Effect of Salts on the Gelatinization and Rheological Properties of Sago Starch

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The effects of various salts on the gelatinization and rheological properties of sago starch have been studied using differential scanning calorimetry, small deformation oscillation, and large deformation techniques. The presence of salts affected the gelatinization peak temperature, T_p, gelatinization enthalpy, ΔH, swelling properties, storage modulus, G', gel strength, GS, and gelation rate constants, k, depending on the type of salt and the concentration. Their influence followed the Hofmeister series, and the effect of anions was more pronounced than that of cations. Sulfate ions increased T_p, G', GS, and k and reduced the swelling properties, whereas iodide and thiocyanate ions reduced T_p, G', GS, and k but increased the swelling properties. For all of the salts studied except for Na_2SO_4, T_p increased to a maximum and then decreased again at higher salt concentrations while ΔH reduced with concentration. In the presence of $MgCl_2$, $CaCl_2$, and LiCl complex behavior was observed such that at ~3.5 M $MgCl_2$ and $CaCl_2$ and 8 M LiCl the starch samples were gelatinized at room temperature, whereas at much higher concentration T_p increased again and the transition became exothermic.

Keywords: *Sago starch; differential scanning microscopy; rheology; gelatinization; gelation; Hofmeister series*

INTRODUCTION

Sago starch is isolated from the sago palm, *Metroxylon* spp., which is distributed throughout Southeast Asia. Generally *M. sagu* and *M. rumphii* give the highest starch yield and are widely used for starch extraction. There are very few reports in the literature concerning the physicochemical properties and characteristics of sago starch. In a recent study of 12 sago starches from various sources, we showed that the granules have an average diameter of 30 μm and exhibit a C-type X-ray diffraction pattern similar to that of pea starch rather than the A-type patterns found for cereal starches. This may be a consequence of its slightly higher amylose content, which was shown to be in the range from 25 to 31%. The gelatinization peak temperature (the temperature at which the crystalline structure of the granules is disrupted) was ~70° C (Ahmad et al., 1999).

Salts have been shown to have a significant effect on the gelatinization and rheological properties of starches generally, and it has been found that they can cause an elevation or depression of the gelatinization temperature, T_p, (Wooton and Bamunuarachchi, 1980; Evans and Haisman, 1982; Chuncharoen and Lund, 1987; Paredes-Lopez and Hernandez-Lopez, 1991; Jane, 1993), and gelatinization enthalpy, ΔH (Wooton and Bamunuarachchi, 1980; Evans and Haisman, 1982; Chuncharoen and Lund, 1987; Jane, 1993) and similarly might increase or decrease the rate and degree of gelation (Katsuta, 1998) and retrogradation (Ciacco and Fernandes, 1979; Chang and Lui, 1991). Surprisingly, as far as we aware there are no studies that compare the effect of salt type and concentration on both the gelatinization and gelation properties of starches generally. The purpose of this investigation, therefore, has been to undertake a comprehensive study of the effect of electrolytes on the swelling, gelatinization, and gelation of sago starch. The electrolytes were chosen on the basis of their ability to influence solvent quality according to the Hofmeister (lyotropic) series.

EXPERIMENTAL PROCEDURES

Materials. The sago starch used in this study was a food grade sample and was a gift from Netsei Sago Industry, Sarawak, Malaysia. The amylose content for the sample was 31%, with an average particle size around 30 μm and molecular mass of the amylose fraction 7.9×10^5 Da. The sample was used as provided without any further treatment.

All salts used in this study were of analytical grade and purchased from Sigma Chemical Co.

Differential Scanning Calorimetry (DSC). DSC measurements were performed using a micro DSC (Setaram, Lyon, France). Starch samples were prepared on a dry weight basis, and 10% (w/v) starch was used for all experiments. Salt solutions at the required concentration were prepared on a molar basis. An appropriate amount of starch was added to the salt solutions and the pH of the suspension adjusted to 5.5 by adding 0.02 M HCl or NaOH. The suspensions were shaken thoroughly before being weighed into the DSC cell. An aliquot of the sample (~0.95 g) was transferred to the DSC measurement cell, the top sealed, and the weight recorded. An equal mass of solvent was added into the reference cell. The cells were heated from 0 to 99 °C at a rate of 0.5 °C/min. The temperature at which the gelatinization process began, T_o, the peak temperature, T_p, the conclusion temperature, T_c, and the gelatinization enthalpy, ΔH, were determined. Two measurements were performed for each sample, and the results are given here as an average. Good reproducible results were obtained for each measurement and agreed within ±0.1%.

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Swelling Factor. Salts in the required concentration were prepared (0.5 M), and starch was added to give a 0.5% starch suspension. The pH of the suspension was adjusted to 5.5 by adding dilute HCl or dilute NaOH and gently stirred. The suspension was heated for 30 min at 95 °C and stirred at 200 rpm using a mechanical stirrer. Excessive stirring was avoided to minimize fragmentation of the swollen granules. After the heating period, hot distilled water was added to compensate for evaporation, and the samples were then centrifuged for 15 min at 2200 rpm (using an MSE Centaur 2 centrifuge) and the weight of the sedimented fraction was determined. The swelling factor was calculated as the ratio of the weight of the swollen starch granules to the weight of the dry starch. The results reported are the mean of triplicate measurements. Good reproducible results were obtained for each measurement. All of the measurements agreed within ±1%.

Mechanical Spectroscopy. The storage and loss moduli (G' and G') were monitored using a Carri-Med CSL500 controlled stress rheometer (TA Instruments, Leatherhead, U.K.). Measurements were performed on 6% w/v starch samples. Salt solutions (molar basis) were prepared at the required concentration and starch was added. The starch suspensions were adjusted to pH 5.5 using dilute HCl or dilute NaOH prior to heating. All samples were heated for 30 min at 95 °C with constant stirring at 400 rpm. The beaker was reweighed and the volume corrected for evaporation loss on heating using hot distilled water. Hot samples were placed immediately into the rheometer measuring system (cone and plate, 4 cm diameter, 2° angle), which was equilibrated to 25° C. All measurements were performed within the linear viscoelastic region. For all samples, measurements were made at a frequency of 1.0 Hz with an amplitude of 1 mrad over a 6 h period without disturbing the samples. A solvent trap was used to eliminate the evaporation of water. At the end of the run a frequency sweep was performed in the range between 0.1 and 10.0 Hz. All measurements were undertaken twice and agreed within ±1%. Results reported are an average of the two measurements.

Gel Strength. Sample preparation was similar to the above. Hot samples were transferred into storage jars, cooled to 25 °C in a circulating water bath, and stored at that temperature for 6 h before measurement of the gel strength. Measurements were performed using a texture analyzer (Stevens, Leatherhead Food Research, Surrey, U.K.) using a 1 cm probe with a penetration speed of 1 mm/s, a penetration depth of 20 mm, and a gel depth of 30 mm. The force required to break the gel was determined. Triplicate measurements were performed, and the results given here are an average. Good reproducible results were obtained and agreed within ±1%.

RESULTS

Differential Scanning Calorimetry. Figures 1, 2, and 3 show DSC endotherms for sago starch in the presence of Na_2SO_4, NaCl, and NaI, respectively. In the presence of Na_2SO_4, T_p increased with concentration and the endotherms became sharper. For NaCl, T_p increased with concentration to a maximum value (~2 M NaCl) and then decreased at higher concentrations. The intensities of the peaks decreased with increasing NaCl concentrations. In the presence of NaI, generally T_p decreased with increasing concentration. The intensities of the peaks reduced with concentration, and at ~2 M NaI no peak was observed. A similar observation was noted for KI, NaSCN, and KSCN, and light microscopy studies revealed that gelatinization had occurred at room temperature.

For NaCl, KCl, and $NaNO_3$ (DSC curves not shown) at lower concentration, T_p increased slightly to a maximum value then decreased with increasing concentration. The different electrolyte concentration ranges
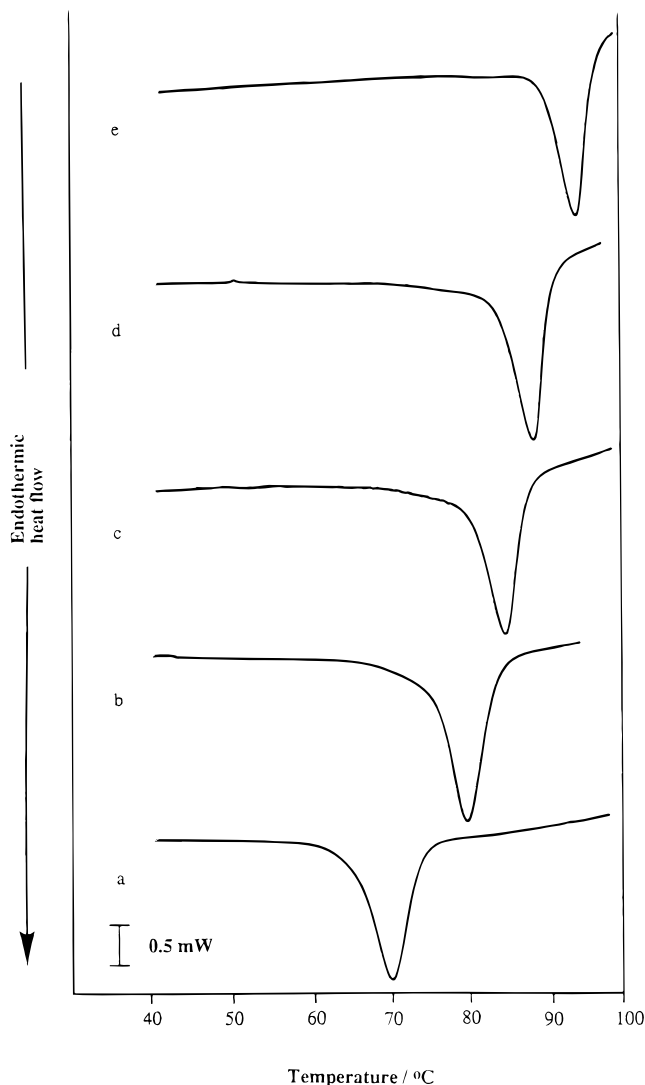

Figure 1. Effect of Na_2SO_4 on DSC endotherms for 10% sago starch: (a) control; (b) 0.25 M Na_2SO_4; (c) 0.5 M Na_2SO_4; (d) 0.75 M Na_2SO_4; (e) 1.0 M Na_2SO_4. Heating rate = 0.5 °C/min.

used were a consequence of their solubility. The effect of various salts on T_p is summarized in Figure 4.

The ΔH for the gelatinization process in the presence of these salts is shown in Figure 5. For Na_2SO_4, NaCl, KCl, and $NaNO_3$, ΔH increased slightly at low salt concentrations but decreased at higher concentration. For KSCN and NaI, ΔH decreased to a greater extent compared to the other salts.

Figure 6 shows DSC endotherms for sago starch in the presence of $MgCl_2$. Similar curves were obtained for $CaCl_2$ and LiCl (data not shown). Figure 7 shows the effect of $CaCl_2$, $MgCl_2$, and LiCl on T_p. In the presence of these salts complex behavior was observed. Initially T_p increased at the lower concentrations to a maximum value, then decreased to pass through a minimum, and finally increased again at much higher concentration, which for $CaCl_2$ and $MgCl_2$ was >4 M and for LiCl was >12 M. For $MgCl_2$ and $CaCl_2$ at ~3.5 M and for LiCl at ~8 M the sago starch was gelatinized at room temperature. For other salts, the effect on T_p at higher concentrations could not be studied due to their solubility.

Complex behavior was also observed for the gelatinization enthalpy in the presence of $CaCl_2$, $MgCl_2$, and LiCl as shown in Figure 8. The endothermic peak
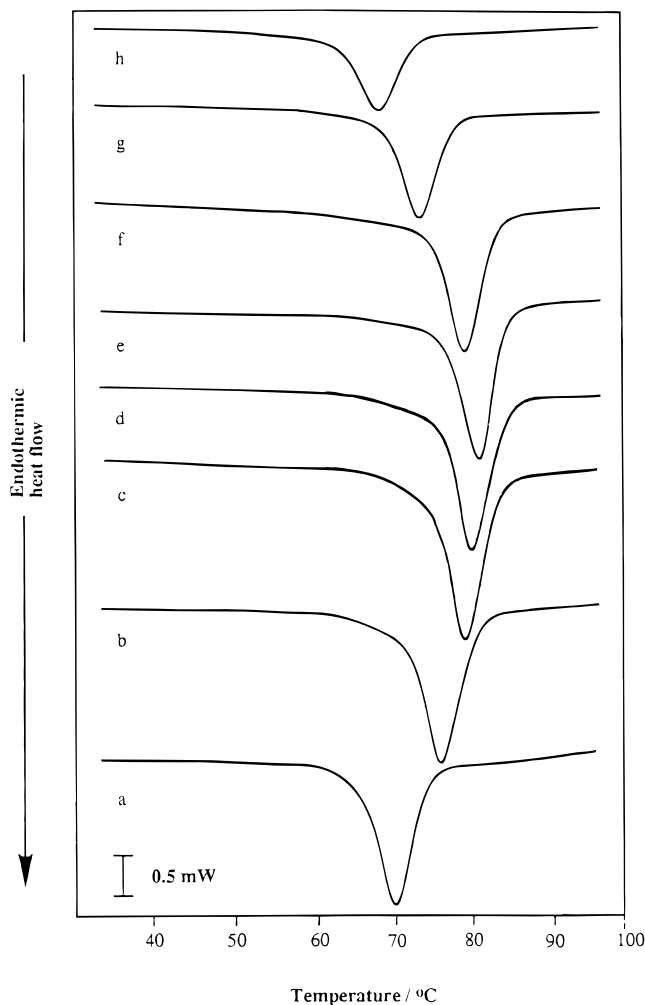
Figure 2. Effect of NaCl on DSC endotherms for 10% sago starch: (a) control; (b) 0.25 M NaCl; (c) 0.5 M NaCl; (d) 1 M NaCl; (e) 2 M NaCl; (f) 3 M NaCl; (g) 4 M NaCl; (h) 5 M NaCl. Heating rate = 0.5 °C/min.
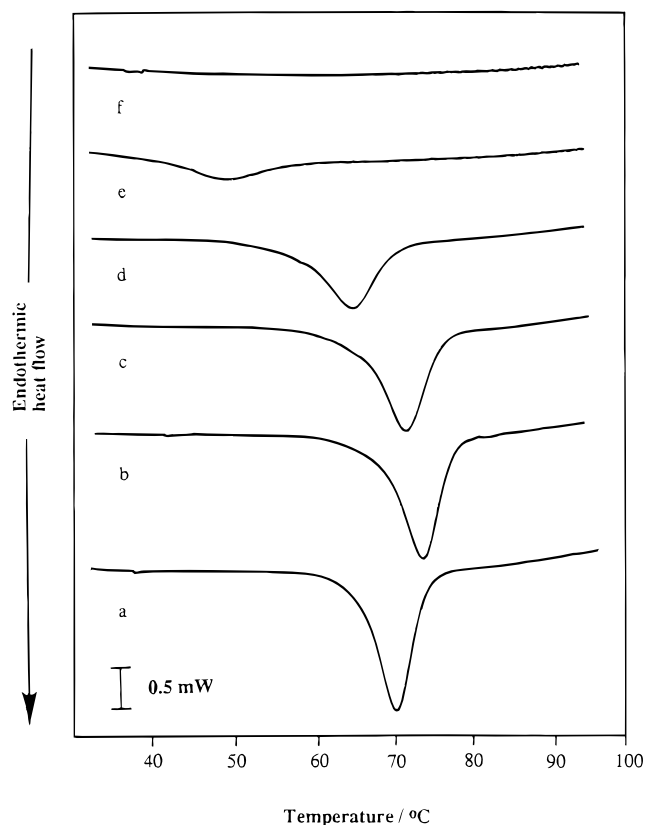

Figure 3. Effect of NaI on DSC endotherms for 10% sago starch: (a) control; (b) 0.25 M NaI; (c) 0.5 M NaI; (d) 1 M NaI; (e) 1.5 M NaI; (f) 2 M NaI. Heating rate = 0.5 °C/min.
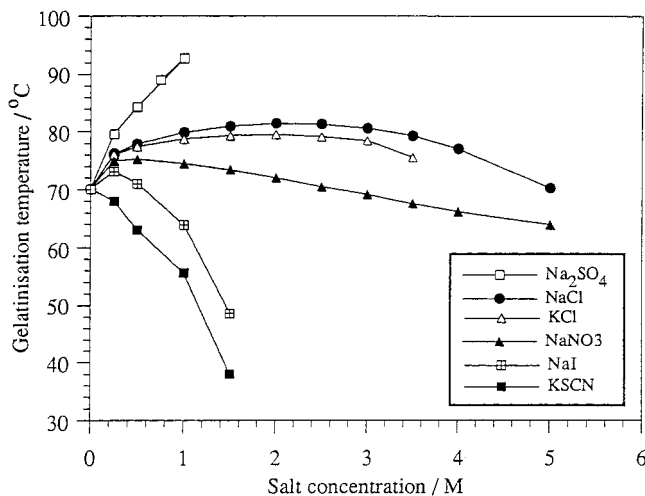

Figure 4. Effect of various salts on the gelatinization temperature for 10% sago starch. Heating rate = 0.5 °C/min.

associated with the gelatinization process reduced in intensity with increasing salt concentration, and at high concentrations an exothermic peak was observed that shifted to higher temperatures as the salt concentration increased. For $CaCl_2$ and $MgCl_2$ the change from an endothermic to an exothermic transition occurred at ~4 M, whereas for LiCl it occurred at ~12 M. There was no corresponding endothermic peak obtained when these solutions cooled, indicating that the enthalpy was due to a nonequilibrium process. Interestingly, after the mixtures had stood for 24 h and the DSC experiment had been repeated, the exothermic peak no longer appeared. Instead, a small endothermic peak was obtained at a temperature that corresponded to the sample changing from a turbid to a crystal clear viscous solution and was, presumably, due to the dissolution process. There was no corresponding exothermic peak obtained on cooling, but the sample gradually became more turbid over time.

Table 1 compares the effect of various salts at a concentration of 1 M on T_o, T_p, T_c, ΔT ($T_c - T_o$), and ΔH. Generally ΔT increased (except for Na_2SO_4 and $AlCl_3$) in the presence of salt, especially with I^- and SCN^- ions.

The influence of the ions was in accordance with the Hofmeister series. Thus, for the sodium salts of the various anions T_p and ΔH decreased in the order SO_4^{2-}

> $Cl^- > Br^- > NO_3^- > I^- > SCN^-$. A similar trend was observed for ΔH, that is, $SO_4^{2-} \sim Cl^- > Br^- > NO_3^- > I^- > SCN^-$, and for the cations T_p decreased in the order $Al^{3+} > Mg^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+ > Cs^+$, whereas ΔH did not show any specific trend but decreased in the order $Al^{3+} > K^+ \sim Na^+ \sim Li^+ > Ca^{2+} > Mg^{2+} \sim Cs^+$.

Anions had a greater effect compared to the cations on the gelatinization process.

Swelling Properties. The swelling factor for sago starch in 0.5 M salts is shown in Figure 9. For the anions, the swelling factor decreased in the order $SCN^- > I^- > NO_3^- > Br^- > Cl^- > SO_4^{2-}$ and for cations $K^+ > Na^+ > Li^+$, consistent with the Hofmeister series. Generally the salting-out ions reduced the swelling,

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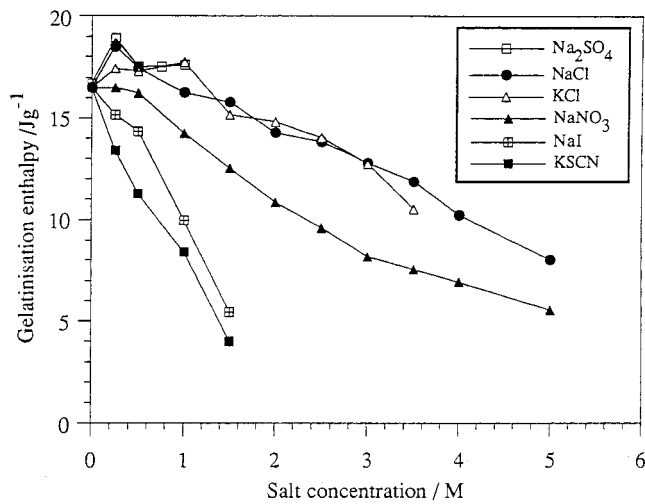**Figure 5.** Effect of various salts on the gelatinization enthalpy for 10% sago starch. Heating rate = 0.5 °C/min.

Figure 6. Effect of $MgCl_2$ on DSC endotherms for 10% sago starch: (a) control; (b) 0.25 M $MgCl_2$; (c) 1 M $MgCl_2$; (d) 2 M $MgCl_2$; (e) 2.5 M $MgCl_2$; (f) 3 M $MgCl_2$; (g) 3.5 M $MgCl_2$; (h) 4 M $MgCl_2$; (i) 5 M $MgCl_2$. Heating rate = 0.5 °C/min.

whereas the salting-in ions increased the swelling. The most significant effect can be observed by comparing the highest and lowest ranking ions in the Hofmeister series. SO_4^{2-} reduced the swelling significantly compared to the control, whereas I^- and SCN^- gave rise to an increase.

Rheological Properties. *Small Deformation Oscillation Measurements.* The effect of NaCl concentration on G' is shown in Figure 10. The symbols represent the experimental data points; the solid lines have been
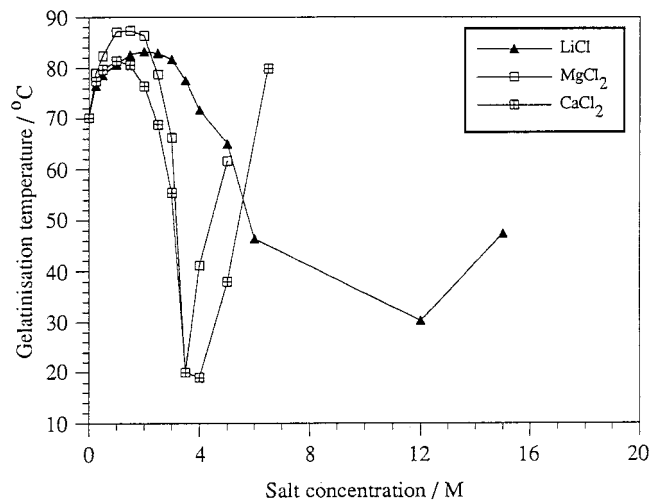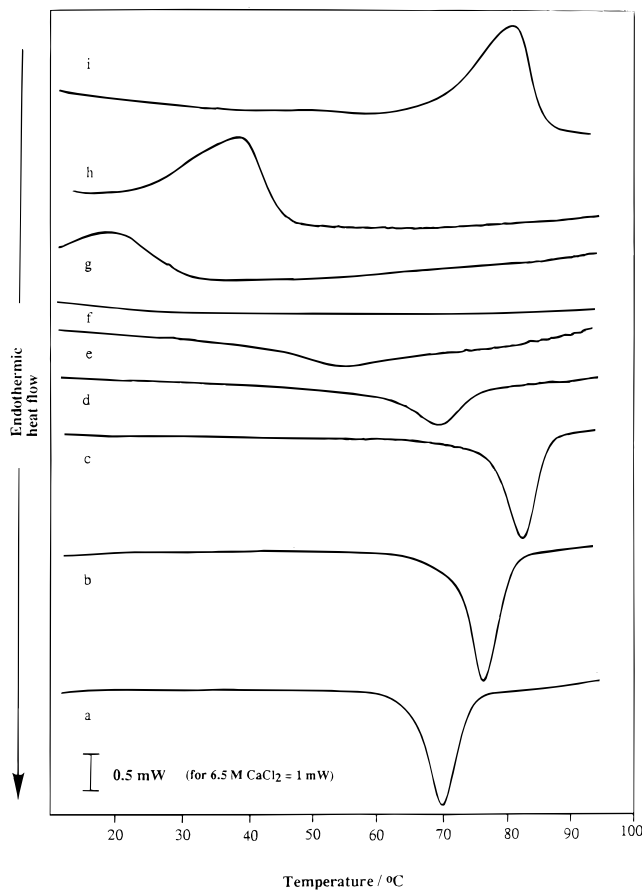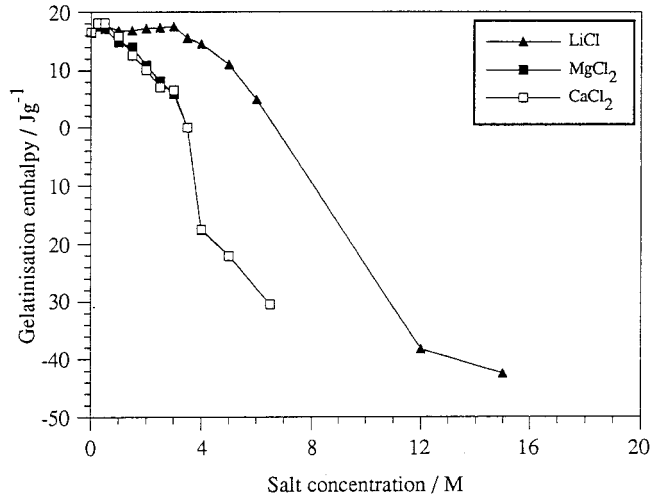

Figure 7. Effect of $MgCl_2$, $CaCl_2$, and LiCl on gelatinization temperature for 10% sago starch. Heating rate = 0.5 °C/min.

Figure 8. Effect of $MgCl_2$, $CaCl_2$, and LiCl on gelatinization enthalpy for 10% sago starch. Heating rate = 0.5 °C/min.

Table 1. Effect of Various Salts at 1 M on Gelatinization Properties for 10% Sago Starch

salt	T_o (°C)	T_p (°C)	T_c (°C)	ΔT $(T_c - T_o)$	ΔH (J g^{-1})
control	59.0	70.1	76.7	17.7	16.5
LiCl	68.4	80.7	87.4	19.0	16.3
NaCl	66.5	79.8	87.9	21.3	16.3
KCl	64.4	78.7	86.5	22.1	16.7
CsCl	63.3	78.0	85.6	22.3	14.8
LiBr	62.4	76.7	84.6	22.3	16.6
NaBr	61.0	75.5	83.2	21.3	14.9
KBr	60.0	73.7	82.3	22.3	12.3
LiI	50.5	64.5	73.0	22.5	10.7
NaI	50.0	63.9	72.0	22.0	9.5
KI	47.4	60.9	68.9	21.4	8.6
CsI	45.2	60.2	67.8	22.6	8.1
NaSCN	39.7	56.5	66.9	27.2	8.5
KSCN	38.7	55.6	66.1	27.4	8.4
NaNO$_3$	58.6	74.4	82.3	23.7	14.2
MgCl$_2$	74.9	87.1	93.4	18.6	14.8
CaCl$_2$	64.2	81.4	88.8	24.6	15.8
AlCl$_3$	81.5	93.5	99.5	18.0	17.4
Na$_2$SO$_4$	82.1	92.7	99.5	17.4	16.5

calculated using the first-order rate equation (Yoshida et al., 1990)

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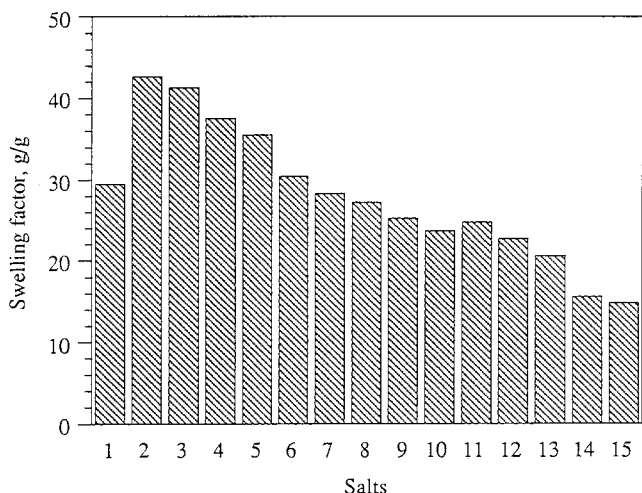*J. Agric. Food Chem.,* Vol. 47, No. 8, 1999 **3363**

Figure 9. Effect of various salts on swelling factor for sago starch at 95° C (starch concentration = 0.5%; salts concentration = 0.5 M): (1) control; (2) KSCN; (3) NaSCN; (4) KI; (5) NaI; (6) KNO$_3$; (7) NaNO$_3$; (8) KBr; (9) NaBr; (10) LiBr; (11) KCl; (12) NaCl; (13) LiCl; (14) K$_2$SO$_4$; (15) Na$_2$SO$_4$.
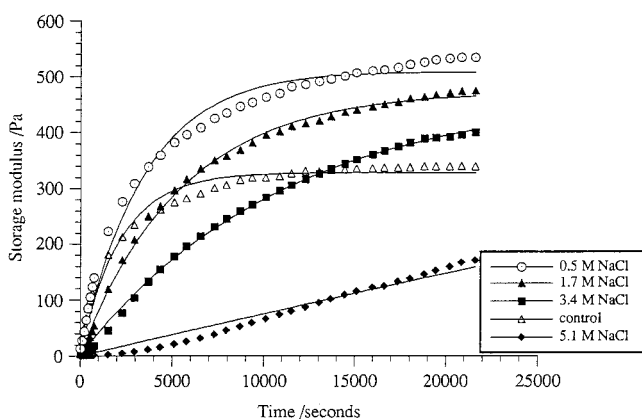

Figure 10. Effect of NaCl concentration on G' (frequency = 1 Hz, temperature = 25° C) as a function of time for 6% sago starch.

$$G_t = G_{sat} (1 - e^{-kt}) \tag{1}$$

where G_{sat} = plateau value of storage modulus, G$'$, k = rate constant for gelation, and t = time. For NaCl concentrations up to 3.4 M the curves showed the normal initial sharp increase in G' followed by a pseudoplateau region. G_{sat} increased in magnitude with increasing salt concentration. The initial rise in G' decreased above 0.5 M NaCl, and this is reflected in Figure 11, which is a plot of k as a function of NaCl concentration and shows that k decreases with increasing NaCl concentration.

The effect of various metal chlorides at a concentration of 0.5 M on G' is shown in Figure 12. Both the divalent and monovalent ions gave rise to characteristic curves with an initial rapid increase in G' followed by a pseudoplateau region. G'_{max} was found to increase compared to the control, with the divalent ions having a greater influence than the monovalent ions. In the case of AlCl$_3$, gelation did not occur even though the starch was fully gelatinized.

For the various metal chlorides, G'_{sat} decreased in the order Mg^{2+} > Ca^{2+} > Na$^+$ > K$^+$ ≫ Al^{3+}; however, the gelation rate constant, k, remained almost constant for all of the cations at ∼3.0 × 10^{-4} s^{-1}.
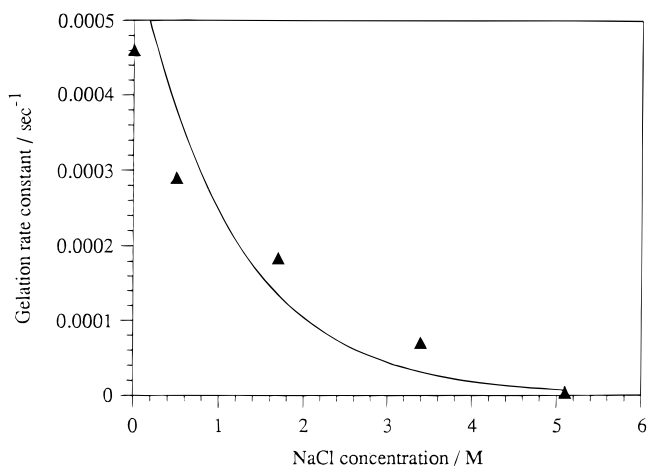

Figure 11. Effect of NaCl concentration on gelation rate constants for 6% sago starch.
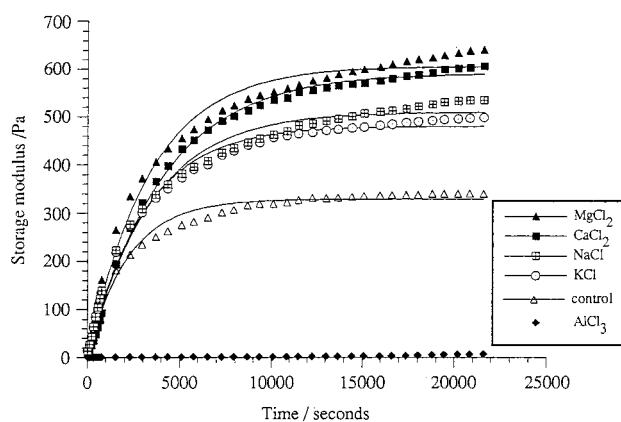

Figure 12. Effect of various metal chlorides at 0.5 M on G' (frequency = 1 Hz, temperature = 25° C) as a function of time for 6% sago starch.
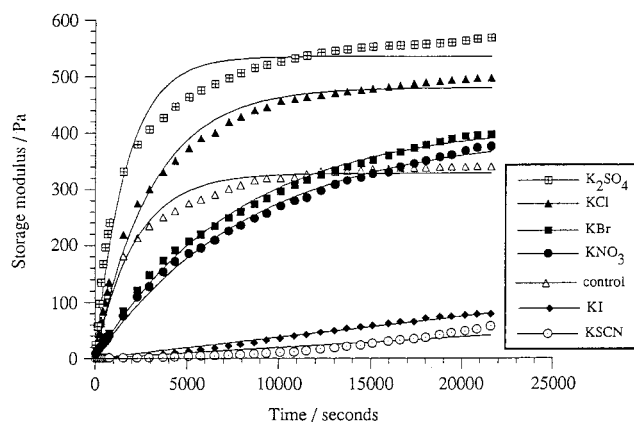

Figure 13. Effect of various potassium salts at 0.5 M on G' (frequency = 1 Hz, temperature = 25° C) as a function of time for 6% sago starch.

The effect of various potassium salts on G' was studied, and the results are given in Figure 13. Similar data were obtained for the corresponding sodium salts. The presence of SO$_4^{2-}$ and Cl$^-$ ions increased G'_{max} significantly compared to the control. Br$^-$ and NO$_3^-$ ions gave rise to a slight increase, whereas I$^-$ and SCN$^-$ significantly reduced G'. For all of the salts except for SO$_4^{2-}$ ions the rate constant for gelation, k, was reduced compared to the control as shown in Table 2. For the sodium and potassium salts G' and k decreased in the

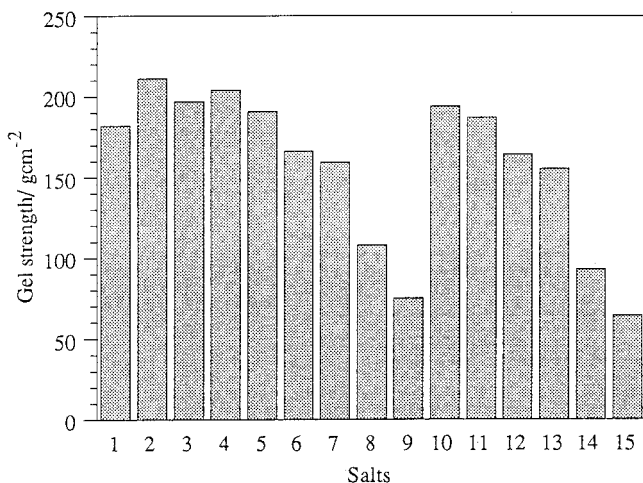**3364** *J. Agric. Food Chem.*, Vol. 47, No. 8, 1999

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Figure 14. Effect of various salts at 0.5 M on gel strength for 6% sago starch after 6 h: (1) control; (2) MgCl₂; (3) CaCl₂; (4) Na₂SO₄; (5) NaCl; (6) NaBr; (7) NaNO₃; (8) NaI; (9) NaSCN; (10) K₂SO₄; (11) KCl; (12) KBr; (13) KNO₃; (14) KI; (15) KSCN.

Table 2. Effect of Various Sodium and Potassium Salts at 0.5 M on Gelation Rate Constant for 6% Sago Starch

salt	rate constant $(s^{-1}) \times 10^4$	salt	rate constant $(s^{-1}) \times 10^4$
control	4.6	K₂SO₄	6.0
Na₂SO₄	6.6	KCl	3.3
NaCl	2.9	KBr	1.3
NaBr	1.6	KNO₃	1.2
NaNO₃	1.2	KI	0.08
NaI	0.19	KSCN	0.01

Table 3. Effect of NaCl Concentration on Gel Strength of 6% Sago Starch

concn (M)	gel strength $(g\ cm^{-2})$	concn (M)	gel strength $(g\ cm^{-2})$
control	182	3.4	148
0.5	191	5.1	80
1.7	181		

order $SO_4^{2-} > Cl^- > Br^- > NO_3^- > I^- > SCN^-$, in keeping with the Hofmeister series.

Gel Strength. The effect of NaCl concentration on gel strength is shown in Table 3. The results clearly show that the gel strength was higher in 0.5 M NaCl compared to the control but a further increase in NaCl concentration decreased the gel strength significantly.

The effect of the various salts on the gel strength of sago starch is shown in Figure 14. Good agreement was obtained between these results and the small deformation oscillation measurements. This figure clearly shows that the salting-out ions increased the gel strength while the salting-in ions decreased the gel strength significantly and the order followed the Hofmeister series as for $\check{G}$.

DISCUSSION

Swelling and Gelatinization. The degree of granule swelling in 0.5 M salt appears to follow the Hofmeister series, with the anions having a greater influence than the cations as expected. The so-called salting-out ions such as SO_4^{2-} inhibited swelling, whereas salting-in ions such as I^- and SCN^- promoted swelling. A similar effect was also observed for T_p and ΔH at salt concentrations up to ~1 M. Salting-out ions increased T_p and ΔH, whereas salting-in ions resulted in a decrease.

Jane (1993a) also reported similar trends for T_p and ΔH for corn starch. She suggested that the increase in T_p and ΔH in the presence of SO_4^{2-} ions was due to their strong interaction with water molecules and the consequent reduction in the fraction of free water molecules as indicated from infrared spectroscopy studies (Paquette and Jolicoeur, 1977; Kleeberg and Luck, 1983). She argued that the solution viscosity also increased, thus retarding the diffusion of ions into the granule, and that there would be repulsion between the hydroxyl groups of the starch and the SO_4^{2-} groups. The decrease in T_p and ΔH in the presence of I^- and SCN^- ions has been attributed to their interaction with the starch molecules, which induces formation of a single helical conformation as inferred from ¹³C NMR studies with amylodextrin (Chinachoti et al., 1991; Jane, 1993b), which facilitated chain dissociation. Jane (1993a) argued that KI and KSCN solutions have an increased fraction of free water and hence the solution has a lower viscosity and therefore ions can readily diffuse into the granules. Interestingly, it was noted that gelatinization began at the hilum rather than the periphery of the starch granules (Jane, 1993a).

The influence of salts on the solubility of polymers is commonly found to follow the Hofmeister series regardless of the nature of the polymer (Collins and Washabaugh, 1985), although it should be pointed out that the sequence is not universally applicable with dramatic variations occurring (Garvey and Robb, 1979). The origins have been explained in terms of the positive or negative excess of ions at the polymer−solution interface and their consequent influence on the interfacial energy (Piculell and Nilsson, 1990). This conclusion is corroborated by the fact that a similar sequence is observed for the interfacial tensions for salt solutions in contact with liquid alkanes (Aveyard and Saleem, 1976), decanol (Aveyard et al., 1977), and air (Jarvis and Scheiman, 1968). Salting-out ions tend to be depleted from the polymer−solution interface (i.e., they are negatively adsorbed), whereas salting-in ions are in excess (i.e., they are positively adsorbed). The effect of the distribution of ions on the free energy of the system is predicted by the Kirkwood−Buff theory (Hall, 1971, 1974). The standard chemical potential of the solute, S, in solution is given by

$$d\mu_S^\circ = -\Sigma_i N_{Si}\, d\mu_i \qquad (2)$$

and for this to be positive the condition $d\mu_S^\circ > 0$ must apply. This would be the case for salting-out ions when the excess concentration, N_{Si} of the species i near the solute S is negative, that is, there is negative adsorption. The tendency of salts to positively or negatively adsorb is believed to depend on water−ion interactions. The salting-in ions, therefore, promote polymer−solvent interaction at the expense of polymer−polymer interaction by reducing the polymer−solvent interfacial energy and hence induce granule swelling and decrease T_p and ΔH, whereas salting-out ions have the opposite effect.

In the case of chloride salts, T_p and ΔH were found to increase with salt concentration up to ~2 M (for ΔH < 1 M), but as the concentrations increased further they decreased. In the case of Mg^{2+}, Ca^{2+}, and Li^+ chlorides the gelatinization process occurred at room temperature (~3.5 M for CaCl₂ and MgCl₂ and ~8 M for LiCl). At very high concentrations some metal salts (MgCl₂, CaCl₂, and LiCl) showed an exothermic peak in the DSC heating curve rather than an endothermic peak char-

Effect of Salts on the Properties of Sago Starch

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acteristic of the gelatinization process. Jane (1993a) found similar trends for LiCl and CaCl$_2$ and noted that gelatinization started at the periphery of the granules rather than the hilum as was the case in the presence of SCN$^-$ and I$^-$. Gough and Pybus (1973) observed similar behavior in studies on wheat starch. They found that three types of gelatinization occurred. Type I proceeded by tangential swelling, progressing from the hilum to the periphery. For type II, swelling proceeded from the periphery to the hilum, and for type III there was apparent solubilization of the starch granules at low temperature to give a starch solution. They found that for certain metal chlorides such as CuCl$_2$, CaCl$_2$, and AlCl$_3$ all types of gelatinization were observed with increasing concentration. The T_p initially increased with increasing concentration to a maximum value, then decreased to a minimum value, and finally increased again at much higher concentration. Type I gelatinization was observed until the minimum T_p was reached and was followed by type II and type III gelatinization at much higher concentration. A number of workers have reported that interaction and complex formation occur between carbohydrate hydroxyl groups and alkali/alkali earth metal ions (Rendlemen, 1966). Jane (1993a) concluded that at high salt concentrations the interaction was sufficiently exothermic to induce the crystalline regions at the periphery of the granule to melt, thus reducing T_p. At very high concentrations she argued that the water molecules became highly structured and, hence, higher temperatures were required. She gave no explanation as to why the peak became exothermic. A possible explanation is that although the crystalline structure of the granule is disrupted at room temperature, some crystalline regions remain as noted by observation under a polarizing microscope. On heating, these remaining crystalline regions are disrupted but an endothermic peak is not observed, because at the same time as the amylopectin chains disaggregate through disruption of intermolecular hydrogen bonds, the hydroxyl groups which become exposed to the solvent interact exothermically with the metal ions present in solution. The fact that the exothermic process is nonreversible supports this view. As noted earlier, on standing for 24 h complete gelatinization of the starch occurred at room temperature and the exothermic peak was no longer observed. It appears, therefore, that there is an optimum salt concentration for gelatinization at room temperature and that the process is retarded as the concentration increases further.

Rheology. G'_{sat} values and the gelation rate constant were significantly affected in the presence of salts, and the effect was found to depend on the salt concentration. At NaCl concentrations between 0.5 and 3.4 M, G'_{sat} after 6 h was higher compared to the control, but at much higher concentrations G'_{sat} was reduced significantly. Similar observations were reported by Russell and Oliver (1989) for wheat starch. Gelation in starch occurs initially as a consequence of the aggregation of amylose molecules, which are released from the granules at the gelatinization temperature. The increase in G'_{sat} at the lower NaCl concentrations may be attributed to salting-out effects, which will enhance the aggregation of amylose chains and the formation of a three-dimensional network. The aggregation process is believed to predominantly involve hydrogen bonding and, at very high NaCl concentrations, interaction between sodium ions with the hydroxyl groups in the starch

molecules to form complexes is likely to become significant, thus reducing the possibility of aggregation. The rate constant for gelation was found to decrease even in the presence of low concentrations of NaCl. This may in part be attributed to the increase in viscosity of the salt solution compared to water, which will retard the diffusion of the amylose chains in solution and hence reduce the rate of aggregation. Complexation of hydroxyl groups with the metal ions will also have a significant influence.

In the presence of various salts at 0.5 M concentration, the effect on gelation followed the Hofmeister series with salting-out ions such as SO$_4^{2-}$ increasing G'_{sat}, k, and GS and the salting-in ions such as I$^-$ and SCN$^-$ causing these to decrease significantly. In the case of AlCl$_3$, gelation did not occur. This was probably due to the fact that Al^{3+} ions can form strong complexes with the amylose hydroxyl groups, thus inhibiting aggregation. The increase in G'_{sat} in the presence of salting-out ions can be attributed to greater aggregation of amylose chains, whereas the salting-in ions inhibit the aggregation and reduce G'_{sat} as discussed above. A similar influence of ions has been reported for the retrogradation of wheat starch (Ciacco and Fernandes, 1979) and corn starch (Morsi and Stirling 1963).

Conclusions. Salts have been found to have a complex effect on the gelatinization and rheological properties of sago starch. It has been argued that there are two factors that might contribute to the observations found in this study: (i) the effect of salts on polymer–solvent interactions, which are influenced to a greater extent by the anions; (ii) the interaction of cations with the hydroxyl groups of the starch molecules to form complexes that disrupt polymer chain aggregation. The former gives rise to an increase in T_p and G' in the presence of salting out ions (e.g., sulfate) but a decrease in the presence of salting in ions (e.g., iodide). The latter causes T_p and G' to decrease.

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