques, it was possible to construct a phase diagram for the maltodextrin–SDS system (Figure 8). At low surfactant concentrations (SDS < T_1), there was no interaction between SDS and maltodextrin. At intermediate surfactant concentrations (T_1 < SDS < T_2), SDS bound to maltodextrin, and there was an equilibrium between surfactant molecules present in the maltodextrin–SDS complex and those that existed as monomers in the aqueous phase. At higher surfactant concentrations (T_2 < SDS < CMC*), the maltodextrin became saturated with SDS, and the excess surfactant existed as monomers in the aqueous phase. Above the apparent critical micelle concentration of the surfactant (SDS > CMC*), the maltodextrin was saturated with SDS, and the excess surfactant existed as a mixture of monomers and micelles in the aqueous phase.

The construction of the phase diagram helps us to interpret some of the finer details of the $\Delta H/\Delta[SDS]$ versus [SDS] profiles determined by ITC (Figure 5). The first injection of SDS into the maltodextrin solutions always resulted in a surfactant concentration in the reaction cell that was greater than T_1; therefore, the region where no interaction between surfactant and maltodextrin occurred was not observed in the ITC experiments. The break in the $\Delta H/\Delta[SDS]$ versus [SDS] plots, which occurred at relatively low surfactant concentrations where the enthalpy change was still highly exothermic, corresponded to the surfactant concentration where the maltodextrin became saturated with SDS. For example, this break occurred at approximately 2.3 mM SDS for the 1% (w/v) maltodextrin solution (Figure 5), which was close to the saturation concentration of 2.4 mM SDS determined from the CMC* measurements (Figure 6).

Influence of SDS−Maltodextrin Interactions on Functional Properties. Turbidity measurements were used to determine if any phase separation occurred in the maltodextrin−SDS solutions. No significant change in the turbidity (at 600 nm) of 1% (w/v) maltodextrin solutions was observed when the SDS concentration was increased from 0 to 20 mM, which suggested that there was no appreciable aggregation of maltodextrin−SDS complexes and no thermodynamic incompatibility of the components. Ultrasensitive DSC measurements were used to determine whether SDS altered the conformational stability of maltodextrin molecules, e.g., the helix−coil transition. No enthalpy peaks were observed when 1% (w/v) maltodextrin solutions were scanned from 10 to 110 °C in the presence of 0, 3 and 6 mM SDS, which suggested that any helix−coil transitions were either too small to measure or occurred outside the measurement temperature range.

CONCLUSIONS

This study has shown that isothermal titration calorimetry and surface tension measurements can provide valuable information about the interactions between maltodextrin and an anionic surfactant. A phase diagram for the SDS−maltodextrin system was constructed using data from the two techniques. The ITC measurements indicated that the binding of SDS to maltodextrin was exothermic and that on average one SDS monomer was bound per 24 glucose units of maltodextrin at saturation. Surface tension measurements indicated that there was a critical surfactant concentration below which surfactant and maltodextrin did not interact and that the amount of SDS bound to the maltodextrin above this concentration increased with increasing maltodextrin concentration. In future work, it would be useful to correlate the data from binding measurements to changes in maltodextrin conformation resulting from binding.

LITERATURE CITED

(1) Goddard, E. D.; Ananthapadmanabhan, K. P. *Interactions of Surfactants with Polymers and Proteins*; CRC Press: Boca Raton, FL, 1993.

(2) Biswas, S. C.; Chattoraj, D. K. Polysaccharide−surfactant interaction. 1. Adsorption of cationic surfactants at the cellulose−water interface. *Langmuir* **1997**, *13*, 4505−4511.

(3) Biswas, S. C.; Chattoraj, D. K. Polysaccharide−surfactant interaction. 2. Binding of cationic surfactants to carboxymethyl cellulose and dextrin. *Langmuir* **1997**, *13*, 4512−4519.

(4) Caram-Lelham, N.; Hed, F.; Sundelof, L. O. Adsorption of charged amphiphiles to oppositely charged polysaccharides−A study of the influence of polysaccharide structure and hydrophobicity of the amphiphile molecule. *Biopolymers* **1997**, *41*, 765−772.

(5) Merta, J.; Stenius, P. Interactions between cationic starch and anionic surfactants 2. Viscosity and aggregate size in dilute solutions. *Colloids Surf. A* **1997**, *122*, 243−255.

(6) Maulik, S.; Dutta, P.; Chattoraj, D. K.; Moulik, S. P. Biopolymer-surfactant interactions: 5. Equilibrium studies on the binding of cetyltrimethyl ammonium bromide and sodium dodecyl sulfate with bovine serum albumin, β-lactoglobulin, hemoglobin, gelatin, lysozyme and deoxyribonucleic acid. *Colloids Surf. B* **1998**, *11*, 1−8.

(7) Waninge, R.; Paulsson, M.; Nylander, T.; Ninham, B.; Sellers, P. Binding of sodium dodecyl sulfate and dodecyl trimethly ammonium chloride to β-lactoglobulin: A calorimetric study. *Int. Dairy J.* **1998**, *8*, 141−148.

(8) Kwak, J. C. T. *Polymer-Surfactant Systems*; Marcel Dekker: New York, 1998.

(9) Kastner, U.; Zana, R. Interactions between quanternary ammonium surfactant oligomers and water soluble modified guars. *J. Colloid Interface Sci.* **1999**, *218*, 468−479.

(10) Dalgleish, D. G.; Srinivasan, M.; Singh, H. Surface-properties of oil-in-water emulsion droplets containing casein and Tween-60. *J. Agric. Food Chem.* **1995**, *43*, 2351−2355.

(11) Cornec, M.; Wilde, P. J.; Gunning, P. A.; Mackie, A. R.; Husband, F. A.; Parker, M. L.; Clark, D. C. Emulsion stability as affected by competitive adsorption between an oil-soluble emulsifier and milk proteins at the interface. *J. Food Sci.* **1998**, *63*, 39−43.

(12) Demetriades, K.; McClements, D. J. Influence of sodium dodecyl sulfate on the physicochemical properties of whey protein-stabilized emulsions. *Colloids Surf. A* **2000**, *161*, 391−400.

(13) Demetriades, K.; McClements, D. J. Influence of pH and heating on physicochemical properties of whey protein-stabilized emulsions containing a nonionic surfactant. *J. Agric. Food Chem.* **1998**, *46*, 3936−3942.

(14) Dickinson, E. Adsorbed protein layers at fluid interfaces: interactions, structure and surface rheology. *Colloids Surf. B* **1999**, *15*, 161−176.

(15) Dickinson, E.; Ritzoulis, C. Creaming and rheology of oil-in-water emulsions containing sodium dodecyl sulfate and sodium caseinate. *J. Colloid Interface Sci.* **2000**, *224*, 148−154.

(16) Lairon, D. Dietary fibers: effects on lipid metabolism and mechanisms of action. *Eur. J. Clin. Nutr.* **1996**, *50*, 125−133.

(17) Potty, V. H. Physio-chemical aspects, physiological functions, nutritional importance and technological significance of dietary fibres−A critical appraisal. *J. Food Sci. Technol.* **1996**, *33*, 1−18.

(18) Dongowski, G. Effect of pH on the in vitro interactions between bile acids and pectin. *Z. Lebensm.-Unters. Forsch. A* **1997**, *205*, 185−192.

(19) Jenkins, D. J. A.; Vuksan, V.; Wolever, T. M. S. Diet and cardiovascular disease risk reduction: A place for fibre? *Nutr., Metab. Cardiovasc. Dis.* **1995**, *5*, 251−259.

(20) Jenkins, D. J. A.; Kendall, C. W. C.; Ransom, T. P. P. Dietary fiber, the evolution of the human diet and coronary heart disease. *Nutr. Res.* **1998**, *18*, 633−652.

(21) Baines, Z. V.; Morris, E. R. Suppression of perceived flavor and taste by hydrocolloids. In *Food Colloids*; Bee, R. D., Richmond, P., Mingins, J. Eds.; Royal Society of Chemistry: Cambridge, UK, 1989; p 184.

(22) Kinsella, J. E.; Whitehead, D. M. Proteins in whey: chemical, physical and functional properties. *Adv. Food Nutr. Res.* **1989**, *33*, 343−400.

(23) Bakker, J. Flavor interactions with the food matrix and their effects on perception. In *Ingredient Interactions: Effects on Food Quality*; Gaonkar, A. G., Ed.; Marcel Dekker: New York, 1995.

(24) Gaonkar, A. G. *Ingredient Interactions: Effects on Food Quality*; Marcel Dekker: New York, 1995.

(25) Boudaud, N.; Dumont, J. P. Interaction between flavor components and β-lactoglobulin. In *Flavor-Food Interactions*; McGorrin, R. J., Leland, J. V., Eds.; American Chemical Society: Washington, DC, 1996; Chapter 4.

(26) Guichard, E. Interactions between pectins and flavor compounds in strawberry jam. In *Flavor-Food Interactions*; McGorrin, R. J., Leland, J. V., Eds.; American Chemical Society: Washington, DC, 1996; Chapter 11.

(27) Donnelly, J. L.; Decker, E. A.; McClements, D. J. Iron-catalyzed oxidation of Menhaden oil as affected by emulsifiers. *J. Food Sci.* **1998**, *63*, 997−1000.

(28) Goddard, E. D. Polymer-Surfactant Interaction Part I: Uncharged water-soluble polymers and charged surfactant. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1993; pp 123−170.

(29) Goddard, E. D. Polymer-Surfactant Interaction Part II: Polymer and surfactant of opposite charge. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1993; pp 171−202.
(30) Lindman, B.; Thalberg, K. Polymer-Surfactant Interactions−Recent Developments. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1993; pp 203−276.
(31) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1992.
(32) Bergethon, P. R. *The Physical Basis of Biochemistry*; Springer-Verlag: New York, 1998.
(33) Singh, S. K.; Caram-Lelham, N. Thermodynamics of κ-carrageenan-amphiphilic drug interaction as influenced by specific counterions and temperature: A microcalorimetric and viscometric study. *J. Colloid Interface Sci.* **1998**, *203*, 430−446.
(34) Wyman, J.; Gill, S. J. *Binding and Linkage: Functional Chemistry of Biological Molecules*; University Science Books: Mill Valley, CA, 1990.
(35) Goddard, E. D. Applications. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1993; pp 395−414.
(36) Whistler, R. L. *Starch: Chemistry and Technology*; Academic Press: San Diego, CA, 1984.
(37) Zobel, H. F. Molecules to granules: A comprehesive review. *Starch* **1988**, *40*, 44−50.
(38) Banks, W.; Greenwood, C. T.; Khan, K. H. The interaction of linear amylose oligomers with iodine. *Carbohydr. Res.* **1971**, *17*, 25−35.
(39) Yamamoto, M.; Sano, T.; Harada, S.; Yasunaga, T. Kinetic studies of the complex formation in the ternary system of amylose, SDS, and iodine. *Biopolymers* **1984**, *23*, 2083−2093.
(40) Kuge, T.; Takeo, K. Complexes of starchy materials with organic compounds. Part II. Complex formation in aqueous solution and fraction of starch by 1-menthone. *Agric. Biol. Chem.* **1968**, *32*, 1232−1242.
(41) Raphaelides, S.; Karkalas, J. Thermal dissociation of amylose-fatty acid complexes. *Carbohydr. Res.* **1988**, *172*, 65−75.
(42) Godet, M. C.; Buleon, A.; Tran, V.; Colonna, P. Structural features of fatty acid−amylose complexes. *Carbohydr. Polym.* **1993**, *21*, 91−95.
(43) Biliaderis, C. G.; Seneviratne, H. D. On the supermolecular structure and metastability of glycerol monostearate-amylose complex. *Carbohydr. Polym.* **1990**, *13*, 185−195.
(44) Galloway, G. I.; Biliaderis, C. G.; Stanley, D. W. Properties and structure of amylose-glyceryl monostearate complexes formed in solution or on extrusion of wheat flour. *J. Food Sci.* **1989**, *54*, 950−960.
(45) Kowblansky, M. Calorimetric investigation of inclusion complexes of amylose with long-chain aliphatic compounds containing different function groups. *Macromolecules* **1985**, *18*, 1776−1786.
(46) Kugimiya, M.; Donovan, J. W. Calorimetric determination of the amylose content of starches based on formation and melting of the amylose-lysolecithin complex. *J. Food Sci.* **1981**, *46*, 765−774.
(47) Krog, N.; Olesen, S. K.; Toernaes, H.; Joensson, T. Retrogradation of the starch fraction in wheat bread. *Cereal Foods World* **1989**, *34*, 281−285.
(48) Mercier, C.; Charbonniere, N.; Grebaut, J.; de la Gueriviere, J. F. Formation of amylose complexes by twin-screw extrusion cooking of manioc starch. *Cereal Chem.* **1980**, *57*, 4−10.
(49) Eliasson, A. C. Starch gelatinization in the presence of emulsifier. A morphological study of wheat starch. *Starch* **1985**, *37*, 411−421.
(50) Seneviratne, H. D.; Biliaderis, C. G. Action of α-amylose on amylose-lipid complex superstructures. *J. Cereal Sci.* **1991**, *13*, 129−138.
(51) Szczodrak, J.; Pomerranz, Y. Starch-lipid interaction and formation of resistant starch in high-amylose barley. *Cereal Chem.* **1992**, *69*, 626−632.
(52) Cui, R.; Oates, C. G. The effect of amylose-lipid complex formation on enzyme susceptibility of sago starch. *Food Chem.* **1999**, *65*, 417−425.
(53) Kitahara, K.; Suganuma, T.; Nagahama, T. Susceptibility of amylose-lipid complexes to hydrolysis by glucoamylase from *Rhizopus niveus*. *Cereal Chem.* **1996**, *73*, 428−432.
(54) Chronakis, I. S. On the molecular characteristics, compositional properties, and structural-functional mechanisms of maltodextrins: a review. *Crit. Rev. Food Sci. Nutr.* **1998**, *38*, 599−637.
(55) Reineccius, G. A. Carbohydrates for flavor encapsulation. *Food Technol.* **1991**, *3*, 144−154.
(56) Alexander, R. J. Fat replacers based on starch. *Cereal Foods World* **1995**, *40*, 366−370.
(57) Svensson, E.; Gudmundsson, M.; Eliasson, A. C. Binding of sodium dodecylsulphate to starch polysaccharides quantified by surface tension measurements. *Colloids Surf. B* **1996**, *6*, 227−233.
(58) Bijma, K.; Engberts, J. B. F. N.; Blandamer, B. J.; Cullis, P. M.; Last, P. M.; Irlam, K. D.; Soldi, L. G. Classification of calorimetric titration plots for alkylmethylammonium and alkylpyridinium surfactants in aqueous solution. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1579−1586.
(59) Jones, M. N.; Chapman, D. *Micelles, Monolayers, and Biomembranes*; Wiley: New York, 1995.
(60) Bulpin, P. V.; Cutler, A. N.; Lips, A. Cooperative binding of sodium myristate to amylose. *Macromolecules* **1987**, *20*, 44−49.
(61) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; Wiley: New York, 1980.
(62) Biliaderis, C. G.; Galloway, G. Crystallization behavior of amylose-V complexes: Structure−property functions. *Carbohydr. Res.* **1989**, *189*, 31−48.
(63) Lagendijk, J.; Pennings, H. J. Starch−Lipid interactions. *Cereal Sci. Today* **1970**, *15*, 354−358.

Received for review March 13, 2001. Revised manuscript received July 26, 2001. Accepted August 2, 2001.

JF0103471