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The Influence of Electrolytes on Certain Characteristics of Corn Starch

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THE INFLUENCE OF ELECTROLYTES ON CERTAIN CHARACTERISTICS OF CORN STARCH

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ABSTRACT

The survey of literature shows that very little work has been done showing the effect of small amounts of electrolytes on the properties of native corn starch. The literature seems to be in agreement in that electrolytes do effect gelatinization when added in small amounts before cooking. Just what role the anion or cation plays seems to be controversial.

Varying amounts of electrolytes with different cations but the same anion were added to different concentrations of native corn starch before cooking. Viscosities were then taken after cooking under a standard cooking procedure. The results seem to indicate that the mono valent cation electrolyte has slightly more effect on viscosity than the di valent cation electrolyte. The tri valent cation added resulted in a decided decrease in pH thus a decided decrease in viscosity. Upon further investigation it was found that the addition of this tri valent cation electrolyte has more effect than the corresponding cooks with the same pH derived by the addition of the related acid . This would seem to indicate further decrease in viscosity caused by the electrolyte.

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Introduction

This survey of literature has been undertaken in an effort to compile the known facts available concerning the effect of small amounts of electrolytes on certain properties of corn starch. An additional objective of this work was to ascertain whether the control of electrolytes can be utilized effectively in the consumption of starch in sizing. This paper is primarily a study of the effects of anions and cations on properties of corn starch and not of the effects of hydrogen ion concentration. Although the literature seemed to be very sparce and academic in nature, it proved of value in shedding some definite light on the subject.

Kerr (1) states that considerable effort has been made in research directed toward the development of starches with increased efficiency for use in sizing of paper. This effort has been rewarded by the development of starches modified by acid hydrolysis, oxidation, heat dextrinization, milling, or enzyme conversion. Products produced by the aforementioned process have provided a virtually limitless range of starch viscosities, all of which can be produced within the purity and consistency standards required by modern industry.

Due to the many types of starch available, it was deemed necessary

to start with a thorough investigation of a native product. Although the effects of electrolytes on many different starches were studied in the literature survey, only native corn starch was considered for experimental use.

The Effect of Anions and Cations

According to Kerr (1), the mechanism of swelling is not known. The addition of small amounts of electrolytes tends to alter the gelatinization temperature greatly (1), (2). Samec (2) states that the anion determines the direction of the change, while the cation determines the quantitative influence on the swelling process caused by the anion. Salts which hydrolyze in water, thus producing excess OH groups, seem to show a general tencency to promote swelling below the original gelatinization temperature.

Lepeschkin (3) showed quite definitely that water is necessary in order to have gelatinization. He cooked starch with sodium carbonate and tried to obtain swelling. The starch would not gelatinize until it had been treated with cold water. Lepeschkin states further that the gelatinization of starch increased with the addition of small amounts of salts according to the lytropic anion series (SCN, I, Br, Cl, SO_4). He states that the property of salts to change the di-electric constant of water seems to be important in the influence of these salts on gelatinization.

Kerr (1) reiterates this theory when discussing the H bond theory of starch. He cites the recent contribution by Buswell et al (4) on the effect of ions on the coordinated structure of water. He states that the

anions may have a dissociating effect on both the starch and the water therefore increasing the tendency for gelatinization. It should be kept in mind that Kerr's statements on Buswell's work were pertaining to the reaction of electrolytes on water at about four molar concentration.

Katz (5), Koets and Kruyt (6), and Harris and Jesperson (7) also agree that small amounts of electrolytes have a great effect on viscosity and swelling power. Koets and Kruyt (6) found a large decrease in viscosity caused by the addition of milliequivalents of cations. They also stated that the drop in the viscosity of starch pastes increased as the valency of the cation added increased. These results led them to believe that the electrical density charge of the starch particles must be small.

Ripperton (8) describes a series of experiments using canna and potato starches in which viscosity and swelling power were determined. The addition of a small amount of electrolytes at the time of cooking alters these properties greatly. It seemed that the positive charge carried by the cation was the important factor since the degree of the effect varied with the valency of the cation.

Harris and Jesperson (7) found there was a fundamental difference between root starches and cereal starches. With additions of electrolytes, root starches decreased in swelling power while an average of eight cereal starches showed an increase in swelling power with increase in valency. (See tables I and II). Swelling power is defined as the volume in cubic centimeters of the swollen granules of one gram of dry starch cooked by a standard procedure. Starches were cooked with various

TABLE I

Comparative Data Secured From Different Starches [1]

Source of Starch	Nitrogen	Moisture	Viscosity as affected by addition of electrolytes[2]		
			untreated	NaCl	$MgSO_4$
	pct.	pct.	t./tw.	t./tw.	t./tw.
Potato - - - - - - - - - - -	.02	14.0	1042.91	12.36	7.02
Rice - - - - - - - - - - - -	.01	11.1	2.50	2.20	2.98
Barley - - - - - - - - - -	.03	10.0	1.96	1.89	4.02
Soft red winter wheat - -	.06	13.3	1.53	1.63	2.06
Hard red spring wheat - -	.05	13.7	2.01	2.09	2.77
1943 Crop					
Durum wheat - - - - -	.07	10.9	1.98	1.61	2.32
Hard red spring wheat	.05	16.0	2.13	1.90	2.65
1944 Crop					
Barley (Wisconsin 38)	.03	10.0	2.02	1.89	2.90
Hard red winter wheat	.03	12.4	1.88	1.93	3.04
Average viscosity of cereal starches - - - -			2.25	1.89	2.84

[1] Arranged in order of decreasing swelling power of untreated starch.
[2] Electrolyte concentration in cooking solution = 0.001N, one per-cent (dry basis) starch solutions used. Viscosity is time of fall of ball in one-per cent starch solution divided by time of fall in redistilled water.

From Harris and Jesperson, reference 7.

TABLE II

Effect of Valency of Cation on Swelling Power of Various Starches[1]

Source of Starch	Control	Electrolyte treatment			
		NaCl	$MgSO_4$	$Al_2(SO_4)_3$	$Th(NO_3)_4$
	cc	cc	cc	cc	cc
Potato - - - - - - - - - - - -	450.0	210.0	128.9	80.6	130.1
Rice - - - - - - - - - - - -	40.7	42.5	38.0	54.8	61.6
Barley - - - - - - - - - - - -	33.6	30.2	31.2	42.9	63.7
Soft red winter - - - - - -	32.4	33.2	38.4	52.1	66.2
Hard red spring, 1943 crop -	29.7	27.6	36.3	38.5	67.9
Durum - - - - - - - - - - - -	27.0	28.8	42.1	39.5	73.0
Hard red spring, 1944 crop -	26.8	27.7	34.5	40.5	64.7
Barley (Wisconsin 38)- - - -	26.0	28.3	29.0	50.4	59.2
Hard red winter - - - - - -	25.8	29.9	38.7	42.2	59.9
Mean swelling power of cereal starches - - -	30.3	31.0	36.0	45.1	64.5
Potato[2] - - - - - - - - - - -		-240.0	-321.1	-369.4	-319.9
Cereal[2] - - - - - - - - - - -		-0.7	-5.7	-14.8	-34.2

[1] Arranged in order of decreasing swelling power of untreated starch.
[2] These figures show the changes in swelling power induced by added electrolyte.

From Harris and Jesperson, reference 7.

types of anions to determine their effect. It can be seen in table III that no appreciable effect on swelling power could be detected with anions of differing valency. They also found that washing with water or sodium citrate would annul the effect caused by the electrolytes added at the time of cooking. (See table IV). It will be noted that the sodium citrate, with the tri valent anion, seemed to nullify the effects even more than the distilled water. The co-authors state that there seemed to be no significant changes in gel strength due to the addition of small amounts of electrolytes before gelatinization of the starch. Katz (5), while attempting to stabilize the viscosity of potato pastes, found that the acidity of the potato starch as well as the electrolytes in soft and hard water had a marked effect upon the viscosity throughout the cooking process. (See Fig. I) In this work a sample of the potato starch was first neutralized with sodium carbonate, using phenolphthalein as an indicator. Equivalent amounts of sulfates were then added to samples of the starch at cooking. An appreciabl e decrease in viscosity was noted.

Effects of Alkali

Alkalies are strong swelling agents for starch (2), (9), (10). It has been mentioned above that metallic salts will hydrolyze to form bases which in turn will induce swelling of the starch granule. According to Samec (2), bases in very dilute solutions show the greatest relative influence on the starch granule. Jambuserwala (10) states that when modifying starch with alkali in concentration from one to ten per cent,

TABLE III

Effect of Valency of Anion on Swelling Power of Cereal Starches

Source of starch	Control	Electrolyte treatment			
		NaCl	Na_2SO_4 [1]	Sodium citrate [1]	$K_4Fe(CN)_6$ [1]
	cc	cc	cc	cc	cc
Hard red spring - - - - - -	26.8	27.7	27.6	27.1	27.4
Barley - - - - - - - - - - -	26.0	28.3	29.2	29.9	29.4

[1] Average of four determinations.

TABLE IV

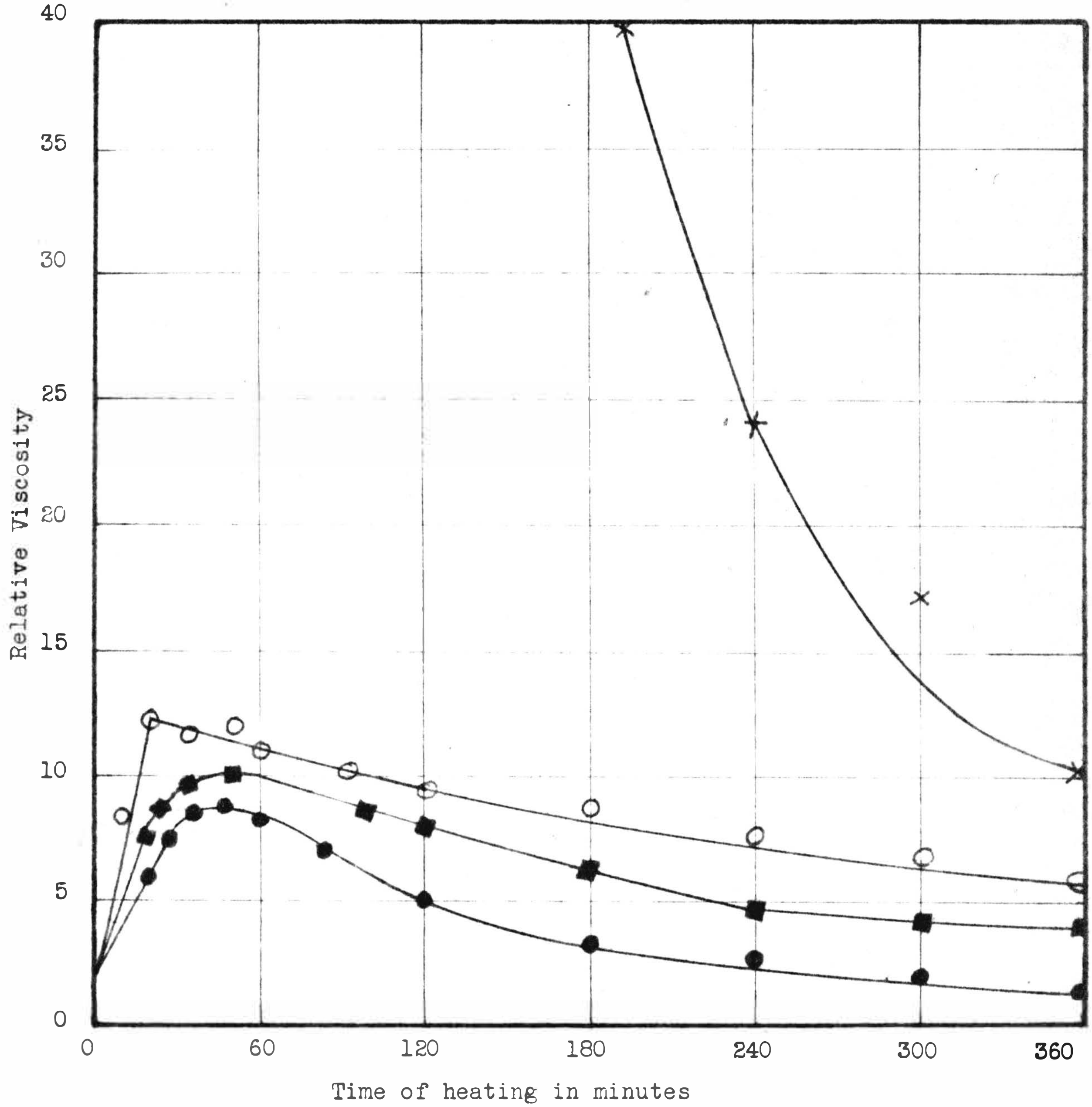
Effect of Reduction of Cation on Swelling Power of Cereal Starches[1]

Source of starch	Electrolyte added at cooking	Washing liquid	Control	Number of washings		
				1	2	3
			cc	cc	cc	cc
Durum - - - - - - - - -	$MgSO_4$	Na citrate	41.8	32.0	24.3	16.0
		Distilled water	43.4	34.0	25.5	21.5
Durum - - - - - - - - -	$Th(NO_3)_4$	Na citrate	68.5	45.0	38.0	35.3
		Distilled water	61.0	51.5	45.5	42.0
Hard red spring - - -	$MgSO_4$	Na citrate	31.0	26.5	25.5	22.9
		Distilled water	35.0	30.0	27.9	25.5
Hard red spring - - -	$Th(NO_3)_4$	Na citrate	63.0	40.0	36.0	36.0
		Distilled water	63.0	57.0	48.0	40.0

[1] Average of four determinations.

From Harris and Jesperson, reference 7.

Effect of sulfates found in hard and soft water upon viscosity of potato starch



From Katz, reference 5.

Key

X ------- untreated high grade potato starch
O ------- sodium sulfate added
■ ------- calcium sulfate added
● ------- magnesium sulfate added

FIG-I

the relation between alkali concentration and viscosity of the starch paste is almost linear.

Effects of Acid

Samec (2) has reported that acids have no greater effect on gelatinization than do the salts of the same concentration. (The anion in this case still has the directional effect.) According to Harris and Jeaperson, Ripperton (8) showed that the effect of hydrogen as a cation on swelling power was similar to that of the other mono valent ions. It has been shown that hydrogen ion concentration plays an important part in gelatinization. Bechetel and Kesler (11) state that the effect of pH is not so great on unmodified corn starch as on modified corn starches. The conclusion seems probable that electrolytes do not effect native corn starch as drastically as they do modified corn starches.

Effects of Electrolytes on Starch Used on Beater Sizing

It is of interest to note an article by Rowland (12) which discusses the effect of hard water of high alkalinity on the retention of starch in the beater. He explains that the hard water tends to increase the retention of starch because alumina is formed when alum is added to the hard water in the furnish. The resulting alumina with its plus charge helps in the retention of the negative starch granule on the negative cellulose fibers. Accordingly, the pH in the final condition would not correlate effectively with this phenomenon. The pH history or the electrolytes present seem to be the important factor.

Summary

The survey of literature shows that very little work has been done

integrating the effects of electrolytes on different properties of starch, i.e. gelatinization temperature, swelling power, viscosity and ultimate film strength. Some studies made of the effect of electrolytes on certain specific properties have been indicated. The literature seems to be in agreement in that electrolytes do effect gelatinization when added in small amounts before cooking. Just what role the anion or cation plays seems to be controversial to a certain extent.

It is of interest to note that a fundamental difference was detected between the behavior of cereal starches and potato starch. It can be supposed that corn starch, being a cereal starch, would follow in line with those cereal starches that were tested.

One study (7) states that no significant difference in gel strength was apparent with the addition of electrolytes in small amounts. A study of the ultimate film strength should prove of interest in substantiating this finding.

Application of the tests discussed herein to native corn starch should prove of interest to users of this commodity for sizing purposes.

Kalamazoo, Michigan
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LABORATORY EXPERIMENTAL PROGRAM

The literature survey which precedes this report shows that some information has been published concerning the influence of electrolytes on gelatinization temperature, swelling power, and viscosity of various starches. The purpose of this experimental work was to ascertain the effect, if any, of small amounts of certain electrolytes on the viscosity of native corn starch. Several concentrations of native corn starch were used and varying amounts of the following materials were added before cooking.

$NaCl$
$CaCl_2$
$AlCl_3$
HCl

Keeping in mind the effect of the cation, as reported in the literature, the anions of each compound were kept constant for comparative purposes.

Experimental Procedure

The moisture content of the native corn starch to be used was obtained by placing the air dry starch in a constant temperature oven at 135° C for three hours. The concentration of the starch was then calculated on an oven dry basis throughout the experimental work.

Stainless steel beakers and glass stirring rods were tared and the amount of starch necessary was added. Distilled water was added to bring the total weight to 1000 grams. The cold slurry was then put in a steam bath at atmospheric pressure and agitated for 30 minutes.

Following the cooking period, the starch was cooled in a cold water bath to within five degrees of 50° C. At this point the can and contents were weighed and enough distilled water added to make 1000 grams of cooked

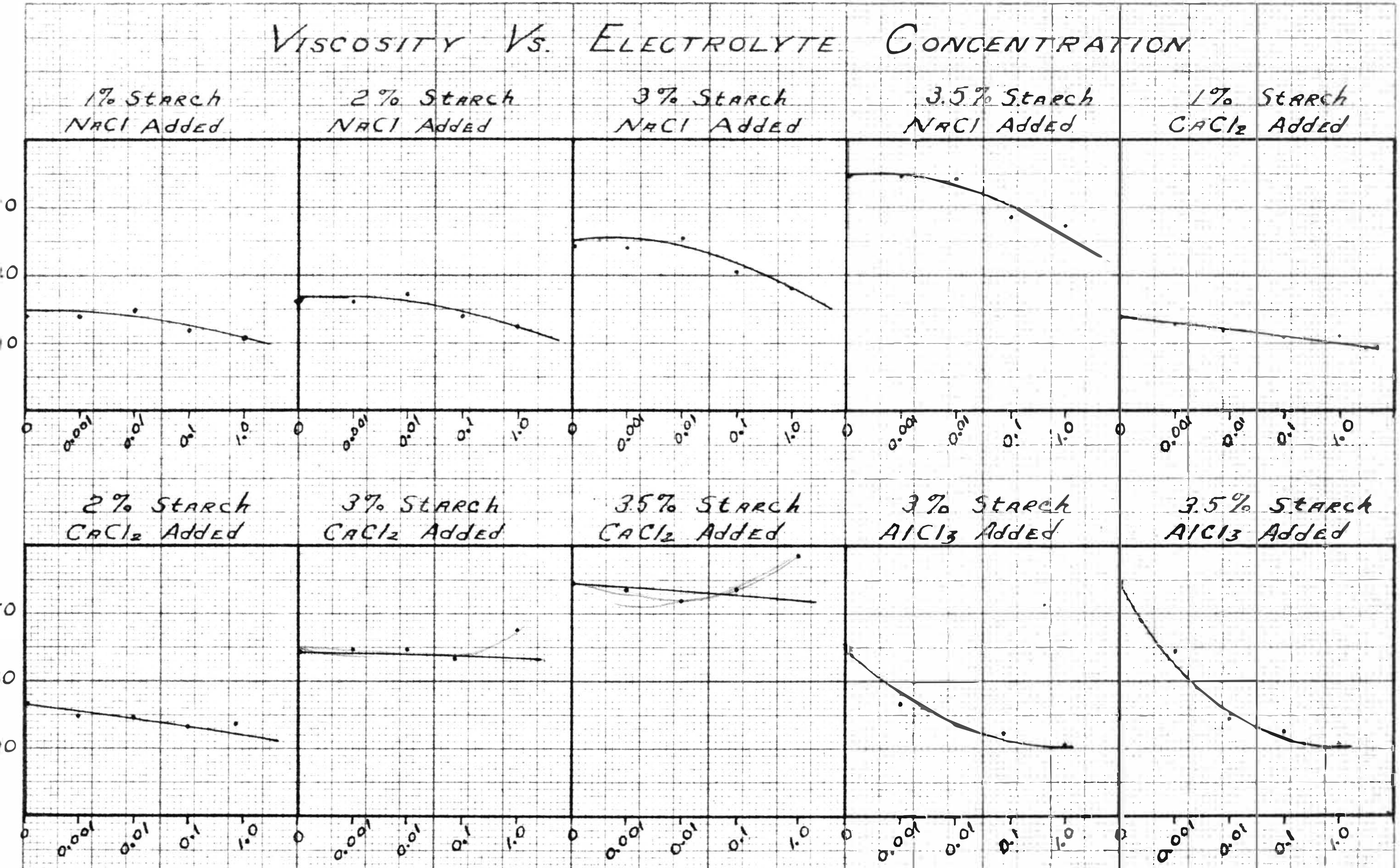
VISCOSITY VS. ELECTROLYTE CONCENTRATION
1% Starch NaCl Added
2% Starch NaCl Added
3% Starch NaCl Added
3.5% Starch NaCl Added
1% Starch CaCl2 Added
2% Starch CaCl2 Added
3% Starch CaCl2 Added
3.5% Starch CaCl2 Added
3% Starch AlCl3 Added
3.5% Starch AlCl3 Added
0 0.001 0.01 0.1 1.0

FIGURE II

APPENDIX I

Concentration of starch		1%		2%		3%		3.5%	
Chemical	Concentration	u	pH	u	pH	u	pH	u	pH
Blank		34.0	7.1	36.4	7.1	44.3	6.9	54.6	7.1
NaCl	0.001N	34.2	7.0	36.1	7.0	44.2	7.0	54.6	-
	0.01N	35.0	7.0	37.3	6.6	45.6	-	54.2	-
	0.1N	32.0	6.9	34.0	6.3	40.5	6.2	48.3	6.0
	1.0N	30.9	-	32.5	6.1	38.1	6.0	47.1	5.7
$CaCl_2$	0.001N	32.8	6.8	35.0	7.1	44.7	7.2	53.6	6.6
	0.01N	32.0	6.6	34.9	6.3	44.9	7.2	52.0	6.3
	0.1N	31.0	-	33.4	-	43.2	-	53.6	-
	1.0N	31.1	6.2	34.0	5.9	47.4	5.9	58.9	5.9
$AlCl_3$	0.001N	31.4	3.7	32.8	4.2	36.8	3.8	44.5	4.1
	0.01N	-	-	32.5	3.4	33.4	3.4	34.4	3.4
	0.1N	-	-	-	-	32.3	3.2	32.7	3.2
	1.0N	-	-	-	-	30.7	2.6	30.6	2.7
HCl	0.001N	30.1	3.3	31.8	3.2	35.9	3.4	41.1	3.2
	0.005N	-	-	29.8	2.4	30.8	2.4	31.2	2.4

Note: Water @ 50° C - 28.8 seconds

starch. The viscosities of the starches were then determined on a 100 ml Dudley pipette which expelled water at 50° C in 28.8 seconds.

Starch cooks were made at one, two, three and three and one half percent consistency. Three and one half percent consistency was considered to be the upper limit of the Dudley pipette from the standpoint of reproducibility. Various concentrations of the electrolytes were added before cooking, namely, 0.001, 0.01, 0.1 and 1.0 Normal based on 1000 grams of cooked starch. Hydrogen ion concentrations were checked at various intervals throughout the work by allowing a portion of the cooked starch to cool to 25° C and using an electrometric method for determination.

Experimental Results

As shown in Appendix I, the addition of electrolytes before cooking does alter the viscosity of the cook. As can be seen in Figure II, the effect of the mono valent cation electrolyte seems to show a trend of decreasing the viscosity more pronouncely than the di valent cation electrolyte; however, the tri valent cation electrolyte seems to alter the viscosity greater than either of the aforementioned compounds. Reference should be made to Appendix I, which shows a decided decrease in pH in the case of $AlCl_3$ which would seem to provide a possible explanation for the extreme drop. Upon further inspection of Appendix I it is found that the corresponding pH of a cook to which HCl has been added shows an higher viscosity than the cook of the same pH with $AlCl_3$. This would tend to indicate that the el ectrolyte itself has some influence upon the viscosity change.

Conclusions

The results of this work, under the conditions and limitations outlined, seem to indicate that the electrolyte composed of a mono valent cation decreases the viscosity slightly more than an electrolyte with a di valent cation. No significant change in viscosity was noticed, until a salt concentration of 0.01 to 0.1 Normal was added, except in the cases where the pH was altered. As for the addition of $AlCl_3$, the trend seems to show that the electrolyte itself does effect the viscosity in that corresponding cooks with the same pH derived by the addition of HCl have viscosities which are consistently higher.

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