The Influence of Polysaccharides on the Glass Transition in Frozen Sucrose Solutions and Ice Cream

H. D. GOFF, K. B. CALDWELL,[1] and D. W. STANLEY
Department of Food Science
University of Guelph
Guelph, ON, Canada N1G 2W1

T. J. MAURICE
Ault Foods Ltd.
London, ON, Canada N6B 1N8

ABSTRACT

The objective of this study was to describe further the mechanism by which polysaccharide stabilizers contribute to stability of frozen dairy desserts. The influence of stabilizers on the thermal properties and viscosity of carbohydrate solutions at subzero temperatures, on the thermal properties of ice cream mix, and on ice crystallization and growth in ice cream were investigated. Polysaccharide stabilizers did not influence the thermal properties of sucrose solutions as measured by differential scanning calorimetry. Stabilizers provided resistance to thermal deformation and increased subzero viscosity above the glass transition temperature but did not influence the experimental glass transition temperature of the solutions or ice cream mix as determined by thermomechanical analysis. The effect of stabilizers on ice crystals in ice cream was demonstrated by low temperature scanning electron microscopy, which showed that the initial ice crystal size and the rate of growth after 24 wk of storage at abusive temperatures were smaller in stabilized ice creams than in unstabilized ice creams. The influence of stabilizers on ice crystal size in ice cream above its glass transition temperature was postulated to be a function of the kinetic properties of the freeze-concentrated, viscoelastic liquid surrounding the ice crystals.

(**Key words**: glass transition, ice cream, stabilizers, thermomechanical analysis)

Abbreviation key: **DSC** = differential scanning calorimeter (or calorimetry), **SEM** = scanning electron microscope (or microscopy), T_g' = the glass transition temperature of a maximally freeze-concentrated solution, **TMA** = thermomechanical analyzer (or analysis).

INTRODUCTION

During storage, ice cream can suffer deleterious effects, such as ice crystal growth and structural collapse. These deteriorations in quality become more prevalent with higher freezer temperatures, greater temperature fluctuations, and increased storage time. Polysaccharide stabilizers, such as locust bean gum, guar gum, sodium carboxymethyl cellulose, sodium alginate, carrageenan, and xanthan, are commonly added to ice cream to control ice crystal growth during hardening and storage, especially in abusive temperatures, to give body and stiffness during freezing for air incorporation, and to impart smoothness in body and texture (1). The idea that stabilizers restrict the growth of crystals of ice and lactose in frozen desserts is common; however, the behavior of stabilizers is difficult to relate to the thermodynamics of ice nucleation and crystal growth (2). Several researchers (3, 4, 6, 19, 20) have examined the role of stabilizers in controlling the amount of ice formed (i.e., modifying phase equilibria), in affecting the ice crystal nucleation process, in modifying the growth kinetics of the ice crystals themselves, and in controlling the rate at which recrystallization occurs during storage. Those researchers have concluded that theoretical considerations and experimental results discount any expectation

Received March 26, 1992.
Accepted January 8, 1993.
[1]Present address: Ault Foods Ltd., London, ON, Canada N6B 1N8.

that stabilizers modify phase equilibria and that no consistent effect accounts for the modification of ice crystal structure or growth by stabilizers. However, some authors (6, 16) suggested that stabilizers exert a desirable influence on the sensory texture of frozen desserts by some mechanism other than control of ice crystal size or amount of ice formed, possibly solely because of organoleptic perception of texture.

Stabilizers may perform a more important role in changing the rheological properties of the mix. Many attempts were made to correlate an increase in mix viscosity with polysaccharide action in ice cream, but the results were inconclusive (5, 9, 15, 24, 27). Shirai et al. (24) examined the effects of polymers on secondary nucleation of ice crystals and reported that a decrease in the secondary nucleation rate of water was related to increased solution viscosity. However, Harper and Shoemaker (15) reported no correlation between locust bean gum concentration and ice recrystallization rates and suggested that the influence of stabilizers on texture may be due to considerations other than ice crystal size alone. Budiaman and Fennema (5) also reported that viscosity was not an adequate predictor of ice crystallization and suggested that some attribute other than ice crystal size may influence the beneficial effect of stabilizers on ice cream texture. As the concentration of the stabilizer rises in the freeze-concentrated serum phase, helical coil overlap or entanglement of the stabilizers may occur, thus diminishing the rates of diffusion of the polysaccharide, other solutes, and water and inhibiting crystal growth (17). Thus, diffusion kinetics may be more important than thermodynamic considerations (12, 13, 16, 17, 25, 26).

Current research (14) in the area of low temperature stability of frozen foods has focused on carbohydrate glass formation as a function of temperature. A glass is characterized as a metastable solid with a high viscosity of $>10^{13}$ Pa·s (16). At the glass transition temperature, polymeric materials change from a viscoelastic liquid (rubber) to an amorphous solid (glass) with an associated increase in viscosity. For frozen food systems, this temperature is defined as the glass transition temperature of a maximally freeze-concentrated solution (T_g') (16, 17). At temperatures above T_g', the constituents in the frozen system increase in mobility. The T_g' of ice cream may range from –23 to –43°C, depending on formulation (17). In the glassy state (temperatures below T_g'), the sample is stable to both recrystallization and deteriorative reactions because of the high viscosity (2). Cryostabilization of frozen dairy dessert products can be accomplished by elevation of T_g' through ingredient formulation or by storage at temperatures below T_g' (16).

The overall objective of this study was to describe further the mechanism by which polysaccharide stabilizers contribute to the stability of frozen dairy dessert products. This study describes the determination of the influence of polysaccharides on the T_g' of model carbohydrate systems and ice cream mixes by thermal analyses, determination of the subzero viscosity of the model systems and ice cream mixes by parallel plate rheometry, and examination of the effect of the stabilizers on ice crystal growth in ice cream during storage at abusive temperatures through low temperature scanning electron microscopy (SEM) techniques.

MATERIALS AND METHODS

Manufacture of Carbohydrate Solutions and Ice Cream

Solutions of 20% sucrose (wt/wt) were prepared with or without .6% added stabilizers (gelatin, guar gum, locust bean gum, carrageenan, and xanthan; Food Specialties, Halton Hills, ON, Canada). The dry solids (sucrose and stabilizer) were blended. Deionized water was warmed to the appropriate temperature for each stabilizer before the solids were added slowly. The stabilizers were incorporated by vigorous mixing using mechanical agitators, and the solutions were heated to 80°C, held for 10 min, and homogenized at 6.8 MPa, single stage. All solutions were then chilled to 5°C and held for 24 h before use.

The composition of the ice cream mix consisted of 11% milk fat, 11% milk SNF, 12% sucrose, 4% 42 dextrose equivalent corn syrup solids (Casco, Inc., Etobicoke, ON, Canada), .23% vanilla (Bowes Ltd., Toronto, ON, Canada), and, when stabilized, .15% locust bean

gum plus .02% carrageenan (Food Specialties). Mix was prepared using fresh cream (18% milk fat), skim milk, and instantized low heat NDM, pasteurized at 75°C for 15 min, homogenized at 17.2 MPa for the first stage and at 3.4 MPa for the second stage (Cherry Burrell, Chicago, IL), cooled to 5°C, and aged for 24 h. Continuous freezing was performed on a Vogt VA80 (Cherry Burrell) freezer to 85% overrun and a draw temperature of –5°C. The ice cream was packaged into 340-ml paper cups, hardened at –25°C, and stored under abusive temperature conditions that involved moving the ice cream from –25 to –10°C for 8 to 10 h daily for storage periods of up to 24 wk. The center temperature of the 340-ml cup reached the freezer temperature after the allotted time in each case.

Differential Scanning Calorimetry

A DuPont 1090 thermal analyzer (TA Instruments, New Castle, DE) equipped with a DuPont 910 differential scanning calorimeter (**DSC**) cell base was utilized. This equipment was later upgraded to the DuPont Thermal Analyst 2000 with DuPont 2910 cell base, confirming earlier results. The DSC was calibrated with indium, heptanol, ethylene glycol, and glycerol standards. Samples of approximately 3.0 mg, weighed accurately, were hermetically sealed in aluminum pans using the DuPont sample encapsulation press. Deionized water and 20% sucrose solutions with or without added polysaccharides or gelatin were cooled at a cooling rate of 20°C/min, using liquid nitrogen in the quench cooling assembly, and scanned at heating rates of 1, 2, 3, and 5°C/min from –80 to 20°C. Each treatment was replicated three times. The four response variables extracted from the DSC curves included the T_g', the onset of the melting endotherm, the peak temperature of the melting endotherm, and the melting enthalpy. The T_g' was determined by expansion of the baseline shift prior to the melting peak and measurement of the half height between the two baselines. The T_g' was also confirmed from the first derivative peak.

Thermomechanical Analysis

The thermomechanical analyzer (**TMA**) measures the dimensional change of a sample as a function of temperature or time. DuPont model 943 and model 2940 TMA modules (TA Instruments) with parallel plate rheometer attachments were utilized. A frozen slab of sample approximately 500 μm thick and 1 cm in diameter was placed between two circular plates. An expansion probe with a linear variable differential transformer capable of measuring small changes in sample height was lowered from above (model 943) or below (model 2940) to rest on top of these plates, which were shrouded by a liquid nitrogen quench cooling assembly and the TMA furnace. Force was applied either with weights (model 943) or electronically (model 2940). The dimensional change as a function of temperature was then recorded. Results from each instrument were compared.

The sample loading procedure involved a machined parallel plate holder that gave consistent sample dimensions (500 ± 10 μm) and consisted of four drilled wells in a brass base. The wells were deep enough to hold the parallel plates with a sample depth of .5 mm. The bottom rheometer plates were first loaded into the base of the brass loader. The upper rheometer plates were held into the top of the brass form with set screws. A 35-μl drop was spread over the whole surface of the bottom plate, and the brass form top was placed on the base. The sample form was then placed in the freezing environment. The freezing rate could be varied readily with this holder. After the sample was frozen, the set screws were unscrewed, and the top brass form was removed to permit removal of sample and plates. The plates were then removed from the base with a teflon plunger pushed up through the base. After removal, the plates were caged and transferred to the prechilled stage of the TMA. Extra samples were stored in the freezing environment.

The study consisted of a comparison of 20% sucrose solutions with or without .6% guar gum under various instrumental and processing conditions. Ice cream mixes were also studied in the presence or absence of stabilizer. Ice cream samples could not be studied in the TMA because of the overriding effect of overrun. Two extremes in freezing rate were studied, one rate by quench freezing with liquid nitrogen and a second slower rate by placing the holder on a plate freezer at –20°C. Samples were then equilibrated to

−70°C for 5 min in the TMA and heated at a heating rate of 2°C/min to temperatures above 0°C. Each solution was analyzed with either a 0, .1, .2, or .5 N (newtons) of force acting on the system. Each treatment was replicated five times. The expansion of the parallel plates during warming was subtracted from all curves prior to analysis.

The T_g' of the solutions was determined by tangents drawn to the curve both preceding and following the change in slope associated with the relaxation. The rate of deformation above the T_g' was characterized by the area under the curve from −30 to −10°C and the normalized height (after all curves were adjusted to the same vertical scale). Height and time data were taken at intervals of 1°C. The viscosity, η, was calculated from the data points of the TMA curve using the following equation:

$$\eta = \frac{4F}{3\pi r^4} + \frac{\Delta l/h^2}{\Delta t}$$

where F is the applied force (kilogram meters per second^2), r is the sample radius (.00475 m), h is the height of the sample (meter), and Δt is the time change (seconds) (11).

Low Temperature SEM

After hardening and at 3 and 24 wk of storage at abusive temperatures, ice cream samples were examined using low temperature SEM (EMscope SP2000A Sputter-Cryo Cryogenic Preparation System; Emscope, Ltd., Kent, England; Hitachi S-570 SEM; Hitachi Ltd., Tokyo, Japan), and image analysis (Zidas, Zeiss, Germany) according to the methods outlined by Caldwell et al. (7). Samples from the 340-ml cups were removed from a position at least 2.54 cm (1 in) from the top and sides of the container. Ice cream manufacture was performed only once; two containers of each ice cream were sampled at each time. For each sample in the SEM, 10 fields were examined and photographed. Ten crystals from each micrograph were then measured.

Statistical Analyses

For the DSC study, the general linear models procedure and Duncan's multiple range test of SAS (Statistical Analysis Systems, Cary, NC) were used to determine significance for the four response variables based on three replicates of six treatments. For the TMA experiment, the same statistical procedure was performed for the T_g' and for area response variables from five replicates of two solutions (sucrose and sucrose plus guar) each at four applied forces.

RESULTS

Thermal Analysis of Polysaccharide Solutions

DSC. The interpretations of the low temperature thermal events occurring during a DSC scan of sucrose solutions are a subject of current debate in the literature (14). The midpoint of the baseline shift occurring in a typical low temperature DSC scan of a sucrose solution (Figure 1) at temperatures lower than the onset of the ice melting peak has been defined as the T_g' (16). However, this transition temperature has also been interpreted solely in terms of the onset of ice melting (21, 25). We are presently investigating thermal events occurring at lower temperatures; thus, we use the T_g' definition with caution. Heating rates of 1, 2, 3, and 5°C/min were examined, and a heating rate of 2°C/min gave enthalpy results closest to those for calibration standards. Thus, this heating rate was used throughout the study. The sucrose curves had a baseline shift associated with the T_g' of sucrose occurring at approximately −34°C (Table 1), as reported by Levine and Slade (16). The presence of polysaccharide stabilizer did not significantly ($P > .05$) alter the T_g' relative to that of the sucrose solution, as has been previously shown for similar samples (26). However, the solution containing gelatin had the highest T_g', −33.5°C, which was significantly higher ($P \leq .05$) than those of the sugar solutions containing polysaccharide. The presence of any stabilizer did not significantly ($P > .05$) alter the onset temperature of the ice melting endotherm in the 20% sucrose solution. The solution containing xanthan gum had a significantly higher ($P \leq .05$) ice melting temperature than did all of the other solutions. The melting enthalpies of the stabilized solutions were not significantly different ($P > .05$) from that of the sucrose solution.

TMA. A typical TMA scan demonstrated a near constant plateau and then an abrupt drop

as the melting temperature of the sample was approached. The region of importance to frozen stability was along the plateau prior to the large melt relaxation. Expansion of the dimension axis in the temperature region preceding the ice melt revealed a characteristic inflection point or transition corresponding to the T_g' as defined herein. Thermal lag and physical movement of the sample are important considerations. Factors such as sample dimension, scanning rate, and thermocouple location contribute to thermal lag and need to be controlled. As a result of warming, the sample underwent a slight thermal expansion until it reached a maximum height and then began to decrease in height as a result of flow. This inflection in height occurred at the T_g' (18) as defined by Levine and Slade (16). Figure 2 shows characteristic TMA plots of 20% sucrose solutions with or without .6% guar gum. The stabilizer did not significantly ($P > .05$) alter the T_g' of the sample (data not shown); however, it did lead to a significant increase ($P \leq .05$) in the area under the curve (Table 2) and, hence, an increased resistance to thermal deformation of the sample, which was the case for all values of imposed force (Table 2). The optimal force for greatest difference between the two samples was between .1 and .2 N (Table 2). Samples frozen rapidly in liquid

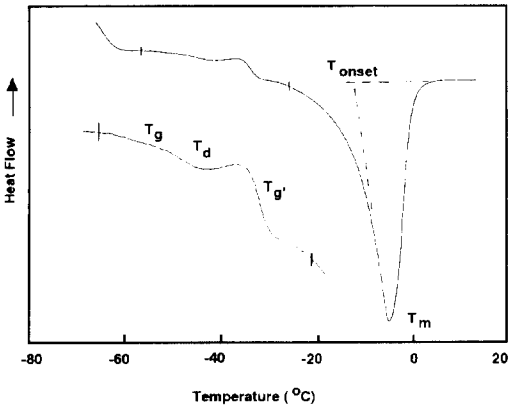

Figure 1. A typical differential scanning calorimetry scan, generated with a DuPont 2000 Thermal Analyzer with DuPont 2910 Cell Base, (TA Instruments, New Castle, DE) of a 20% sucrose solution showing the various thermal events occurring between –60 and 0°C. The temperature axis refers to the upper curve. The lower curve is an expansion of the upper line from –55 to –25°C, as indicated by the vertical slash marks on the curve. T_g' = Glass transition temperature of a maximally freeze-concentrated solution, as the midpoint of the baseline shift; T_g = thermal event at temperatures less than T_g', possibly a glass transition temperature of glass formed during nonequilibrium freezing process; T_d = devitrification temperature of a glass formed during nonequilibrium freezing process, resulting in a small epotherm; T_{onset} = temperature of the onset of the melting endotherm, by extrapolation back to the baseline; T_m = melting temperature taken as the peak temperature of the melting endotherm.

TABLE 1. Differential scanning calorimetry data[1] for 20% sucrose solutions with .6% added stabilizer scanned from –60 to 20°C at a heating rate of 2°C/min.

Solution[2]	Baseline shift (T_g')[3]		Temperature				Enthalpy of melting	
			Onset[4]		Melt[5]			
	(°C)						(J/g of solution)	
	$\bar{X}$	SE	$\bar{X}$	SE	$\bar{X}$	SE	$\bar{X}$	SE
20% Sucrose	–34.18	.03	–5.48	.05	–1.48	.03	279.0	9.3
20% Sucrose +								
Locust bean gum	–34.62	.38	–5.32	.05	–1.55	.00	275.0	1.7
Guar	–34.02	.19	–5.42	.07	–1.52	.03	283.0	2.8
Carrageenan	–34.35	.09	–5.75	.13	–1.52	.10	274.7	3.4
Xanthan	–34.32	.03	–5.52	.07	–1.25	.00	278.0	1.3
Gelatin	–33.50	.09	–5.28	.07	–1.55	.05	285.0	3.1

[1]Obtained with the DuPont 1090 Thermal Analyzer with DuPont 910 Cell Base (TA Instruments, New Castle, DE).

[2]n = 3.

[3]Glass transition temperature of a maximally freeze-concentrated solution.

[4]Temperature at the onset of the melting endotherm.

[5]Melting temperature taken as the peak temperature of the melting endotherm.

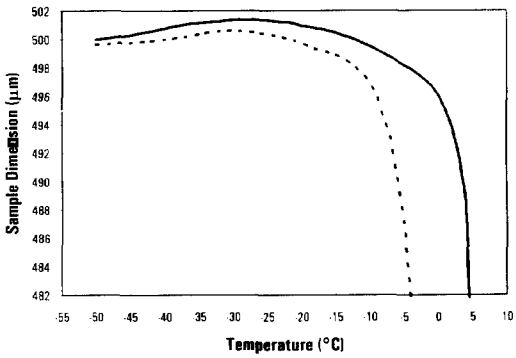

Figure 2. Comparison of average thermomechanical analysis curves for slowly frozen 20% sucrose solutions with (—) or without (---) .6% guar gum scanned at a heating rate of 2°C/min with an applied force of .1 N. The vertical axes of the curves have been shifted slightly to illustrate the differences in shape (n = 5).

nitrogen showed greater deformation than those frozen slowly (Figure 3). This difference may have been related to the relaxation of a larger amount of glass that formed during rapid freezing (8) and also to a smaller ice crystal size.

The maximum viscosity calculable using the parallel plate rheometry was 10^8 Pa·s and was recorded at the first achievable change in height. A glass is characterized by a viscosity of about 10^{13} Pa·s; however, the plated sample did not show flow at temperatures below the T_g'. Sample dimension had a large influence on calculated viscosity and was held constant (± 10 μm) throughout the study with the use of the machined sample preparation unit. Viscosity data are shown as a function of temperature (Figure 4) for sucrose and sucrose plus guar gum solutions. The presence of stabilizer results in a much greater increase in subzero viscosity than the sucrose solution.

Thermal Analysis of Mix and Microstructure of Ice Cream

The stabilized ice cream mix did not display the same degree of thermal expansion upon traversing the T_g' in the TMA as did the control ice cream mix, which showed a more predominant thermal expansion at the T_g'. The T_g' determined for the stabilized ice cream mix was approximately –30°C. However, the T_g' was difficult to assess accurately, given the low level of thermal deformation in the region of the transition. Figure 5 demonstrates the increase in viscosity, as determined by the TMA, that occurred within the stabilized mix as a function of subzero temperature. Similar to the sucrose plus polysaccharide solution, viscosity was higher in the stabilized sample and rose rapidly at temperatures below –20°C. As the stabilizer concentration increases because of freeze-concentration, a critical value may be reached beyond which molecular entanglement (26) results in this dramatic increase in subzero viscosity.

Low temperature SEM and image analysis showed that the addition of stabilizer to the ice cream mix led to smaller ice crystal size at the time of ice cream manufacture and greater resistance to the growth of ice crystals during storage at abusive temperatures (Table 3), as we reported earlier (8). The SEM provides much detail regarding the microstructure of ice cream, but SEM is a lengthy and detailed procedure. Light microscopy may be better suited for a quantitative study of ice crystal

TABLE 2. Area under the thermomechanical analysis curve for slowly frozen 20% sucrose solutions with or without .6% guar gum, using applied forces of 0, .1, .2, and .5 N.

Solution[1]	Force				Mean
	0 N	.1 N	.2 N	.5 N	
	(μm^2)				
Sucrose	349.6	297.4	300.5	295.0	310.5[b]
Sucrose plus guar	363.7	336.7	348.5	317.8	341.7[a]
Mean	356.7[a]	317.1[b]	324.5[b]	306.2[b]	

[a,b]Means with identical letters are not significantly different ($P > .05$).

[1]n = 5 for each solution at each force.

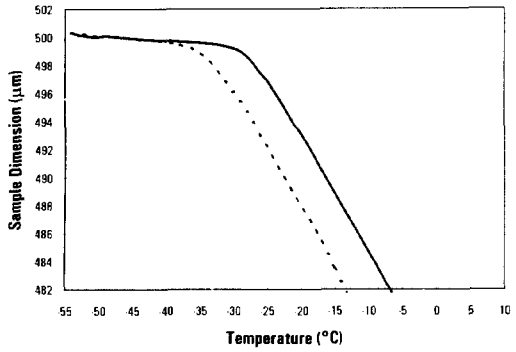

Figure 3. Comparison of average thermomechanical analysis curves for rapidly frozen 20% sucrose solutions with (—) or without (---) .6% guar gum scanned at a heating rate of 2°C/min with an applied force of .1 N (n = 5).

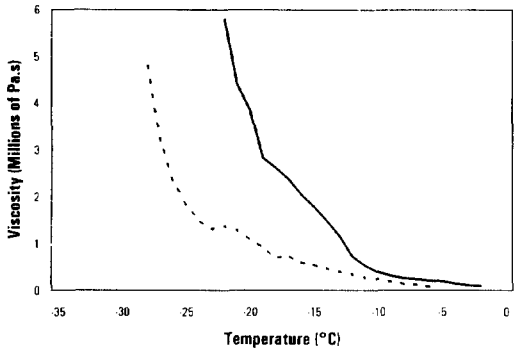

Figure 5. Viscosity of stabilized (—) and control (unstabilized) (---) ice cream mixes, as calculated from an average of thermomechanical analysis data. Mixes were slowly frozen between parallel plates and scanned at a rate of 2°C/min (n = 4).

sizes (10). A regression analysis of the data in Table 3 demonstrated a significantly greater ($P \leq .05$) slope for the control ice cream than for the stabilized ice cream. However, for these two treatments, differences in ice crystal image analysis data are more clearly demonstrated by comparison of the distributions of ice crystal size during storage. As shown in Figure 10 by Caldwell et al. (8), at the end of 3 wk, 25% of the ice crystals in the control ice cream were >80 μm, whereas only 12% of the ice crystals in the stabilized ice cream were >80 μm. At the end of 24 wk, 60% of the ice crystals in the control ice cream were >100 μm, and 30% were >140 μm, but only 40% of the ice crystals in the stabilized ice cream were >100 μm, and only 12% were >140 μm. This distribution of large crystals likely leads to the sensory perception of iciness in unstabilized ice creams; Arbuckle (1) indicated that ice crystals >55 μm were indicative of coarse product. Also, considerable evidence in the unstabilized ice creams indicated that crystals had fused at an interface, presumably because of the weak lamellae surrounding them, which agrees with previous reports (1, 10).

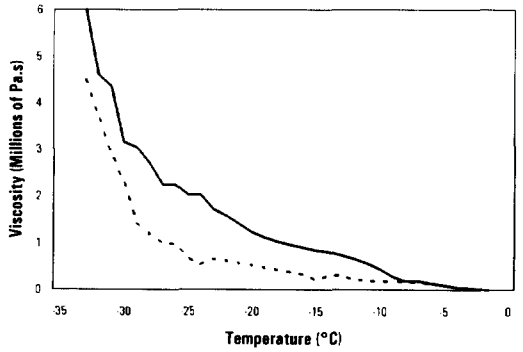

Figure 4. Viscosity of 20% sucrose plus .6% guar gum (—) and 20% sucrose (---) solutions as calculated from an average of thermomechanical analysis data. Solutions were slowly frozen and scanned at a rate of 2°C/min (n = 5).

DISCUSSION

The structure of ice cream can be depicted as a four-phase system that comprises fat globules, air bubbles, ice crystals, and a concentrated serum phase containing many of the soluble components, including sugars and polysaccharide stabilizers (7). As freeze-concentration progresses during the manufacture of ice cream, the sugars and stabilizers are forced into smaller areas surrounding the ice phase. Consequently, the concentration of these carbohydrates increases greatly within this continuous matrix. Polysaccharides are high molecular weight compounds in the form of long, straight-chain, or branched polymers capable of considerable interaction at high concentration. Ice crystals freeze out of solution in pure form, and the nucleation rate is largely a function of the rate of freezing, which is related to the temperature differential within

TABLE 3. Mean ice crystal diameter (± 95% confidence limits) from cryoscanning electron microscopy and image analysis of stabilized[1] and unstabilized (control) ice cream, after manufacture (0 wk) and after storage at abusive temperatures.

Time	Unstabilized ice cream	Stabilized ice cream
(wk)	(μm)	
0	43.3 ± 3.3[2]	35.4 ± 3.2
3	61.9 ± 5.2	57.0 ± 4.6
24	113.7 ± 7.0	95.4 ± 5.1

[1].15% Locust bean gum + .02% carrageenan.

[2]n = 200 (10 per field; 10 fields per sample; 2 samples per treatment).

the freezer barrel and to the conductive and convective heat transfer coefficients of the freezing system (2). However, during storage, especially in the presence of temperature fluctuations, the continuous melting of ice crystals and refreezing of water leads to tremendous growth in the ice crystals, as demonstrated by the low temperature SEM. The polysaccharide stabilizers act within the concentrated serum phase to control this recrystallization process. At sufficiently low temperatures, this freeze-concentrated serum phase may form a glass (17).

The results from the DSC of model solutions of sucrose plus polysaccharide indicate trends reported elsewhere (3, 19, 20); the polysaccharide had no significant effects on ice melting temperatures or amount of ice frozen. Also, the baseline shift defined as the T_g' by Levine and Slade (16) was not influenced significantly by addition of any of the polysaccharides to the sucrose solution. Although the T_g' is a function of the weighted average molecular weight of the solution (26), the addition of low concentrations of stabilizer used in ice cream is not sufficient to produce any significant alteration of the T_g'. This baseline shift is the subject of considerable debate in the literature at present (21, 22, 23, 25). For the model solutions, the T_g' associated with this DSC baseline shift were in the range of –34°C, and similar temperatures were observed in the TMA studies with the model systems and the ice cream samples. Thermal events were noted in DSC scans at temperatures less than the T_g' value (Figure 1), which may represent devitrification and recrystallization events (16). However, theoretically these events should not occur if the system were both maximally freeze-concentrated and in the glassy state, which is under current investigation. The action of gelatin was different from that of the polysaccharides in that it may have significantly altered the T_g', which is also being investigated further.

In contrast to the DSC results, measurements of the thermal deformation and rheological properties of the stabilized model solutions and ice cream mixes by TMA demonstrated strong dependence on the presence or absence of polysaccharide. The polysaccharides greatly increased the resistance to flow of the serum phase surrounding the ice crystals, thereby reducing the rate of thermal deformation during warming of the samples at subzero temperatures. The stabilizers also produced a large increase in calculated viscosity at subzero temperatures, compared with unstabilized samples, and this viscosity increased markedly at temperatures below –20°C. Although ice cream samples were not studied in the TMA, the serum phase surrounding the ice crystals would be similar in frozen mix and in ice cream, differentiated only by the phase separation that can occur around an air bubble, primarily involving fat, but also some protein (7).

Rapid freezing of sucrose solutions using liquid nitrogen resulted in more thermal deformation in the frozen sample than did slower freezing rates for the same solution. Because of the rapid freezing rate, the ice crystals that form are smaller (2) and were probably surrounded by the glassy, incompletely freeze-concentrated serum. Some of the water that could potentially freeze was likely vitrified in the concentrated serum (17). Thus, upon warming to temperatures above the T_g', when the glass changes to a rubbery liquid, the newly transformed water diluted the macromolecules in the unfrozen serum, facilitating serum flow. The deformation resulting from serum flow was probably more rapid than the rate of ice recrystallization. The smaller ice crystals also contributed to reduced physical resistance. In contrast, during slower freezing, the amount of ice formed was probably closer to maximal freeze concentration conditions.

Polysaccharides increase the viscosity of ice cream mix (1). As a result of freeze-

concentration, the polysaccharides likely became more concentrated and entangled, thus increasing further the viscosity of the unfrozen continuous phase surrounding the ice crystals. The polysaccharides had an effect on ice crystal growth in ice cream that was temperature abused, but this effect could not be related to modification of phase behavior of the water or ice. Therefore, the stabilizer's mode of influencing ice crystal growth apparently is by kinetic properties. The molecular diffusion rates would decrease as a result of the large increase in viscosity so that water might have to recrystallize in its entrapped position during temperature fluctuations rather than migrate to existing ice crystals, even though the latter would be favored thermodynamically (3, 13). Glass transitions were noted for the model systems and the ice cream mixes at temperatures below –30°C. Storage of ice cream at this low temperature to maintain the glassy state for enhanced stability is not practical. Polysaccharides at the low concentrations used in the industry have no significant effect on this T_g'. However, knowledge of the action of additional solutes on glass transitions in frozen foods may provide alternative means of stabilizing ice cream for improved shelf-life.

CONCLUSIONS

Polysaccharide stabilizers did not significantly influence the thermal properties of sucrose solutions or ice cream mixes as determined by DSC. However, they did provide a protective effect on the growth of ice crystals during manufacture and storage at abusive temperatures. The initial ice crystal size and the rate of growth of ice crystals were smaller in stabilized ice creams than in unstabilized ice creams. Stabilizers provided resistance to thermal deformation and increased subzero viscosity above the T_g' but did not significantly influence the experimental T_g' of the solutions. The control of ice crystal growth in stabilized ice cream above its T_g' is, therefore, postulated to be a function of the kinetic properties of the freeze-concentrated viscoelastic liquid surrounding the ice crystals.

ACKNOWLEDGMENTS

Financial assistance for this project was provided by the Natural Sciences and Engineering Research Council of Canada and the Ontario Ministry of Agriculture and Food. Appreciation is expressed to Sandy Smith for assistance with the SEM research.

REFERENCES

1 Arbuckle, W. S. 1986. Ice Cream. 4th ed. AVI Publ. Co. Ltd., Westport, CT.
2 Blanshard, J.M.V., and F. Franks. 1987. Ice crystallization and its control in frozen food systems. Page 51 *in* Food Structure and Behaviour. J.M.V. Blanshard and P. Lillford, ed. Academic Press, New York, NY.
3 Blanshard, J.M.V., A. H. Muhr, and A. Gough. 1991. Crystallization from concentrated sucrose solutions. Page 639 *in* Water Relationships in Foods. H. Levine and L. Slade, ed. Plenum Press, New York, NY.
4 Budiaman, E. R., and O. Fennema. 1987. Linear rate of water crystallization as influenced by temperature of hydrocolloid suspensions. J. Dairy Sci. 70:534.
5 Budiaman, E. R., and O. Fennema. 1987. Linear rate of water crystallization as influenced by viscosity of hydrocolloid suspensions. J. Dairy Sci. 70:547.
6 Buyong, N., and O. Fennema. 1988. Amount and size of ice crystals in frozen samples as influenced by hydrocolloids. J. Dairy Sci. 71:2630.
7 Caldwell, K. B., H. D. Goff, and D. W. Stanley. 1992. A low-temperature SEM study of ice cream. I. Techniques and general microstructure. Food Struct. 11:1.
8 Caldwell, K. B., H. D. Goff, and D. W. Stanley. 1992. A low-temperature SEM study of ice cream. II. Influence of ingredients and processes. Food Struct. 11: 11.
9 Cottrell, J.I.L., G. Pass, and G. O. Phillips. 1979. Assessment of polysaccharides as ice cream stabilizers. J. Sci. Food Agric. 30:1085.
10 Donhowe, D. P., R. W. Hartel, and R. L. Bradley, Jr. 1991. Determination of ice crystal size distributions in frozen desserts. J. Dairy Sci. 74:3334.
11 DuPont Instruments. 1981. Instruction Manual 2943 Thermomechanical Analyzer (TMA). DuPont Publ., Wilmington, DE.
12 Franks, F. 1985. Biophysics and Biochemistry at Low Temperatures. Cambridge Univ. Press, New York, NY.
13 Franks, F. 1985. Complex aqueous systems at subzero temperatures. Page 497 *in* Properties of Water in Foods. D. Simatos and J. L. Multon, ed. Martinus Nijhoff Publ., Dordrecht, Neth.
14 Goff, H. D. 1992. Low-temperature stability and the glassy state in frozen foods. Food Res. Int. 25:317.
15 Harper, E. K., and C. F. Shoemaker. 1983. Effect of locust bean gum and selected sweetening agents on ice recrystallization rates. J. Food Sci. 48:1801.
16 Levine, H., and L. Slade. 1988. Principles of cryostabilization technology from structure/property relationships of carbohydrate/water systems. A review. Cyro Lett. 9:21.
17 Levine, H., and L. Slade. 1990. Cryostabilization technology: thermoanalytical evaluation of food ingredients and systems. Page 221 *in* Thermal Analysis of Foods. V. R. Harwalker and C. Y. Ma, ed. Elsevier Appl. Sci. Publ., New York, NY.

18 Maurice, T. J., Y. J. Asher, and S. Thomson. 1991. Thermomechanical analysis of frozen aqueous systems. Page 215 *in* Water Relationships in Foods. H. Levine and L. Slade, ed. Plenum Press, New York, NY.

19 Muhr, A. H., and J.M.V. Blanshard. 1986. Effect of polysaccharide stabilizers on the rate of growth of ice. J. Food Technol. 21:683.

20 Muhr, A. H., J.M.V. Blanshard, and S. J. Sheard. 1986. Effects of polysaccharide stabilizers on the nucleation of ice. J. Food Technol. 21:587.

21 Roos, Y., and M. Karel. 1991. Phase transitions of amorphous sucrose and frozen sucrose solutions. J. Food Sci. 56:266.

22 Roos, Y., and M. Karel. 1991. Nonequilibrium ice formation in carbohydrate solutions. Cyro Lett. 12: 367.

23 Roos, Y., and M. Karel. 1991. Amorphous state and delayed ice formation in sucrose solutions. Int. J. Food Sci. Technol. 26:553.

24 Shirai, Y., K. Nakanishi, R. Matsuno, and T. Kamikubo. 1985. Effects of polymers on secondary nucleation of ice crystals. J. Food Sci. 50:401.

25 Simatos, D., and G. Blond. 1991. DSC studies and stability of frozen foods. Page 139 *in* Water Relationships in Foods. H. Levine and L. Slade, ed. Plenum Press, New York, NY.

26 Slade, L., and H. Levine. 1991. Beyond water activity: recent advances based on an alternative approach to the assessment of food quality and safety. Crit. Rev. Food Sci. Nutr. 30:115.

27 Smith, D. E., and S. A. Wittinger. 1986. Effect of sweeteners and stabilizers on the structure of ice cream mix as determined by acoustic methods. J. Food Process. Preserv. 10:227.