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Study of inclusion complexes of cycloamylose with surfactants by isothermal titration calorimetry

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ABSTRACT

Useful materials can be made from cycloamylose (CA) and the functional properties of CA could be improved by complexation with surfactants. Isothermal titration calorimetry (ITC) was used to investigate interactions between CA and surfactants in buffered solutions. Three surfactants with C_{12} non-polar tail groups and charged [anionic: sodium dodecyl sulfate (SDS); cationic: dodecyl trimethylammonium bromide (DTAB)] or non-charged headgroups [non-ionic: polyoxyethylene 23 lauryl ether (Brij35)] were used in this study. The effects of temperature, pH, and salt concentration were also studied. All three surfactants bound to CA; however, Brij35 binding to CA was negligible. Enthalpy changes associated with binding of surfactants to CA were exothermic except for interactions measured at 50 °C. There was no effect of pH on surfactant demicellization or CA binding. Salt concentration affected surfactant demicellization, but the amount of SDS bound to CA at saturation was unaffected by salt. When the titration curves obtained for CA with SDS and DTAB were fitted, it could be analyzed using a model based on a single set of identical sites.

1. Introduction

Starch, the dominant storage carbohydrate in plants, is widely used in various industries. It is composed of two types of glucose polymer: amylose and amylopectin. Amylose and amylopectin exhibit distinct physical properties, indicating that their glucose polymeric structures underlie their functionality. Accordingly, there is increasing interest in engineering glucose polymers with distinct structures and properties to provide novel applications that cannot be achieved with conventional starch (Fujii et al., 2003; Park et al., 2007; Takaha et al., 1998). Large-ring cyclodextrins, also called cycloamylose (CA), can be produced by disproportionating enzyme(s) and have been attracting attention despite existing difficulties in their synthesis, isolation, and purification (Kitamura, Nakatani, Takaha, & Okada, 1999; Machida et al., 2000; Shimada, Handa, Kaneko, & Takada, 1996; Ueda, 2002). Treatment of amylose with cyclodextrin glucanotransferase produces common cyclodextrin (CD) containing 6–8 glucose residues and small amounts of higher homologs, and disproportionating enzymes such as 4-α-glucanotransferase yield CAs derived from amylose that have much higher degrees of glucose polymerization (Kitamura et al., 1999; Machida et al., 2000; Shimada et al., 1996; Ueda, 2002).

The most notable feature of common CDs (α-, β-, and γ-CD) is their ability to form solid inclusion complexes (host–guest complexes) with a very wide range of solid, liquid, and gaseous compounds by molecular complexation, which promotes the formation of an annular cavity of 5–8 Å (Del Valle, 2004; Szente & Szejtli, 2004). Specifically, CAs can form inclusion complexes with various materials and have several advantages compared to small CDs. First, CAs have different cavity geometries than CDs; second, they are highly soluble in cold water; and third, CAs prepared with disproportionating enzyme are quite heterogenous with respect to their number of glucose residues. Whereas small CDs are composed of molecules of the same size with degrees of polymerization (DP) of 6, 7, and 8 for α-, β-, and γ-CD, respectively, CAs comprise 17 to several hundred glucose residues that can be formed simultaneously. Therefore, it is anticipated that CAs can accommodate a variety of guest molecules in their cavities and may have different binding capacities compared to small CDs (Kitamura et al., 1999; Machida et al., 2000; Shimada et al., 1996; Tomono et al., 2002; Ueda, 2002). The structures of several CAs (δ-CD, CD10, CD14, and CD26) have been reported and suggest that, unlike common CDs, CAs are not annular in shape. Specifically, δ-CD exhibits a distorted boat-like shape, and CD10 and CD14 exhibit an elliptical macrocyclic ring folded in a saddle-like shape. The structure of CD26 is very different from common CDs and has channel-like cavities composed of two short V-amylose helices in antiparallel orientations (Gessler et al., 1999; Nimz et al., 2003, 2004).

CA mixtures with DPs from 22 to 45 and >50 are efficient artificial chaperones for protein refolding (Machida et al., 2000) and are the basis for new practical application CA products such as a protein refolding kit sold in Japan. With this in mind, an

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improved understanding of the nature of the interactions between CAs and guest materials may lead to the development of functional ingredients with enhanced or unique properties. Therefore, in this study we investigated the characteristics of inclusion complexes of CAs formed with surfactants by isothermal titration calorimetry (ITC), which is a powerful technique to study these types of interactions (Fox, Bloor, Holzwarth, & Wyn-Jones, 1998; Ollila et al., 2001; Seng & Tam, 2000; Yan et al., 2007). Surfactants were chosen as a guest material because they may bind and incorporate their non-polar tails into helical regions of polymer chains of cyclodextrins, oligosaccharides, and polysaccharides. Three surfactants with the same type of non-polar tail (C_{12}) but with different types of head groups were used (Wangsakan, Chinachoti, & McClements, 2004). Factors such as temperature, pH, and salt concentration that could affect surfactant–CA interactions were also investigated. Ultimately, we hope that the information obtained from this study will help improve our understanding of CA–surfactant interactions and that this may lead to the development of materials with improved functional attributes or bulk physicochemical properties.

2. Materials and methods

2.1. Materials

Cycloamylose (Lot No. GMH 2107) was obtained from Ezaki Glico Co., Ltd. (Osaka, Japan). As stated by the manufacturer, the weight average molecular weight was 7500. Sodium dodecyl sulfate (SDS, L-6026), dodecyl trimethylammonium bromide (DTAB, D-5047), and Trizma base (T-1503) were purchased from Sigma Chemical Co. (St. Louis, MO). Polyoxyethylene 23 lauryl ether (Brij 35) was purchased from Junsei Chemical Co., Ltd. (Japan). Sodium chloride (NaCl) and hydrochloric acid (HCl) were purchased from Duksan Pure Chemical Co. Ltd. (Korea).

2.2. Solution preparation

A stock buffer solution (20 mM Trizma, pH 7, containing 10 mM NaCl) was prepared in water, and pH was adjusted with HCl. To vary the pH, stock buffer solutions were also prepared at pH 3 and 5, and for salt concentration experiments, NaCl was added to 0, 10, and 100 mM concentrations in pH 7 buffer. CA solution was prepared by dissolving powdered cycloamylose in the stock buffer solution. After stirring for 1 h at room temperature, the final CA concentration was 0.05 mM. Surfactant solutions were prepared by dissolving powdered SDS, DTAB, and Brij 35 in stock buffer solutions. The solutions were stirred overnight at room temperature.

2.3. Matrix assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF MS)

The molecular mass of cycloamylose was determined by using a MALDI-TOF mass spectrometer (Voyager™-DE, Perceptive Biosystem, Framingham, MA). The sample was mixed with a matrix (2,5-dihydroxybenzoic acid, 0.1–5 pmol/μl). The mixture was applied to the probe tip and dried until homogeneous crystals formed. The sample was desorbed/ionized from the probe tip under the following conditions: Grid voltage, 87; Grid wire voltage, 0.3; Delayed extraction, 300 ns; and Laser, 2000.

2.4. Isothermal titration calorimetry

An isothermal titration calorimeter (VP-ITC, Microcal, Inc., Northampton, MA) was used to measure enthalpy changes resulting from titration of the ligand into buffered or CA solutions. Aliquots (10 μl) of 35 mM SDS, 100 mM DTAB, and 8 mM Brij35 solution were injected sequentially into a 1.48-mL titration cell containing either buffer alone or CA solution. The concentration of the surfactants was determined by the method of Wangsakan et al. (Wangsakan, Chinachoti, & McClements, 2004). Each injection lasted 20, and 300 s were allowed between successive injections. The temperature and pH of the solution in the titration cell was 25.0 and 7 °C, respectively. All solutions were degassed prior to measurement. Measurements were performed in duplicate.

3. Results and discussion

3.1. MALDI-TOF MS analysis

The molecular mass of CA measured by MALDI-TOF MS is shown in Fig. 1. The DP of CA ranged from about 24 to 44, and as stated by manufacturer, the average molecular weight of CA was 7500. Among CAs, the structure of CA26 (cyclomaltohexaicosaose) has been reported in several studies. The crystal structure of the hydrated CA26 appears to be a macrocycle folded in a 'number 8' configuration, with $1_{2/3}$ turns of antiparallel V-amylose helices related by a pseudo-C_2 axis (Gessler et al., 1999; Nimz et al., 2003, 2004; Nimz, Geβler, Usón, & Saenger, 2001). Most of the CAs with different DPs have not yet been determined with the exception of CA10, CA14, and CA26. In our study, the fine structure of CA com-

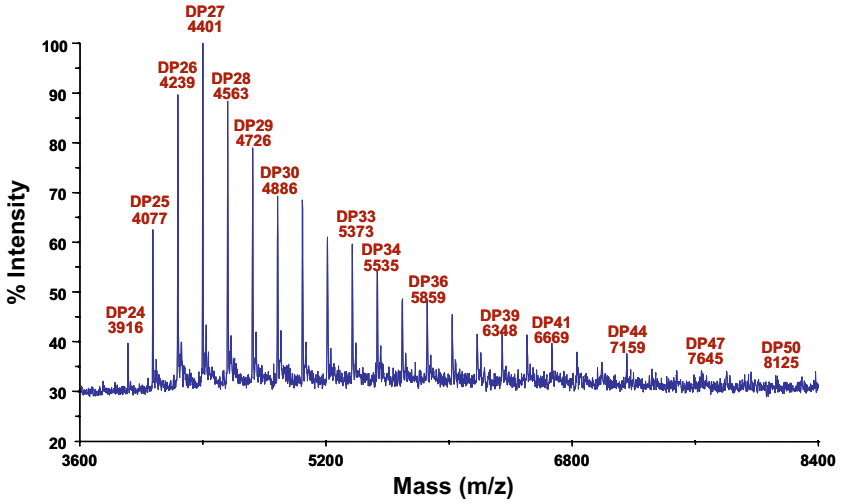

Fig. 1. MALDI-TOF MS analysis of cycloamylose. The number above each peak indicates the molecular mass (in daltons) of the molecule plus 23 Da (sodium ion).

prise 24–44 glucose residues was not define, however, it is likely that CA molecules with larger or smaller cavities than CA26 or with 'number 8' configurations coexist.

3.2. Influence of surfactant types on surfactant–CA interactions

The isothermal titration experiments were conducted by injecting concentrated surfactants (35 mM SDS, 100 mM DTAB, and 8 mM Brij35) in their micellar states into a cell containing Trizma-buffered solution only or 0.05 mM CA in the buffered solution. Titration curves are shown in Fig. 2.

Each of the injections of 35 mM SDS into the buffered solution produced a large endothermic heat signal that continued to increase until the 10th injection. Thereafter, the height of the endothermic peaks declined. Earlier investigations using ITC that examined the titration curves of ionic surfactants in buffered solutions suggested that the titration curves consist of three regions, i.e., region I: complete demicellization of ionic surfactants from the micellar state of the injectant to the critical micelle concentration (CMC); region II: a distinct point at the maximum of the titration curve that corresponds to the transition concentration from monomers to micelles; and region III: simple dilution of the surfactant micelles of the injectant (Wangsakan, Chinachoti, & McClements, 2001; Wangsakan et al., 2004; Yan et al., 2007). Similar regions of the titration curves were observed in our study. A series of large endothermic peaks observed until certain number of injections were the result of micelle dissociation because the surfactant concentration in the reaction cell remained below the CMC. After a certain number of injections, the decrease of endothermic peaks was attributed to the surfactant concentration in the reaction cell which exceeded the CMC, so that micelle dissociation no longer occurred.

In the presence of 0.05 mM CA, there was initially a large exothermic contribution to the enthalpy change. With more SDS injections, the enthalpy change increased until it reached an endothermic maximum, after which it became less endothermic. These results are in agreement with those of previous studies (Wangsakan et al., 2001, 2004; Wangsakan, Chinachoti, & McClements, 2006). They suggest that the transfer of the non-polar tails of the surfactant molecules from a highly polar environment (water) into a less polar environment (inside the helix) would probably be an exothermic reaction at 30 °C and would be opposite to the endothermic enthalpy changes associated with demicellization, which involves transfer of the non-polar tails of surfactant molecules from a less polar environment (inside the micelles) to a more polar environment (water) (Wangsakan et al., 2004). Thus, the exothermic enthalpy changes observed at lower SDS concentrations were ascribed to SDS-CA interactions. As the surfactant concentration increased, the number of available binding sites on CA decreased; hence, the exothermic contribution to the enthalpy change associated with binding decreased. Eventually, all binding sites on CA became saturated, and further SDS micelles injected into the reaction cell dissociated into monomers, leading to an endothermic reaction. Micelle dissociation no longer occurred when the concentration of free SDS monomers in the reaction cell increased above the CMC. These enthalpy changes are similar to those observed for the injection of SDS into the reaction cell above CMC in the absence of CA (Wangsakan et al., 2001).

Analogous experiments were carried out for DTAB and Brij35, but the dependence of the enthalpy changes on surfactant concentration were somewhat different.

The dependence of the enthalpy change per mole of surfactant ($\Delta H/\Delta$[Surfactants]) injected into the reaction cell on the surfactant concentration in the reaction cell was calculated by integration of the heat flow versus time profiles (Fig. 3). The CMC of SDS and DTAB, determined from the inflection point in the $\Delta H/\Delta$[surfactant] versus the surfactant concentration curve, was 2.7 ± 0.2 mM and 14.8 ± 0.0 mM, respectively (Király & Dekány, 2001). The CMC value of SDS was a slightly lower than ~3.3 mM reported in earlier studies (Wangsakan et al., 2004). As stated by manufacturer, the CMC of Brij35 was 92 μM so that it was difficult to determine the CMC of the non-ionic surfactant using ITC even though enthalpy changes were more exothermic in the low concentration of Brij 35, which may have been because of demicellization effects (Wangsakan et al., 2004).

Previous studies have reported that an *effective* critical micelle concentration (CMC*) can be defined as the surfactant concentration

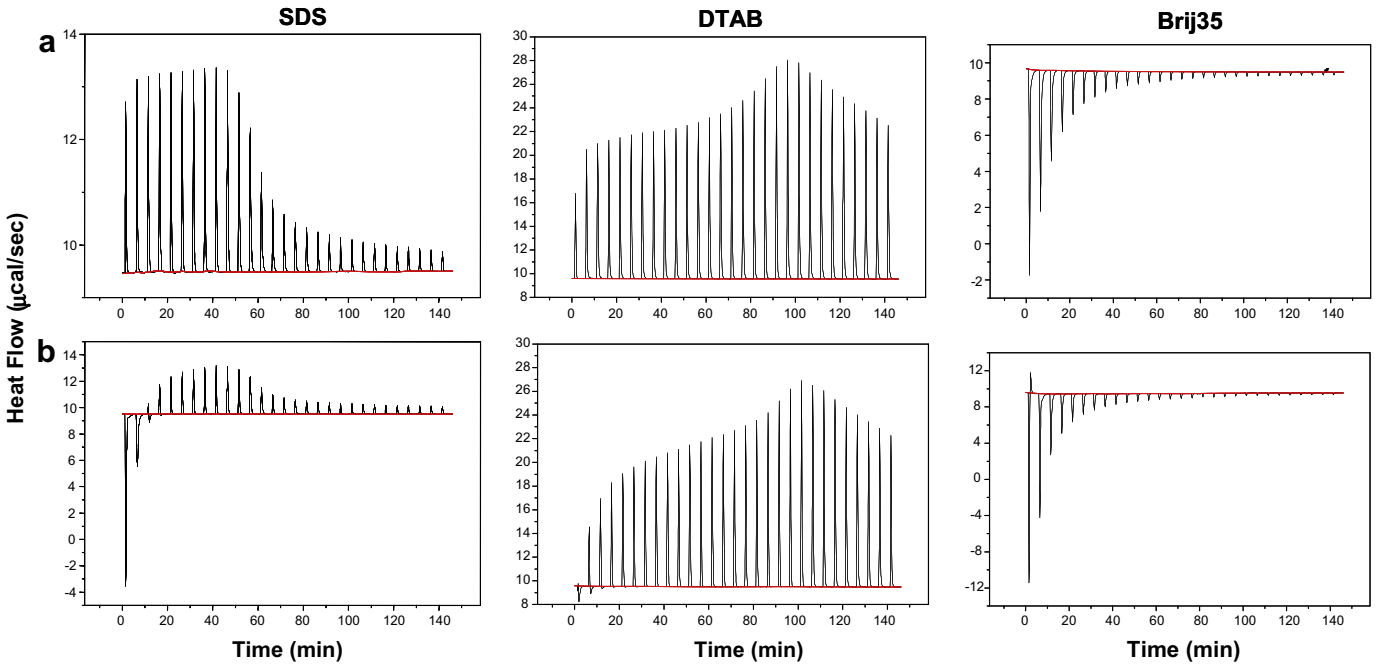

Fig. 2. (a) Titration curves resulting from injection of 10 μl aliquots of 35 mM SDS, 100 mM DTAB and 8 mM Brij35 into a reaction cell containing buffer at 25 °C and pH 7 (b) Titration curves resulting from injection of 10 μl aliquots of 35 mM SDS into a reaction cell containing 0.05 mM cycloamylose at 25 °C and pH 7.

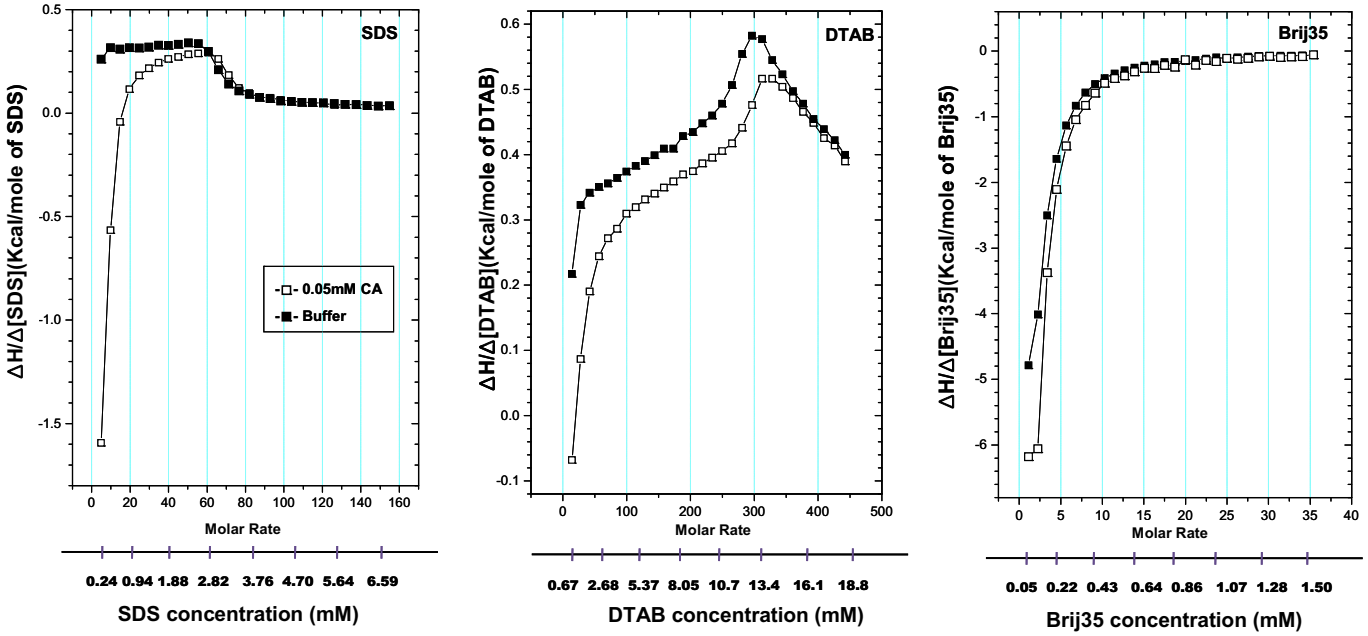

Fig. 3. Dependence of enthalpy change per mole of surfactant on the surfactant concentration in the reaction cell for 35 mM SDS, 100 mM DTAB and 8 mM Brij35 injected into buffer and 0.05 mM cycloamylose solution at 25 °C.

at which micelles first form in the reaction cell in the presence of a polymer. Also, the difference between the CMC of the surfactant in the presence and absence of CA ($\Delta CMC = CMC^{*} - CMC$) should be equal to the amount of surfactant that binds to CA at saturation: $C_{bound} = CMC^{*} - CMC$. Hence, to examine the amount of surfactants that bind to CA at saturation, the CMC^{*} was determined from the inflection point in the $\Delta H/\Delta$[surfactant] versus the surfactant concentration curve; C_{bound} was ≈0.24 mM for SDS and 0.67 mM for DTAB. The amounts of Brij35 bound to the CA could not be determined using ITC because there was no obvious peak associated with surfactant demicellization.

Previous research on the interactions between surfactants and maltodextrin (DE 5) reported that the amount of SDS and DTAB bound to 0.5% maltodextrin (DE 5) was ≈1.57 mM for SDS and 1.59 mM for DTAB and similar amounts of the two ionic surfactants were bound to the maltodextrin. (Wangsakan et al., 2004). But, in our study, larger amounts of DTAB were bound to CA compared to SDS and Brij35. The difference in the amount of surfactant bound to CA observed in our study may be rather due to the structure of CA and the different initial concentrations of surfactant than different head groups of surfactants. In this study, we used a higher DTAB concentration (100 mM) than SDS concentration (35 mM) to discriminate the value of CMC and CMC^{*}; the value of CMC of DTAB is higher than that of SDS. As mentioned above, CA used in this study was composed of DP 24–44. Thus, CA could have multiple cavities with different sizes. It is possible that several molecules of DTAB might be bound to one CA molecule that has larger cavities. A study that used ITC to investigate complex formation between I_3^- and CA26 analogs with 21–32 glucoses (DP21–DP32) suggested that CA26 has two identical binding sites, each occupied by one I_3^- (Kitamura et al., 1999). Therefore, it is possible that several molecules of SDS and DTAB could bind with one CA molecule with larger DP than CA26.

In another study, the slope of the linear plot of ΔCMC versus maltodextrin concentration was determined, and it was calculated that on average, one SDS molecule was bound per 24 glucose units in maltodextrin at saturation (Wangsakan et al., 2001). In our study, 0.24 mM of SDS was bound to 0.05 mM of CA. Therefore, we deduce that one SDS molecule was bound to approximately 9 glucose units in the CA at saturation. Since maltodextrins used in the previous study had an average degree of polymerization of 10 glucose units, an average of one SDS molecule was bound per approximately two maltodextrin molecules. This implied that not all of the maltodextrin molecules were capable of binding with surfactant molecules because commercial maltodextrin usually have considerably-broad chain length distribution. Considering the fact that the hydrocarbon tail of a SDS molecule is approximately 1.7 nm long (Wangsakan et al., 2001) and the one turn height of 6 D-glucosyl residues in the helical conformation of maltodextrin is approximately 0.8 nm (Biliaderis & Galloway, 1989), only those maltodextrin molecules that have a degree of polymerization around 12 or higher may have sufficient glucose units to completely surround the hydrocarbon tail of SDS (Wangsakan et al., 2001). The CA sample used in our study had a degree of polymerization mainly between 24 and 44 (Fig. 1), which was long enough to accommodate SDS molecules.

Shimada et al. (1996) reported that two plausible conformations of CA are a circularized single-helical structure and a double helical structure with foldbacks at each end. According to their molecular modeling work, depending on the DP of CA, the number of loops in a helical structure and arcs in circularized single-helical structure was different. Our finding about average one SDS molecule bound to 9 glucose units in CA and the possibility of multiple loop conformation in CA might lead to the conclusion that several SDS molecules could bind to one molecule of CA. However, further studies concerning the structure and binding ability of CA are needed to verify this hypothesis.

3.3. Thermodynamic data analysis

The purpose of this section was to investigate complexation thermodynamics of CA with SDS and DTAB. ITC has considerable advantages over other methods. Importantly, binding affinity (Ka), heat of binding and entropy (ΔH, ΔS), and the number of binding sites (n) can be determined directly and simultaneously. ITC experiments in this portion of the study were performed using surfactant concentrations in the injector that were below their CMC so that only surfactant monomers were injected into the reac-

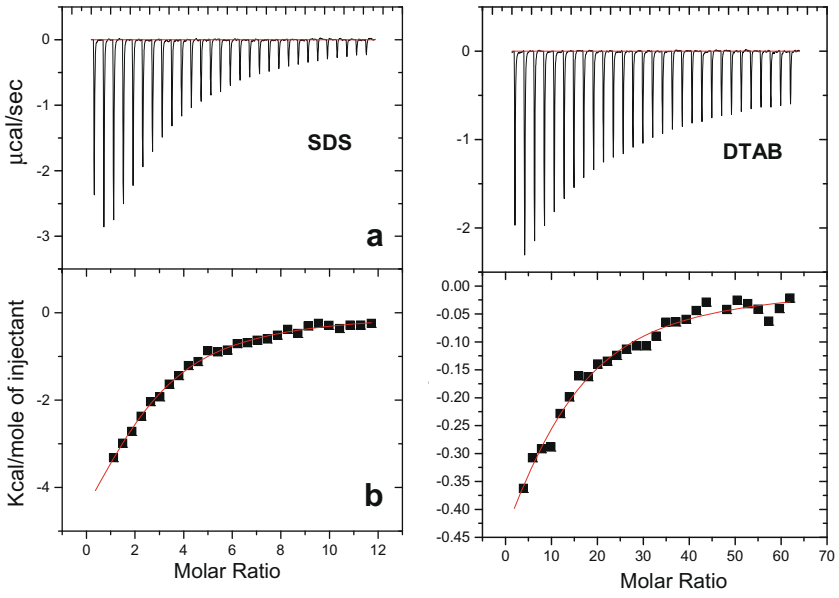

Fig. 4. (a) Experimental data for titrations of 10 µl aliquots of 2.65 mM SDS and 14.5 mM DTAB into a reaction cell containing 0.05 mM cycloamylose. (b) Data point obtained by integration of the injection peaks and the titration curve (solid line) obtained by fitting the data points.

tion cell. These experiments were carried out to avoid the relatively large contribution of demicellization to the overall enthalpy changes, so as to focus on the enthalpy changes directly associated with CA–surfactant binding. Aliquots (10 µl) of SDS (2.65 mM SDS) and DTAB (14.5 mM DTAB) solutions were injected sequentially into a 1.48-mL reaction cell initially containing buffer alone or CA solution (0.05 mM).

The heat of each individual injection, shown in Fig. 4a, are integrated and plotted against molar ratio of components. These are then fitted to the appropriate binding model enabling the calculation of the enthalpy ΔH, the binding constant K, and stoichiometry n (Fig. 4b, Table 1). A simple 1:1 binding model gave the most reasonable fitting parameters. Stoichiometry n values of SDS and DTAB were 2.5 and 5.3, respectively. The stoichiometry n values 2.5 of SDS implied that the binding of average two or three molecules of SDS to one CA molecule occurred. This result was consistent with the result reported in Section 3.2 that one SDS molecule was bound to approximately 9 glucose units in the CA at saturation. Considering the DP distribution of CA (Fig. 1), where major DPs resided in around 27, it seemed to be reasonable that two or three molecules of SDS bound to one CA molecule. The values of enthalpy were negative, indicating that the formation of host–guest inclusion complexes is a weak exothermic process. The water molecules in the hole of a completely hydrated CA molecule were released from the hydrophobic hole to the bulk aqueous phase, which involves an exothermic process (Kitamura et al., 1999; Seng & Tam, 2000). The entropy change (ΔS) and free energy change (ΔG^o) of association were calculated by using the equation:

$$\Delta G^o = -RT \ln Ka = \Delta H^o - T\Delta S^o$$

For the complexation of CA and SDS, ΔS was negative, but for the complexation of CA and DTAB, ΔS was positive. The negative value may be due to the decrease in conformational flexibility of the CA chain when SDS penetrates into the cavities of CA. For the complexation of CA and DTAB, since DTAB penetrated CA cavity further than SDS, a larger number of water molecules to the bulk solvent were released and thus this factor could explain less negative and positive entropy of CA and DTAB complexation (Eli & Chen, 1999; Sun et al., 2006). As mentioned above, the CA used in our study was composed of various DPs ranging mainly from 24 to 44. Therefore, when SDS and DTAB penetrates the cavity of CA molecules that have different DP, the mobility of CA molecules and the amount of surfactants bound to each CA molecule with different DP could vary, thus these factors contributed the value of entropy of each complexation differently. The negative values of ΔG, which are decided by enthalpy and entropy changes, indicated that the formation of CA–surfactant complexes in aqueous solutions is a spontaneous process.

3.4. Influence of temperature, pH, and salt on CA–surfactant interactions

We next investigated the influence of temperature on the binding of surfactants to CA. Aliquots (10 µl) of 35 mM SDS solution were injected into a reaction cell containing either Trizma-buffered solution or 0.05 mM CA in the buffered solution at different temperatures (10, 25, and 50 °C). Fig. 5 shows the enthalpy change per mol of SDS ($\Delta H/\Delta$[SDS]) versus SDS concentration at different temperatures. At 10 °C, each of the injections of 35 mM SDS into the buffer produced large exothermic heat signals up to the 13th injection, which was followed by endothermic signals with subsequent injections. At 50 °C, the peaks were highly endothermic for the first 13 injections but became less endothermic with later injections (Fig. 5). The peaks observed at 25 °C had similar trends to those at 50 °C. In the presence of CA, qualitatively different behaviors in titration curves were observed. At 10 and 50 °C,

Table 1
Thermodynamic parameters for cycloamylose–surfactants complexes at T = 298 K.

Surfactants	n	Ka (M^{-1})	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (kcal/mol)
SDS	2.5 ± 0.3	11416.7 ± 1277.9	−5537.4 ± 62.9	−7099.0 ± 1040.5	−5.2 ± 3.7
DTAB	5.3 ± 0.8	935.4 ± 70.3	−4050.5 ± 42.8	−2312.4 ± 391.5	5.8 ± 1.5

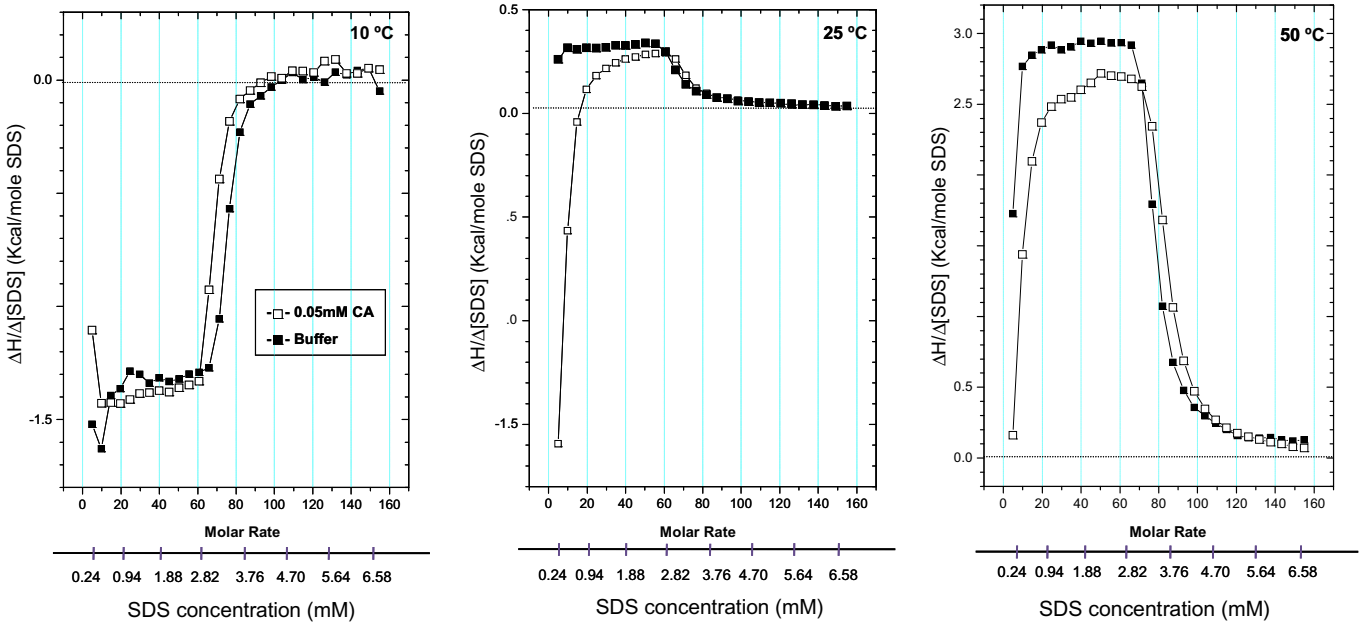

Fig. 5. Dependence of enthalpy change per mol of surfactant on the surfactant concentration in the reaction cell for 35 mM SDS injected into buffer and 0.05 mM cycloamylose solution at various temperatures.

profile curves were similar to those detected in the absence of CA but the peaks showed a lower level of heat flow. This was attributed to the binding of SDS to CA. At 25 °C, a different titration curve in the absence and presence of CA was observed. As mentioned above, whereas the peaks were endothermic at low surfactant concentrations in the absence of CA, the peaks were exothermic at low surfactant concentrations and later became endothermic in the presence of CA.

In the absence of CA, the enthalpy change per mole of SDS was either endothermic or exothermic depending on the temperature at relatively low surfactant concentrations. These results suggest that the enthalpy changes associated with demicellization are highly temperature-dependent and are consistent with results from previous studies (Wangsakan et al., 2006). However, in the presence of CA and at relatively low surfactant concentrations, the enthalpy changes were highly exothermic at 10 and 25 °C, while at 50 °C the enthalpy changes were still endothermic even though the enthalpy was lower than that measured in the absence of CA.

This result could be explained by calculating the CMC* and the amount of SDS bound to CA. CMC* of SDS in the presence of CA was determined at each temperature from the inflection point in the $\Delta H/\Delta$[surfactant] versus the surfactant concentration curve. The difference between the CMC of the surfactant in the presence

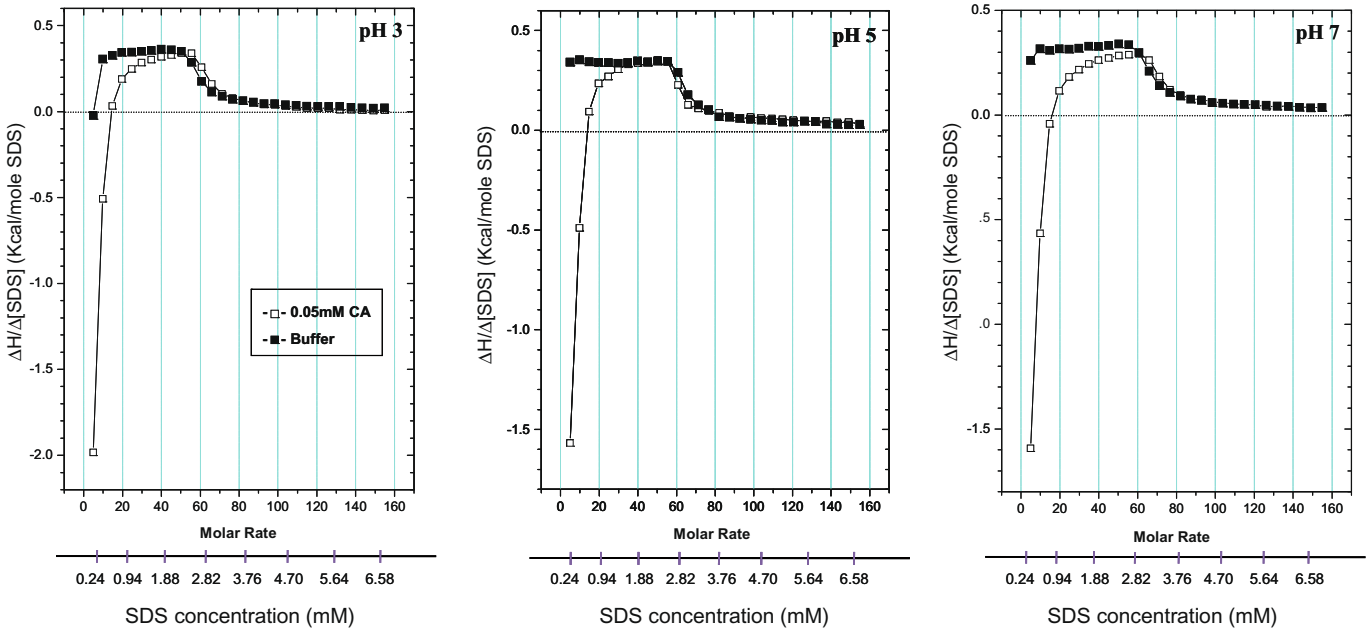

Fig. 6. Dependence of enthalpy change per mole of surfactant on the surfactant concentration in the reaction cell for 35 mM SDS injected into buffer and 0.05 mM cycloamylose solution with different pH at 25 °C.

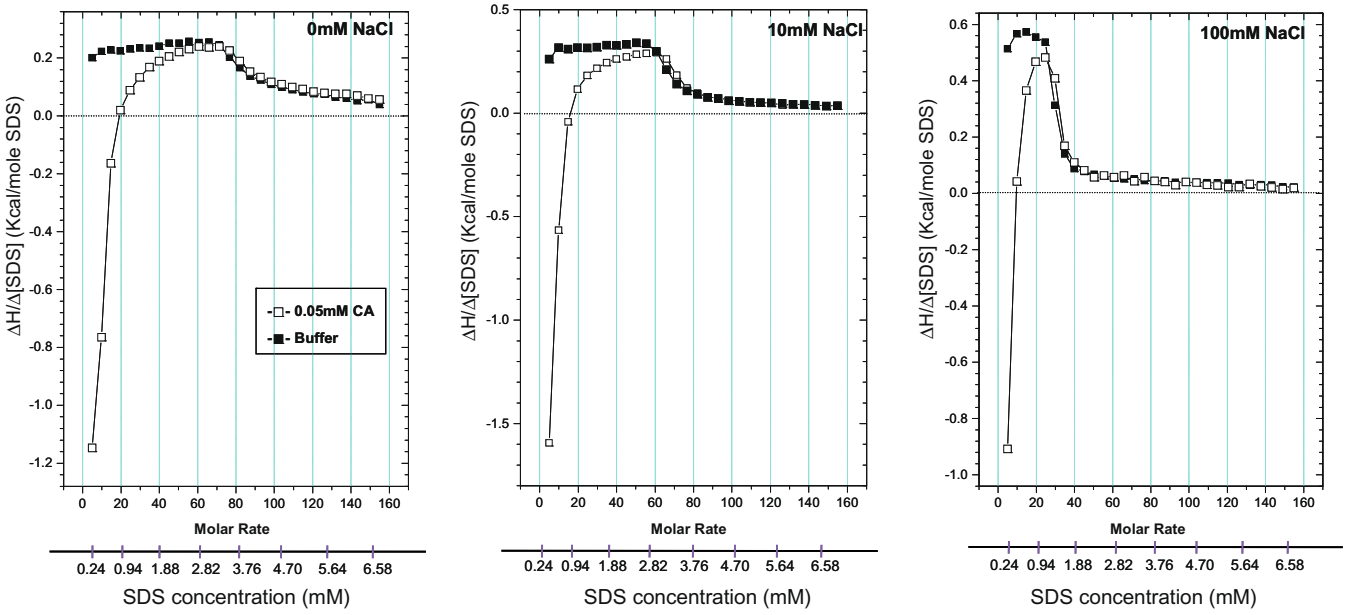

Fig. 7. Dependence of enthalpy change per mole of surfactant on the surfactant concentration in the reaction cell for 35 mM SDS injected into buffer and 0.05 mM cycloamylose solution with different salt concentration at 25 °C.

and absence of CA was 0.24, 0.24, and 0.12 mM at 10, 25, and 50 °C, respectively; these values should be equal to the amount of SDS bound to CA at saturation. At 50 °C, less SDS bound to CA. We postulate that the binding affinity of SDS to CA could be changed by higher temperatures; hence at 50 °C, binding to CA may have been less than binding at 10 and 25 °C.

The influence of pH on the binding of SDS to CA was also investigated by ITC. Aliquots (10 μl) of 35 mM SDS solution were injected into a reaction cell containing either Trizma-buffered solution or 0.05 mM CA in buffer at different pH values, i.e., pH 3, 5, and 7. Fig. 6 shows the enthalpy change per mole of surfactant versus SDS concentration at different pH. The enthalpy change in the absence and presence of CA followed the same trend at all pH values and was not significantly different. These results indicate that pH does not affect SDS demicellization or the binding of SDS to CA.

The enthalpy change per mole of surfactant was determined by integration of heat flow versus time curves at each salt concentration (Fig. 7). The CMC and CMC* of SDS were determined in the absence and presence of CA from the inflection point in the $\Delta H/\Delta$[surfactant] versus surfactant concentration curve as mentioned earlier (Király & Dekány, 2001; Majhi & Blume, 2001).

In the absence of CA, the CMC decreased with increasing salt concentration. The CMC was 3.5, 2.7, and 1.2 with 0, 10, and 100 mM NaCl, respectively. A previous study reported that this effect was probably due to the electrostatic repulsion between the SDS head-groups, thus favoring micelle formation (Wangsakan et al., 2006). The CMC* was also decreased with increasing salt concentration. The CMC* was 3.7, 2.9, and 1.4 with 0, 10, and 100 mM NaCl, respectively. The difference between the CMC of surfactant in the presence and absence of CA (ΔCMC = CMC* − CMC), which is equal to the amount of SDS bound to CA at saturation, was near 0.2 mM. This suggests that the amount of SDS binding to CA is not affected by salt concentration even though the values of CMC and CMC* decreased as the salt concentration increased.

4. Conclusions

Complex formation of CA having DP 24–44 with surfactants in aqueous solutions was studied by ITC. This study shows that SDS, DTAB, and Brij35 bind to CA in aqueous solutions. At saturation, more DTAB bound to cycloamylose compared to SDS and Brij35 (0.64 mM of DTAB and 0.24 mM of SDS per 0.05 mM CA). Complexation thermodynamics of CA with SDS and DTAB revealed values of ΔH and ΔG^{o} that were negative and both positive and negative ΔS values. This may be due to host–guest combinations, the release of water molecules from CA cavities, and decreases in the conformational flexibility of the CA chain. Therefore, these studies provide thermodynamic evidence of CA and SDS and DTAB complexations. There was no effect of pH or salt concentration on the binding of the surfactants to CA, although there was a decrease in the CMC and CMC* with increasing salt concentration. Moreover, temperatures at 50 °C resulted in less surfactant binding to CA than lower temperatures (10 and 25 °C).

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