

Effects of Various Surfactants on Rheological Properties of Maize Starch Granules

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ABSTRACT

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In this study, the formation of complexes between surfactants and the helical chains of amylopectins was confirmed. Nonionic surfactants with hydrophobic and hydrophilic groups of appropriate size and chemical structure enhanced the swelling and gelatinization processes of starch granules. Hydrophobic groups form complexes with the amylose and linear chains of amylopectin by becoming inserted into the hydrophobic inner area of the helical structures. The hydrophilic groups help the approach of the hydrophobic groups into the hydrated molecular chains and thus aid the formation of the complex. Among the anionic surfactants tested, SDS and sodium n-decyl benzenesulfate caused maximum swelling and gelatinization peaks. The average length of the amylopectin exterior chains is almost the same as that of the hydrophobic chains of SDS (16.9 Å) and of sodium decyl benzenesulfate (18.2 Å). This suggests that these anionic surfactants form rigid complexes with the

exterior of the amylopectin by fitting their hydrophobic chains to the hydrophobic inside of the helical structures of these short exterior chains. This process was clarified by NMR analysis and by a decrease in the complex with the addition of iodine. The hydrophobic alkyl chains of anionic and cationic surfactants fix to the edge of the starch molecular chains by forming inclusion complexes with the helical chains of the amylopectin. Cationic ions interact with the starch molecular chains, causing a negative charge that results in a more rapid and efficient swelling of the starch granules. A decrease in setback value occurs due to the inhibition of rearrangement among the starch molecular chains. With SDS, the complex molecular chains become more extensively developed through the repulsion effects of the anionic ions resulting in a larger swelling power and gelatinization peak.

Starch is synthesized as a reverse carbohydrate in the tissues of many species of plant. This synthesized starch consists of amylose ($\approx 20\%$) and amylopectin ($\approx 80\%$). These carbohydrate polymers are arranged in order and packed within starch granules. Exterior molecular chains of amylopectin form orderly double helices that result in a crystalline region and 1-6-linked branch points in the amorphous regions (Imberty et al 1991). These crystalline molecular chains are dissociated by hydration during the gelatinization of starch granules during the heating process, resulting in a high swelling power of the granules. The interaction of these mobile molecular chains then leads to retrogradation during the cooling process. These rheological properties differ in the composition and localization of the amylose and amylopectin, the length of amylose, and the length and distribution of the short linear chains of amylopectin among different types of starch (Orford et al 1987; Takeda and Hizukuri 1987; Mua and Jackson 1997). These properties have been examined and discussed using various methods such modification or treatment of the starch and addition of lipids, using emulsifiers and surfactants in the gelatinization and retrogradation processes, and by cross-linking starch molecules (Sair 1967; Eliasson 1985; Gudmundsson and Eliasson 1990; Jane et al 1992; Rajagopalan and Seib 1992; Hoover and Manuel 1996; Kurakake et al 1997; Villwock et al 1999; Zheng et al 1999; Jackowski et al 2002). The heat-treatment of maize starch with a water-ethanol mixture indicated that rearrangements occur between the amylose and the amylopectin within the starch granules when the starch is treated with various water contents (Kurakake et al 1997).

The interaction between the helical structures of the starch molecule chains and some affinity substances greatly influences the rheological properties and provides important information regarding the structure and position of amylose and amylopectin. Amylose forms complexes with some lipids and surfactants, which results in a depression in the swelling power of the granules and in the retrogradation of gelatinized starch (Eliasson 1985; Godect et al 1995; Ozcan and Jackson 2002) Furthermore, it has been found

that amylopectin forms complexes with surfactants and lipids in the exterior molecular chains (Evans 1986; Eliasson and Ljunger 1988; Gudmundsson and Eliasson 1990). The interaction between surfactant and starch molecular chains were also investigated using their different sizes such as sodium alkyl sulfate and digested amylose and amylopectin (Yamamoto et al 1983; Lundqvist et al 2002). These findings indicate the importance of the helical structures of starch molecular chains on the rheological properties of starch granules. Although the various rheological behaviors caused by it have not yet been clearly elucidated, the insertion of the lipids and surfactants to the helical structures has been.

In this study, changes in the structure of starch molecular chains are investigated using various surfactants with differing chemical structures, the hydrophobic chains of which become inserted into the helical molecular chains. The formation of complexes between the starch molecular chains and surfactants is clarified. Changes in the structure of the starch molecule chains and the consequent influence on the rheological properties are also discussed.

MATERIALS AND METHODS

Starch and Surfactants

Maize starch was supplied from Sanwa Cornstarch Ltd. (Nara, Japan). Amylose A, of maize starch origin was purchased from Wako Pure Chemical Industries. Mean molecular weight was estimated as 2,900 degrees of polymerization ([DP] 18). Nonionic surfactants were supplied by Nippon Oil & Fats Co. and composed of poly-

TABLE I
Effect of Nonionic Surfactants on Swelling Power and Solubility of Maize Starch

Surfactant	HLB ^a	Swelling Power (g/g)	Solubility (%)
None	...	13.7	6.27
SDS	...	40.5	5.47
Nonionic surfactant			
Tween 80	15.0	9.53	9.27
NS-202	5.7	11.1	5.89
NS-206	10.9	29.2	23.0
NS-215	15.0	16.8	13.7
O-4	11.5	7.20	1.26
L-4	13.1	7.98	1.11

^a Hydrophilic-lipophilic balance (HLB).

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oxyethylene nonyl phenol ethers (C₄H₉C₆H₄O(CH₂CH₂O)_nH): Nonion NS-202 (*n* = 2, hydrophilic-lipophilic balance [HLB] 5.7), NS-206 (*n* = 6, HLB 10.9), and NS-215 (*n* = 15, HLB 15.0); polyethylene glycol monooleates (C₁₇H₃₃COO(CH₂CH₂O)_nH): Nonion O-4 (*n* = 4, HLB 11.5); and polyethylene glycol mono-laurate (C₁₁H₂₃COO(CH₂CH₂O)_nH): Nonion L-4 (*n* = 4, HLB 13.1). The value of *n* for Nonion shows the mean DP of the polyoxyethylene. Polyoxyethylene sorbitan monooleate: Tween 80 (HLB 15.0) was purchased from Sigma. The anionic surfactants were purchased from Nakalai Tesque and composed of sodium n-alkyl sulfate (CH₃(CH₂)_nOSO₃Na) (*n* = 5, 7, 9, 11, 13) and sodium n-alkyl benzenesulfate (CH₃(CH₂)_nC₆H₄OSO₃Na) (*n* = 7, 9, 11, 13). The cationic surfactants n-dodecylamine hydrochloride (CH₃(CH₂)₁₁NH₂HCl) and n-dodecyl trimethyl ammonium chloride (CH₃(CH₂)₁₁N(CH₃)₃Cl) were purchased from Kanto Chemical.

Swelling Power and Solubility in 0.2% Surfactant Aqueous Solution

Maize starch samples (2.5%, w/w) dispersed in aqueous solutions each composing of 0.2% surfactant (60–390 mmol/kg of starch) were incubated at 80°C for 30 min. They were then centrifuged at 1,500 × *g* and 25°C for 30 min. The volume of supernatant, the concentration of solubilized starch, and the weight of sediment starch were measured to obtain the swelling power and solubility of the starch granules. The concentrations of dissolved starch were determined using the phenol-sulfuric acid method (Dubois et al 1956). Swelling power was determined by dividing the wet weight of the sediment starch by the dry weight, the dissolved starch was the quantity subtracted (Leach et al 1959).

Rapid Visco Analysis

A Rapid Visco Analyser (RVA; RVA-3D, Foss Electric Japan, Tokyo, Japan) was used to measure changes in viscosity caused by heating and cooling. Samples were added to the RVA vessel to make a 10% suspension in 25 g of water each containing 0.2% of surfactant (15–98 mmol/kg of starch). They were heated to 95°C at 5°C/min after holding period of 1 min at 30°C, they were then held for 6 min at 95°C, cooled to 50°C at –5°C/min, and held again for 10 min at 50°C. One RVA unit (RVU) equals 10 cP.

Blue Value by Iodine-Amylose Complex

Amylose A aqueous solution (2.0%, 0.01 mL) and 0.2–2.0% sodium dodecyl sulfate aqueous solution (0.1 mL) were added to 0.005% iodine and 0.05% iodine chloride aqueous solution (1 mL)

and mixed. After incubation at room temperature for 2 min, the blue value (the absorbance at 680 nm generated by the amylose–iodine complex) was measured using colorimetry. The blue value of another sample containing 2.1% Amylose A aqueous solution (0.018 mL) and 0.1% sodium n-alkyl sulfate aqueous solution (0.2 mL) added to 0.005% iodine and 0.05% iodine chloride aqueous solution (1.8 mL) was measured in the same manner.

Fatty Acid Extracted from Starch by Heat Treatment with Surfactants

After heat treatment at 80°C for 30 min, 1 g of maize starch and 40 mL of 0.2% surfactant aqueous solution were placed in a 50-mL capped tube, the supernatant obtained by centrifugation at 1,500 × *g* for 10 min and the sediment extract washed with ether were gathered into one tube and concentrated to ≈1 mL using an evaporator. Chloroform (20 mL), water (20 mL), and methanol (10 mL) were added to the concentrate and mixed for 2 min to extract lipids into the chloroform layer. After removing the upper layer of the water-methanol mixture, chloroform (20 mL) and water (20 mL) were added to the lower layer and mixed again. After separation, the lipids extracted from the lower chloroform layer were dried using an evaporator. The extracts extracted using surfactants were methylated with the hydrochloric acid-methanol at 90–95°C for 1 hr. Free fatty acids and the fatty acids found in the lipids were converted to methylester and analyzed using gas chromatography (GC 17A, Shimadzu, Kyoto, Japan) with SS-10 column (0.25 mm × 25 m) and column temperature at 150–218°C. A hydrogen flame ionization detector (FID) was used.

Nuclear Magnetic Resonance Spectroscopy (NMR)

¹³C-NMR spectrums were recorded at 400 MHz with AT 300K (Nihon Bruker). Amylose A (1%) and SDS (1%) were dissolved in deuterium oxide and the chemical shifts were calibrated using the signals of acetone, which was used as the internal standard.

RESULTS AND DISCUSSION

Nonionic Surfactants

Table I shows the swelling power and solubility after treatment at 80°C of maize starch with 0.2% of each nonionic surfactant. Among the nonionic surfactants, NS-206 most enhanced the swelling power and solubility properties of the maize starch. The effects were, however, smaller than those of the anionic surfactant SDS. With NS-202, Tween 20, L-4, and O-4, swelling powers

TABLE II
Effect of Nonionic Surfactants on Viscosity Parameters of Maize Starch

Surfactant	HLB ^a	Peak Viscosity Temp. (°C)	Viscosity (RVU)			
			Peak	Breakdown	Setback	End
None	...	92.4	340	205	154	289
SDS	...	91.0	519	393	270	396
Nonionic surfactant						
Tween 80	15.0	91.1	371	242	202	331
NS-202	5.7	90.7	345	229	165	281
NS-206	10.9	82.5	393	282	204	315
NS-215	15.0	86.2	363	241	158	280
O-4	11.5	94.9	349	102	74	247
L-4	13.1	95.1	317	76	61	302

^a Hydrophilic-lipophilic balance (HLB).

TABLE III
Fatty Acids Removed from Maize Starch by Heat-Treatment with Surfactants

Surfactant	Extracted Fatty Acid (mg/g)	Composition (%)					
		C16:0	C16:1	C18:0	C18:1	C18:2	C18:3
SDS	0.23	20.1	0.9	1.4	9.7	62.5	5.3
NS-206	0.47	24.5	3.0	0.5	8.2	58.8	4.9
L-4	2.15	32.9	1.7	1.5	11.7	48.7	3.5

decreased in comparison with the properties of the maize starch without surfactants.

The effect of the surfactants on the rheological properties was also investigated with an RVA viscogram. As shown in Fig. 1, the viscogram of the maize starch presented three types of curve during the heating and cooling processes. First, a viscosity peak occurred with the swelling of the starch granules during the heating process. The viscosity then greatly decreased by the end of the gelatinization process. This decreased viscosity is called breakdown. During the following cooling process when the molecular chains of starch are aggregated and rearranged there was another increase in viscosity. This increased viscosity is called setback, the retrogradation of the gelatinized starch. Peak viscosity, breakdown, and setback were further enhanced by the addition of the anionic surfactant SDS (Fig. 1A). As shown in Fig. 1B, NS-206 also enhanced these values but to a lesser extent than SDS. With L-4, the breakdown following peak viscosity was less pronounced and a high viscosity was maintained during the cooling process. This indicates that the starch granules were not completely gelatinized during heating when L-4 was used. These viscosities are summarized in Table II. NS-206 showed the highest peak viscosity and breakdown values among all the nonionic surfactants. O-4 and L-4 showed increases in peak temperature and lower breakdown and setback values.

A high value for hydrophilic-lipophilic balance (HLB) indicates a high hydrophilic property. Although NS-206 and O-4 show small differences in HLB (10.9 and 11.5, respectively), their rheological

properties, as shown on the RVA, are significantly different. There is little relationship between the HLB values and the viscosities of the starch granules when the nonionic surfactants are of differing chemical structures. Although hydrophobic chain forms the inclusion complex with helical structure of starch (Kumar et al 1991), Tween 80, O-4, and L-4, which have larger molecular hydrophobic groups such as oleate and laurate compared with their hydrophilic polyoxyethylene groups, inhibit the formation of helix complexes with the starch molecular chains.

Among the NS type nonionic surfactants (NS-202, NS-206, NS-215), which have polyoxyethylene groups and relatively smaller sized hydrophobic groups (nonyl phenol ether), NS-206 showed the largest change in viscosity on the RVA viscogram. In surfactants with the same hydrophobic group, HLB values were related to the difference in length of the hydrophilic chains. The mean DP of the polyoxyethylene in NS 202, NS 206, and NS 215 were 2, 6, and 15, respectively. NS-206 with HLB 10.9 and DP 6 values were most effective in the gelatinization of starch.

Within nonionic surfactants, there are appropriate-sized and chemically structured hydrophobic and hydrophilic groups that enhance the effects of swelling and gelatinization in starch granules. This suggests that the hydrophobic groups form complexes with amylose and the linear chains of amylopectin by becoming inserted into the hydrophobic pocket inside the helical structures of the molecular chains. Hydrophilic groups help the approach of these hydrophobic groups and enhance the formation of the complexes.

Table III shows the results of lipids removed from the maize starch by heating with 0.2% of each surfactant. The lipid extraction values are expressed on a fatty acid basis. The removed fatty acids were very small in quantity for SDS and NS-206 treated starches. Some lipids in starch granules have significant effects on the swelling, gelatinization, and retrogradation. Amylose-lipid complexes inhibit the swelling of starch granules (Morrison 1993). If amylose does not form the lipid complexes within the starch granules, the swelling and gelatinization processes would be greatly enhanced. Due to the low defatting effect, the result of the surfactants on the swelling of the starch granules was not attributable to the prevention of the formation of amylose-lipid complexes.

Anionic Surfactants

Sodium n-alkyl sulfates (carbon atom numbers [C] 6, 8, 10, 12, and 14) were added with water to a starch suspension and examined for starch granule swelling and viscosity with the RVA. The swelling power of maize starch increased as the number of carbon atoms in

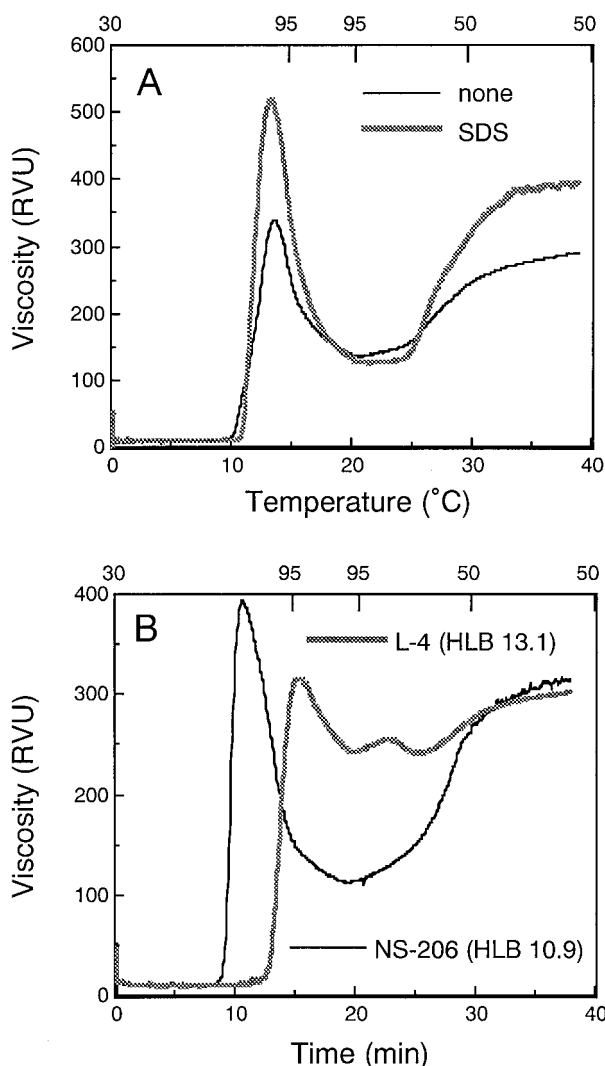


Fig. 1. RVA viscograms of maize starch. Effects of surfactants on starch suspension (10%) with SDS (A) and L-4 and NS-206 (B).

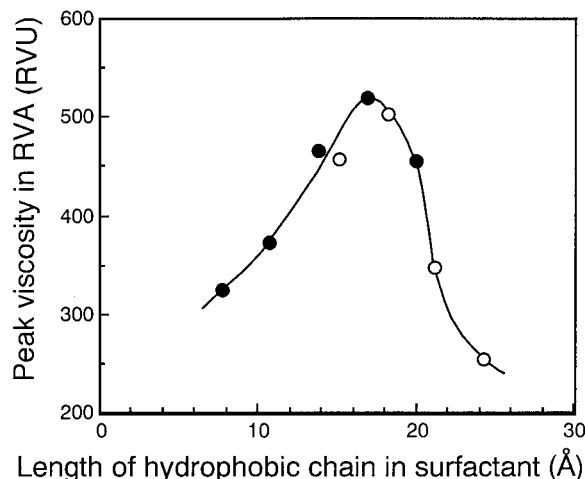


Fig. 2. Relationship between RVA peak viscosity and length of hydrophobic chains of sodium alkyl sulfate (●) and sodium alkyl benzene-sulfate (○).

the alkyl group increased. A maximum was achieved at C12, as shown in Table IV. The peak viscosity, breakdown, and setback measurements taken with the RVA also reached maximum at C12 (Table V). Tables VI and VII shows the effect of sodium n-alkyl benzenesulfates (C8, 10, 12, and 14 of alkyl chain). Sodium n-alkyl benzenesulfates showed results similar to sodium n-alkyl sulfates, although the swelling power and viscosity were maximum at C10.

The relationship between the peak viscosities measured on the RVA and the length of the hydrophobic chains in the surfactants is shown in Fig. 2. The data from samples tested with sodium n-alkyl sulfates and sodium n-alkyl benzenesulfates is expressed with one curve, which indicates the maximum values. These results show that hydrophobic chains have an optimum size in the anionic surfactants, causing an increase in the gelatinization peak viscosity of the maize starch. This optimal size is $\text{\AA} \approx 16.9 \text{\AA}$ for sodium n-alkyl sulfate to $\approx 18.2 \text{\AA}$ for sodium n-alkyl benzenesulfate, in which the benzene ring is included in the hydrophobic chain. Incidentally, the insertion of large molecules like benzene ring expands the helical conformation to be shorter and fatter (Rutschmann and Solms 1990). The benzene ring in sodium n-alkyl benzenesulfate could decrease the helical chain size of amylose by $\approx 1 \text{\AA}$.

The interaction of the surfactants with the helical structures of the starch molecular chains was investigated by testing with iodine. Figure 3A shows the effects of each sodium n-alkyl sulfate on the blue value at 680 nm for Amylose A (MW 2,900, DP 18). As the number of carbon atoms in the surfactant alkyl chains increased to >12 (as in SDS), the blue value decreased. Figure 3B shows the relationship between the relative blue value and the concentration of SDS. The blue value significantly decreased with an increase in surfactant concentrations and was almost constant at $>0.7 \text{ mg/mL}$. This suggests that equilibrium exists in the formation of complexes with surfactants and iodine. SDS would easily form complexes with the short helical chains of Amylose A (DP 18) when iodine does not exist there. Sodium n-alkyl sulfate did not influence the blue value of high molecular amylose separated from the maize starch (data is not shown). The formation of the complex with surfactant depends on a balance between amorphous and helical regions of amylose. When the partial helical chain is longer, the influence of surfactant is small. This finding shows that these surfactants form complexes with the short exterior chains of amylopectin influencing swelling, gelatinization, and retrogradation.

Lipids and amylose form a complex similar to the amylose-iodine inclusion complex. It is characterized by X-ray diffraction (Zobel 1988). The mean DP of Amylose A is ≈ 18 , which corre-

sponds to 24\AA in helix length. As SDS has an alkyl chain of 16.9\AA , when the size of the alkyl chain is $>70\%$ that of Amylose A, the complexes formed with surfactants are rigid and influence the formation of the complex with iodine (Fig. 3A). Sodium tetradecyl sulfate has an alkyl chain of 18.5\AA and fits more strongly to Amylose A helices preventing the insertion of iodine into the helical structure and resulting in a decrease in the blue value. In comparison, in short alkyl chains of $<16.9 \text{\AA}$, the hydrophobic binding strength is too small to cause a decrease in the blue value.

As shown in Fig. 4, the complexes formed between SDS and Amylose A was indicated by ^{13}C -NMR analysis. The formation of the complex was detected by the change in carbon signal (Bulpin et al 1986). Six carbon signals of Amylose A (C1 = 99.1, C2 = 72.9, C3 = 71.1, C4 = 76.3, C5 = 70.7, C6 = 60.0) in concentrations of 1% disappeared by adding 1% SDS, where the mole ratio was 1:10 for Amylose A to SDS, although all carbon signals of the extra surfactants were detected. Signals of SDS (C12 = 69.4) were clearly detected around the region of Amylose A. When alkyl chains of SDS become inserted into the hydrophobic internal components of the helices of Amylose A, they bind tightly with the carbon atoms, resulting in a decline in signal intensity. Only extra surfactants were detected with ^{13}C -NMR analysis. This data clarifies the formation of complexes between sodium alkyl sulfate and short helical chains through hydrophobic binding.

The anionic surfactant SDS had a greater effect than nonionic surfactants. The high hydrophobic ability of the methylene chains and the hydrophilic effect of anionic ions are associated with an increase in the development of molecular chains in starch granules. The existence of an optimum chain length in the hydrophobic groups of sodium alkyl sulfate, which enhances swelling and gelatinization, further supports these claims. During the formation of amylose-lipid complexes, the aliphatic components of the lipids become included into a typical left-handed amylose helix (Eliasson 1985). It is claimed that the hydrophobic chains of the dodecyl group become inserted into the helical ring of the molecular chains in amylopectin, thus accelerating the swelling of the starch granules (Evans 1986; Villwock et al 1999). The interaction between amylopectin and lipids or SDS has also been illustrated through decreased rates of retrogradation (Eliasson and Ljunger 1988; Gudmundsson and Eliasson 1990). However, these reports are discussed only with respect to changes in the rheological properties of starch. In the shorter hydrophobic chains of sodium alkyl sulfate, complexes with exterior molecular chains of amylopectin are not stabilized because of the feeble strength of the hydrophobic bond within the helix. For the amylose, increasing

TABLE IV
Effect of Sodium n-Alkylsulfate on Swelling Power and Solubility of Maize Starch

Sodium n-Alkylsulfate	Swelling Power (g/g)	Solubility (%)
None	13.7	6.27
C6	10.4	4.73
C8	12.1	4.43
C10	16.9	4.19
C12	40.5	5.47
C14	22.2	2.45

TABLE VI
Effect of Sodium n-Alkylbenzenesulfate on Swelling Power and Solubility of Maize Starch

Sodium n-Alkylbenzenesulfate	Swelling Power (g/g)	Solubility (%)
None	13.7	6.27
C8 (alkyl chain)	30.3	6.34
C10	41.0	...
C12	13.2	12.4
C14	12.6	4.92

TABLE V
Effect of Sodium n-Alkylsulfate on Viscosity Parameters of Maize Starch

Sodium n-Alkylsulfate	Peak Viscosity Temp. ($^{\circ}\text{C}$)	Viscosity (RVU)			
		Peak	Breakdown	Setback	End
None	92.4	340	205	154	289
C6	95.3	325	176	138	287
C8	91.9	372	253	122	241
C10	89.2	466	347	135	254
C12	91.0	519	393	270	396
C14	93.0	454	340	224	338

the carbon number of the surfactant increased the melting point of the complex in differential scanning calorimetry (DSC) (Kowblansky 1985). In the longer hydrophobic chains, however, a part of the chain seems to exist outside the helical complexes because the exterior molecular chains of amylopectin are shorter and thus

exposed during the hydrophilic water phase. Therefore, maximum swelling and a gelatinization peak occur at C12 in sodium n-alkyl sulfate and C10 in sodium n-alkyl benzenesulfate (the carbon number is for the alkyl chains).

Amylopectin, which predominates maize starch at $\approx 80\%$, has many short linear chains and forms crystalline structures of 15–45% of the granules (Zobel 1988). The formation of double helix exterior chains leads to the crystalline and rigid region in amylopectin and results in the formation of starch granules (Imberty et al 1991). In general, the average length of the exterior chains is $\approx 20 \text{ \AA}$, 15 glucose units (Richardson et al 2000). This length is almost the same as that of the hydrophobic chains of sodium n-alkyl sulfate (16.9 \AA) and sodium n-alkyl benzenesulfate (18.2 \AA including the benzene ring). This suggests that these anionic surfactants form a rigid complex with the short exterior chains in amylopectin by fitting the hydrophobic chains to the hydrophobic

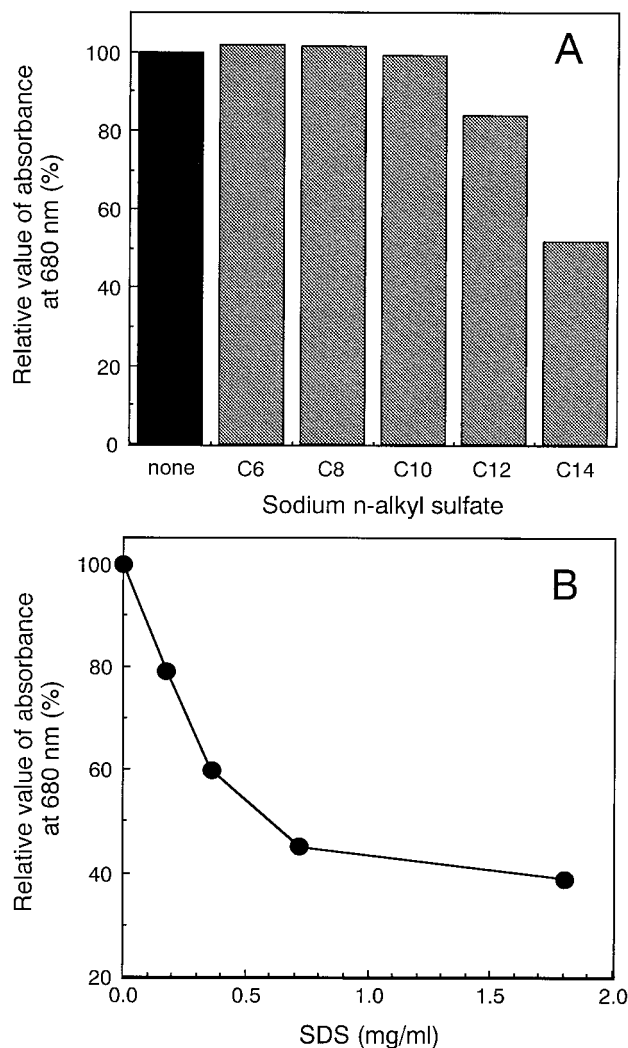


Fig. 3. Effects of sodium alkyl sulfate on the blue value of amylose A complexes tested with iodine. **A**, SDS (0.1 mg/mL) added to a mixture of 0.2 mg/mL of amylose A and 0.04 mg/mL of I_2 and 0.4 mg/mL of KI solution at 25°C. **B**, SDS (0.1–1.8 mg/mL) added to a mixture of 0.2 mg/mL of amylose A and 0.045 mg/mL of I_2 and 0.45 mg/mL of KI solution at 25°C.

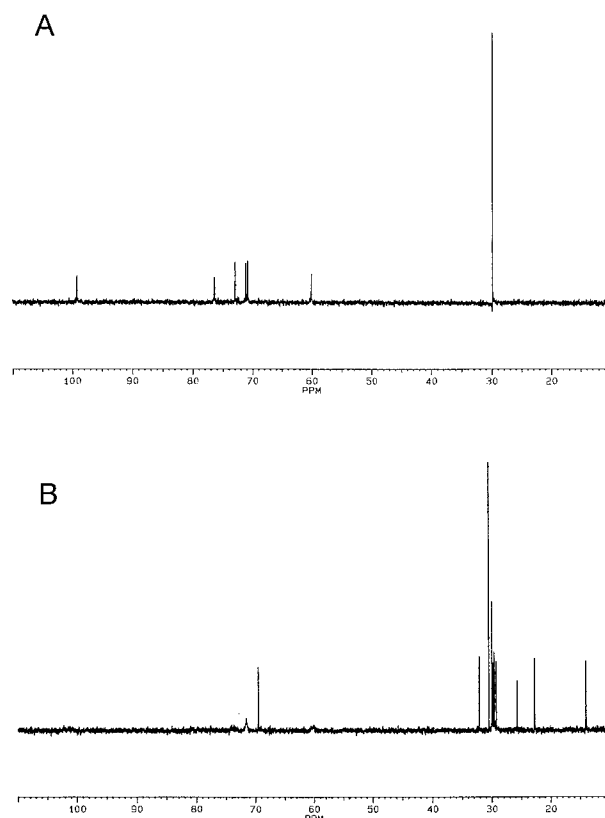


Fig. 4. ^{13}C -NMR spectra of mixture solutions of amylose A and SDS. **A**, 1% amylose A solution; **B**, 1% amylose A and 1% SDS mixture.

TABLE VII
Effect of Sodium n-Alkylbenzenesulfate on Viscosity Parameters of Maize Starch

Sodium n-Alkylbenzenesulfate	Peak Viscosity Temp. (°C)	Viscosity (RVU)			
		Peak	Breakdown	Setback	End
None	92.4	340	205	154	289
C8 (alkyl chain)	90.0	458	345	128	241
C10	88.6	502	395	181	288
C12	93.4	347	233	259	373
C14	95.0	254	151	212	315

TABLE VIII
Effect of Cationic Surfactants on Viscosity Parameters of Maize Starch

$CH_3(CH_2)_{11}R$	Peak Viscosity Temp. (°C)	Viscosity (RVU)			
		Peak	Breakdown	Setback	End
R= SO_4Na (SDS)	91.0	519	393	270	396
R= NH_2HCl	83.0	464	384	128	208
R= $N(CH_3)_3Cl$	88.9	419	326	110	203

internal area of the helical structures in the short exterior chains. This results in the break down of the double helix structures causing a high swelling power and high gelatinization peak viscosity. The effect of molecular size of the SDS also changed the exterior chain length of the amylopectin. The depression of retrogradation caused by SDS decreased as chain length decreased from 15.1 to 10.4 glucose units (Lundqvist et al 2002).

Cationic and Anionic Surfactants with the Same Alkyl Chain

Changes in the rheological properties when treated with cationic surfactants, n-dodecyl amine hydrochloride (with primary amine), and n-dodecyl trimethyl ammonium chloride (with quaternary ammonium), which have the same alkyl chains as SDS, were also investigated. RVA viscosities are shown in Table VIII. Decreases in the peak viscosity and peak temperature values were lower with cationic surfactants than with the anionic surfactant, SDS. The setback values were less than half of those seen with SDS. There was a large difference in the rheological properties of cationic and anionic surfactants despite having the same hydrophobic alkyl chains.

The rheological properties of the cationic surfactants resemble those of waxy starches consisting of only amylopectin. Swelling is enhanced by inserting the alkyl chains into the inside of the short helix chains of amylopectin. Cationic ions existing at the end of the complex interact with the starch molecular chains, which charge negatively and result in more efficient and rapid swelling of the starch granules. It seems that the cationic ion in the complex attracts hydroxyl groups of other molecular chains of starch and depresses the interaction among the molecular chains in the swelling. This action causes a decrease in temperature at the viscosity peak. The decrease in setback value is attributable to the inhibition of rearrangement among the starch molecular chains. In the gelatinized state, the cationic ion of the complex forms networks with amylopectin and amylose through ionic binding. Mobility between these chains for rearrangement is then inhibited. In SDS, the approach of the anionic ions to the starch molecule chains does not proceed rapidly because a repulsion of the negative charge results in an increase in peak temperature and peak viscosity. When the complexes between the alkyl chains of the surfactants and the short helical chains in amylopectin are formed, the swelling of amylopectin is more greatly enhanced by repulsion between the complexed chains. This leads to a high viscosity during gelatinization. The dispersed molecular chains have high mobility and can interact efficiently with the long amylose chains and other amylopectin chains during the cooling process. This results in a high setback value, that is, retrogradation. Highly rigid regions do not, however, form with complexes composed of anion ions. This phenomenon may be associated with the electrostatic effect of anion and cation in neutral salt solutions, where anion repels the hydroxyl groups of starch molecules and cation attracts it (Jane and Ames 1993). A significant feature of anionic and cationic surfactants is that their ions fix to the edge of the starch molecular chains by forming inclusion complexes between the helical chains in amylopectin and the hydrophobic alkyl chains in the surfactant itself. With SDS, complexed molecular chains are more extensively developed due to the repulsion effects of anionic ions resulting in a large swelling power and gelatinization peak.

The structure and size of the hydrophobic chains of the surfactants also influenced interaction with the exterior helical chains of amylopectin. In sodium alkyl sulfate, alkyl chains of SDS caused most significant increases in the gelatinization viscosity of the starch granules. Here, the chain length almost corresponds exactly with the average length of the exterior chains of amylopectin. This clarifies the formation of complexes between the surfactants and the helical chains of amylopectin. The rheological properties of sodium alkyl sulfates with different chain lengths reflect the distribution, size, and mobility of the exterior chains in amylopectin. With respect to the behavior of amylose, the swelling and gelatin-

ization processes seem to depend on amylopectin. The next step would be to clarify the role of amylose during the swelling and gelatinization of starch granules.

CONCLUSIONS

In nonionic surfactants, hydrophobic groups form complexes with the amylose and linear chains of amylopectin by becoming inserted into the hydrophobic inner area of the helical structures. The hydrophilic groups help the approach of the hydrophobic groups into the hydrated molecular chains and thus aid the formation of the complex. SDS and sodium n-decyl benzenesulfate caused maximum swelling and gelatinization peaks. The average length of the amylopectin exterior chains is almost the same as that of the hydrophobic chains of sodium dodecyl sulfate (16.9 Å) and of sodium decyl benzenesulfate (18.2 Å). This suggests that these anionic surfactants form rigid complexes with the exterior of the amylopectin by fitting their hydrophobic chains to the hydrophobic inside of the helical structures of these short exterior chains. Sodium n-alkyl sulfate (C12,14) decreased the blue value at 680 nm for Amylose A (MW 2900, DP18). This effect was also attributable to the fitting size of the hydrophobic chain to helical chain of Amylose A. Anionic and cationic surfactants with the same alkyl chain (C12) cause different rheological properties for starch. Cationic ions outside the complex with helical chain of amylopectin interact with the other starch molecular chains causing a negative charge, which results in a more rapid and efficient swelling of the starch granules and depression of the retrogradation. With SDS of anionic surfactant, the complex molecular chains become more extensively developed through the repulsion effects of the anionic ions resulting in a larger swelling power and gelatinization peak.

LITERATURE CITED

- Bulpin, P. V., Cutler, A. N., and Lips, A. 1986. Physical properties of amylose-fatty acid complexes in solution. Pages 221-232 in: *Gums and Stabilisers for the Food Industry*, 3. G. O. Phillips, D. J. Wedlock, and P. A. Williams, eds. Elsevier Applied Science: Amsterdam.
- Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., and Smith, F. 1956. Calorimetric method for determination of sugars and related substances. *Anal. Chem.* 28:350-356.
- Eliasson, A. C. 1985. Starch gelatinization the presence of emulsifier. A morphological study of wheat starch. *Starch* 37:411-415.
- Eliasson, A. C., and Ljunger, G. 1988. Interaction between amylopectin and lipid additives during retrogradation in a model system. *J. Sci. Food. Agric.* 44:353-361.
- Evans, I. 1986. An investigation of starch/surfactant interactions using viscosimetry and differential scanning calorimetry. *Starch* 38:227-235.
- Godect, M. C., Bizot, H., and Buleon, A. 1995. Crystallization of amylose-fatty acid complexes prepared with different amylose chain lengths. *Carbohydr. Polym.* 27:47-52.
- Gudmundsson, M., and Eliasson, A. C. 1990. Retrogradation of amylopectin and the effects of amylose and added surfactants/emulsifiers. *Carbohydr. Polym.* 12:295-315.
- Hoover, R., and Manuel, H. 1996. The effect of heat-moisture treatment on the structure and physicochemical properties of normal maize, waxy maize, dull waxy maize, and amylo maize V starches. *J. Cereal Sci.* 23:153-162.
- Imberty, A., Buleon, A., Tran, V., and Perez, S. 1991. Recent advances in knowledge of starch structure. *Starch* 43:375-384.
- Jackowski, R., Czuchajowska, Z., and Baik, B. K. 2002. Granular cold water gelling starch prepared from chickpea starch using liquid ammonia and ethanol. *Cereal Chem.* 79:125-128.
- Jane, J. L., Xu, A., Radosavljevic, M., and Seib, P. A. 1992. Location of amylose in normal starch granules. I. Susceptibility of amylose and amylopectin to cross-linking reagents. *Cereal Chem.* 69:405-409.
- Jane, J. L., and Ames, I. A. 1993. Mechanism of starch gelatinization in neutral salt solutions. *Starch* 45:161-166.
- Kowblansky, M. 1985. Calorimetric investigation of inclusion complexes of amylose with long-chain aliphatic compounds containing different functional groups. *Macromolecules* 18:1776-1779.

- Kumar, V. G., Bhandari, M. V., and Bhat, A. N. 1991. Modifications of tapioca starch properties by polyethylene glycol (4000) and polyethylene glycol (4000) stearate additives. *Starch* 43:93-98.
- Kurakake, M., Noguchi, M., Fujioka, K., and Komaki, T. 1997. Effects on maize starch properties of heat-treatment with water-ethanol mixtures. *J. Cereal Sci.* 25:253-260.
- Leach, H. W., McCowen, L. O., and Schoch, T. J. 1959. Structure of starch granule. I. Swelling and solubility patterns of various starches. *Cereal Chem.* 36:534-544.
- Lundqvist, H., Nilsson, G. S., Eliasson, A. C., and Gorton, L. 2002. Changing the amylopectin-sodium dodecyl sulfate interaction by modifying the exterior chain length. *Starch* 54:100-107.
- Morrison, W. R. 1993 Cereal starch granule development and composition. Pages 175-190 in: *Seed Storage Compounds*. P. R. Shewry and K. Stobart, eds. Clarendon Press, Oxford.
- Mua, J. P., and Jackson, D. S. 1997. Relationship between functional attributes and molecular structures of amylose and amylopectin fractions from corn starch. *J. Agric. Food Chem.* 45:3848-3854.
- Orford, P. D., Ring, S. G., Carroll, V., Miles, M. J., and Morris, V. J. 1987. The effect of concentration and botanical source on the retrogradation of starch. *J. Sci. Food Agric.* 39:169.
- Ozcan, S., and Jackson, D. S. 2002. The impact of thermal events on amylose-fatty acid complexes. *Starch* 54:593-602.
- Rajagopalan, S., and Seib, P. A. 1992. Properties of granular cold-water-soluble starches prepared at atmospheric pressure. *J. Cereal Sci.* 16:29-40.
- Richardson, S., Nilsson, G. S., Bergquist, K. E., Gorton, L., and Mischnick, P. 2000 Characterization of the substitution pattern in hydroxypropylated potato amylopectin starch. *Carbohydr. Res.* 328:365-373.
- Rutschmann, M. A., and Solms, J. 1990. Formation of inclusion complexes of starch with different organic compounds. IV. Ligand binding and variability in helical conformations of V amylose complexes. *Lebens. Wiss. Technol.* 23:84-87.
- Sair, L. 1967. Heat-moisture treatment of starch. *Cereal Chem.* 44:8-26.
- Takeda, Y., and Hizukuri, S. 1987. Structures of branched molecules of amyloses of various origins, and molar fractions of branched and unbranched molecules. *Carbohydr. Res.* 165:139-145.
- Villwock, V. K., Eliasson, A. C., Silverio, J., and Bemiller, J. N. 1999. Starch-lipid interactions in common, waxy, ae du, and ae su2 maize starches examined by differential scanning calorimetry. *Cereal Chem.* 76:292-298.
- Yamamoto, M., Sano, T., Harada, S., and Yasunaga, T. 1983. Cooperativity in the binding of sodium dodecyl sulfate to amylose. *Bull. Chem. Soc. Jpn.* 56:2643-2646.
- Zheng, G. H., Han, H. L., and Bhatta, R. S. 1999. Functional properties of cross-linked and hydroxypropylated waxy hull-less barley starches. *Cereal Chem.* 76:182-188.
- Zobel, H. F. 1988. Starch crystal transformations and their industrial importance. *Starch* 40:1-7.

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