THE EFFECT OF HYDROGEN IONS, CALCIUM AND SUCROSE CONCENTRATIONS ON VISCOSITY OF ORANGE PEEL AND PRICKLY PEAR PECTIN SOLUTIONS

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ABSTRACT

The pectic substances of orange peel and prickly pear were extracted. The effect of hydrogen ion, calcium and sucrose concentrations on viscosity and hence ability to form gel from dilute solutions was studied. The addition of calcium ions to the dilute pectin solutions tends to form non sugar gels, while excess of calcium ions caused precipitation (not gelation) and synersis usually occurred. Maximum vicosity of pectin was attained at pH 2.55 for both types of pectins. There was a positive relationship between sucrose concentration and viscosity of dilute pectin solutions. Besides, any increase in pectin concentration (orange peel and prickly pear pectin "B") required a proportional decrease in the added sugar and vice versa to obtain the same colloidal character of the resulting gel. Prickly pear "fraction B" and orange peel pectins can be used to form firm gel, while prickly pear pectin "A" can be used in the purposes which require low content of anhydrogalacturonic acid (A.G.A.).

INTRODUCTION

Polysaccharides are used widely in the food industry to creat gels in aqueous phase (Glicksman, 1969) in addition to that the most important commercial property of pectins is their ability to form gels.

Heneglein (1950), Pilnik (1964), Smit and Bryant (1968) and Sarhan (1975), have studied the relationship between acidity and jelly formation. Since viscosity of a pectin solution affects its jelly grade, the effect of hydrogen ion concentration on the viscosity of pectin solutions was investigated in this study.

The manufacturing of either low sugar jellies or non sugar jellies for persons suffering from diabetus depends mostly upon the reaction between calcium ions and carboxyl groups of low ester pectins (Lopez and Li-Hsing-Li, 1968). Therefore, the effect of calcium ion on the relative viscosity in this study was carried out.

Schweiger (1964), Kohn & Furda (1967); Rees (1972) and Arnott et al. (1982), reported that the binding of divalent ions involved the carboxyl and hydroxyl groups and that both inter and intramolecular chelates were formed.

Pectins is usually graded according to sugar carrying power (Sarhan, 1975). Therefore, sugar is considered a limiting factor in grading pectin from the economical and technological view points. Moreover, it is necessary to study the effect of sucrose concentration on viscosity of a pectin solutions.

MATERIALS AND METHODS

The pectic substances under investigation were isolated from two sources. The first source was the prickly pear (*Opuntia ficus indica*) plnat and the second source was the sweet orange (*Citrus sinensis*) variety (Baladi). The modified stems (leaves) of prickly pear and the orange peel were obtained from the experimental station of the Fac. of Agric., Moshtohor, Zagazig University.

Isolation of orange peel pectin (Baladi variety) was carried out according to the method reported by Aspinall et al. (1968), Prickly pear pectins (Fraction "A" and Fraction "B") were isolated according to the method of Khalifa (1968).

The forementioned polysaccharides were purified by redisolving in water and the solution was centrifuged to separate insoluble materials then treated with ethyl alcohol to precipitate polysaccharides. These polymers were washed three times with a mixture of 70% ethyl alcohol and 30% dimethylformamide (Shalom et al., 1984) to solubilize hesperidin and other flavonoids which may be bound tightly to these polymers. After that the polysaccharides were washed with chloroform and methanol 1:1 followed by ethyl alcohol, acetone and finally with diethyl ether. Chemical and physical properties and the information about the chemical structural features of these polymers were carried out according to Saad (1985).

Estimation of viscosity was carried out using an Ostwald capillary viscometer placed vertically in a water-bath maintained at 27°C±0.5°C. Measurements were made triplicate or more to obtain reliable measurements.

The relative viscosity was calculated according to the following equation:

$$\text{Relative viscosity } (\eta r) = \frac{\text{Flow time in seconds for the solution}}{\text{Flow time in seconds for the } \sout{\text{solution}} \text{ Solvent}}$$

Tridistilled water (produced by distillation of water in presence of potassium permanganate 3 times in all pyrex glass appartus) was used as a solvent.

RESULTS AND DISCUSSION

A- Effect of calcium ion concentration:

The relative viscosities were plotted against calcium ion concentration of pectin solutions. The results are shown in table (1) and Figure (1), these results indicate that a gradual increase in the relative viscosities with the increase in calcium ion concentration for the different types of pectins. However, a sharp increase in ~~teh~~ the viscosities of orange peel and prickly pear "Fraction B" pectin solutions occurred when the concentration of calcium ions was increased from 6 to 11 mg per 100 ml. pectin solution. A further increase in Ca^{++} ions caused gel formation with unmeasured realtive viscosities. The excessive addition of Ca^{++} ions more than 12.5 mg/100 ml. (containing 0.1 g. pectin) caused the precipitation of pectin since obovious weeping "synersis" was noticed. While in case of prickly pear pectin "Fraction A" it has been noticed a gradual increase in relative viscosities until 15 mg calcium ions/100 ml. pectin solution. The low values of relative viscosities of prickly pear pectin "A", compared with others, may be attributed to the differentiation in chemical structures, especially, anhydrogalacturonic acid content (A.G.A.) which amounted to 78%, 73% in orange peel and prickly pear "Fraction B" pectins while prickly pear "Fraction A" contained 27%, respectively (Saad, 1985).

The increase in the relative viscosities of pectin solutions upon addition of minute amounts of calcium ions may be due to the electrostatic attraction between the

Table (1)

The effect of calcium ion :n relative viscosities (η_r) of pectin

Calcium Conc. mg/100ml sol.	Orange peel pectin Conc. 0.1% - (η_r)	Prickly pear pectin "A" Conc. 0.1% - (η_r)	Prickly pear pectin "B" Conc. 0.1% - (η_r)
0	1.357	1.318	1.365
1	1.433	1.350	1.394
2	1.480	1.422	1.502
3	1.604	1.550	1.640
4	1.691	1.630	1.700
5	2.060	1.750	2.140
6	2.460	2.050	2.640
7	3.120	2.190	3.285
8	3.590	2.460	3.850
9	4.230	2.460	4.520
10	5.010	2.900	4.985
11	5.690	2.960	6.760
12.5	jel	3.260	jel
15	synersis	4.020	synirsis

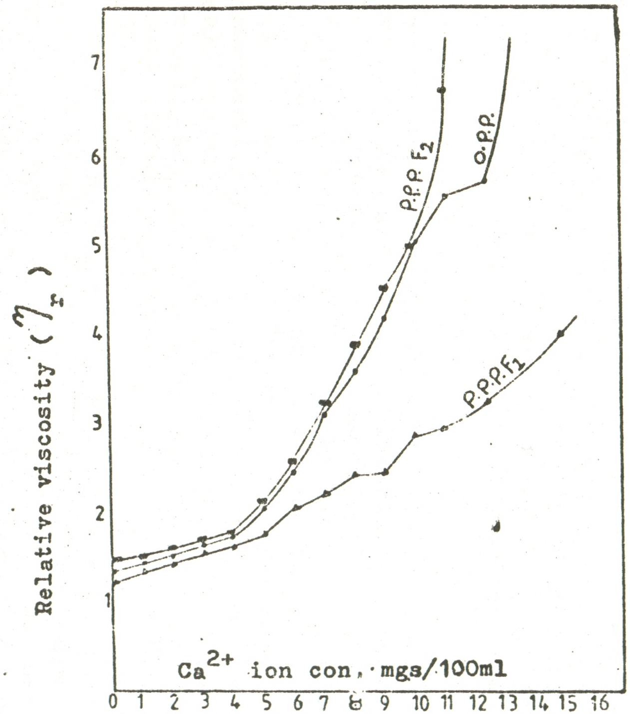

Fig.(I) , The effect of calcium ion concentration on the relative viscosities of 0.1% solution of orange peel (O.P.P.) , prickly pear "A" (P.P.P.F_1) and prickly pear "B" (P.P.P.F_2) pectins

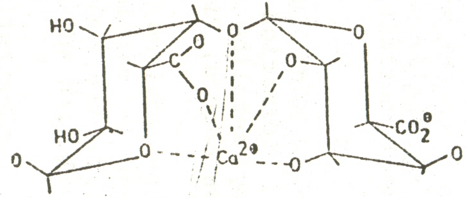

Fig.(II,a) , Proposed structure of Ca^{2+} galacturante (Rees, 1972)

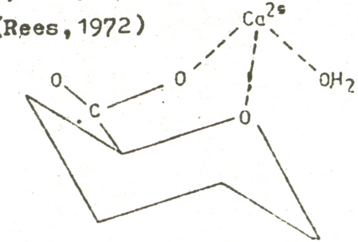

Fig.(II,b) , Proposed structure of Ca^{2+} polyuronate (Arnott et al. , 1982)

particles of pectin and calcium ions leading to an increase in aggregation of the particles. Such conclusion was earlier reported by Schwiger (1964) and Kohn and Furda (1967, 1968). Rees (1972) and Arnott et al. (1982), suggested the optimum binding of Ca^{++} using model building as showing in Fig. (IIa, b).

The addition of calcium ions in higher amounts than those responsible for gel formation caused precipitation (not gelation) followed by settling of calcium salt from solution and hence, synersis occurs, Pilnik (1964).

Therefore, it could be advised that the addition of calcium ions to pectin must be carried out accurately and it is preferable to estimate the calcium requriements for each sample for obtaining gel with suitable characteristics.

b- Effect of hydrogen ion concentration:

The results reported in table (2) and Fig. (IIIa, b) show the effect of hydrogen ion concentration on the relative viscosities of orange and prickly pear pectins. From these results, it could be observed that there is no great change in the relative viscosities with increasing hydrogen ion concentration from the initial pH (3.25, 3.14) for orange peel and prickly pear "Fraction B" pectins to pH 2.55. On the other hand, an appreciable decrease in the viscosities of pectin solutions occurred when hydrogen ion concentration was increased above the optimum pH (2.55). In case of prickly pear pectin "Fraction A" there is a gradual increase in the relative viscosities with the increase of ion concentration. Also, the optimum pH was 2.55.

The increase in the relative viscosities with increasing the hydrogen ion concentration of pectin solution might be due to the effect of hydrogen ions in lowering the dissociation of pectinic acid solutions which reduced the particles charge (common ion effect) and increased the tendency of molecules to form hydrogen bonds. This leads to either aggregation or swelling of pectin molecules, accompanied by an increase in the relative volume occupied by the dispersed pectin which favours the increase in the viscosity. Similar explanation was offered by Heneglein (1950). However, the decrease in the relative viscosity of pectin solution with increasing hydrogen ion concentration (beyond the optimum pH) was explained by Pilnik (1964). The former author believed that the decrease in viscosity with increasing hydrogen ion concentraion was most likely due to change

Table (2)

The effect of pH on relative viscosities (η_r) of pectins

Orange peel pectin (Conc. 0.1%)				Prickly pear pectin "A" (Conc. 0.1%)				Prickly pear pectin "B" (Conc. 0.1%)			
pH	η_r	pH	η_r	pH	η_r	pH	η_r	pH	η_r	pH	η_r
3.25*	1.357	3.25	1.357	3.61*	1.318	3.61	1.318	3.14*	1.365	3.14	1.365
3.0	1.357	3.50	1.57	3.35	1.318	4.0	1.318	2.90	1.365	4.00	1.349
2.85	1.360	4.0	1.333	3.10	1.346	4.57	1.310	2.75	1.389	4.70	1.270
2.75	1.365	4.5	1.325	2.90	1.365	5.5	1.286	2.65	1.413	5.50	1.270
2.65	1.373	5.5	1.254	2.75	1.39	6.5	1.222	2.55	1.508	6.50	1.254
2.55	1.459	6.5	1.246	2.65	1.413	7.2	1.190	2.45	1.476	7.00	1.230
2.45	1.413	7.0	1.246	2.55	1.429	7.6	1.174	2.35	1.429	7.50	1.222
2.3	1.350	7.5	1.238	2.40	1.397	8.1	1.119	2.30	1.429	8.00	1.222
2.15	1.333	8.0	1.238	2.10	1.349	9.0	1.079	2.00	1.317	8.50	1.091
2.00	1.286	8.5	1.183	2.00	1.333	9.6	1.079	1.50	1.206	10	1.111
1.45	1.175	10	1.143	1.50	1.210						

* Initial pH

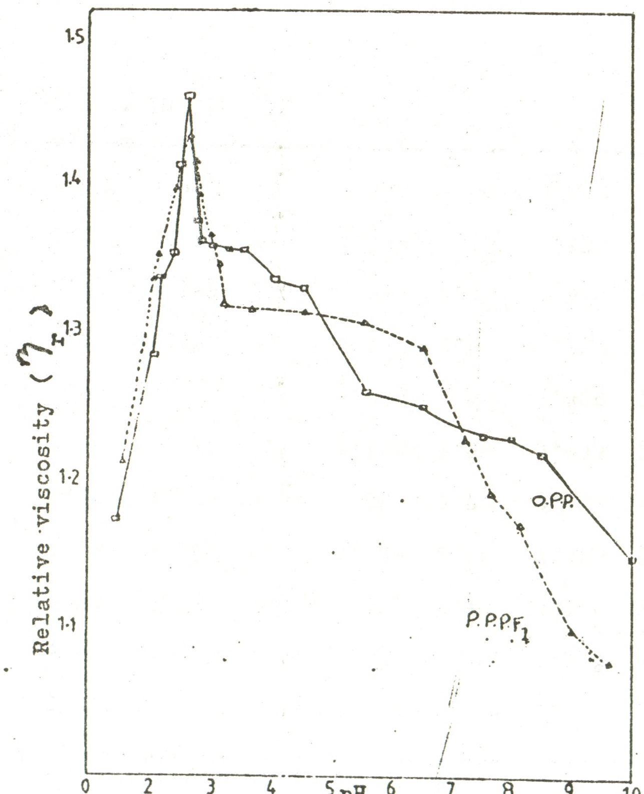

Fig.(III,a) , The effect of pH on the relative viscosities of 0.1% of orange peel(O.P.P.)and prickly pear "A"(P.P.P. F_1) pectins

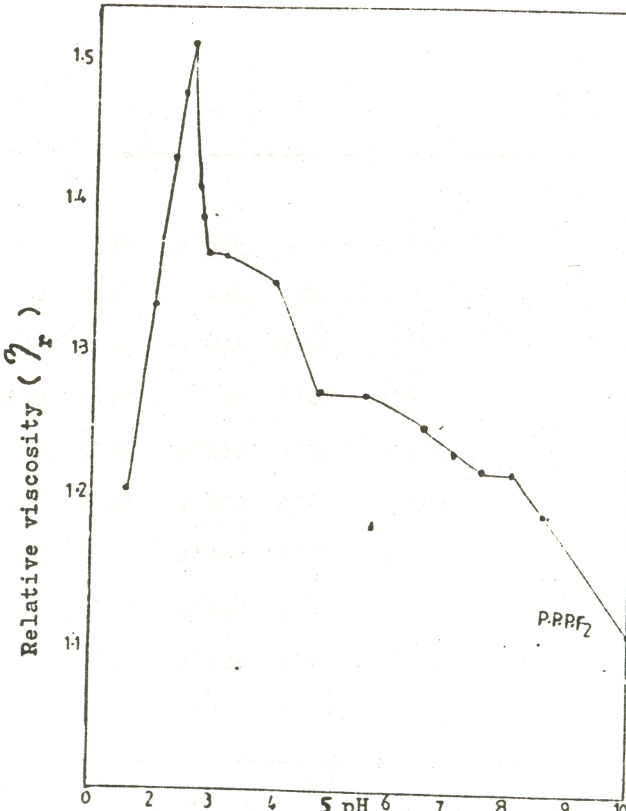

Fig.(III,b) , The effect of pH on the relative viscosities of 0.1% of prickly pear "B"(P.P.P.F_2) pectin solutions in the physical conditions of the pectin (such as the dispersion and hydration), while Pilnik (1964), attributed the drop in viscosity with increasing the hydrogen ion con centration to the more rapid aggregation of molecules tending to precipitate and hence, weeping (synersis) would occur.

On the other hand, it appears that the addition of base caused a decrease in viscosity for the different types of pectins under this study. This observation might be due to the effect of sodium ions (from NaOH) replacing the hydrogen ions of pectin carboxylic groups and this lowering the possibility of hydrogen bonds formation (Heneglein, 1950). Also hydroxyl ion would cause deesterification of pectin, forming insoluble pectate (Neukom & Deuel, 1958 and Neukom, 1963).

c- Effect of sucrose concentration:

In this experiment, the relative viscosities for orange and prickly pear pectins were estimated and plotted against sucrose concentration. The results are recorded in table (3) Fig. (IV). From these results, it has been observed that the relative viscosities of 0.1% pectin solutions of orange peel and prickly pear "Fraction B" increased gradually with the increase in sucrose concentration, till the concentration of sucrose reached to 30% (orange peel pectin) and 35% (prickly pear pectin, Fraction B), where a sharp increase in viscosities of pectin solution occurred, the increase in sucrose concentration more than 45% (orange peel pectin) and 40% (prickly pear pectin, Fraction B) caused unmeasured increase in the relative viscosities of 0.1% pectin solution, this is due to gel formation.

The effect of sucrose on the relative viscosities of pectin solutions might be similar to its effect on the colloidal character of jelly which was explained by Jackman (1983), who reported that the polyhydroxy compounds (such as sucrose) form hydrogen bridges between the pectin molecules and stablize the structure i.e. the sucrose molecules act as bridges linking between molecules. The same data also indicated that the increase in pectin cocnentration from 0.1% to 0.2% reduced the amount of sugar required to that obtain the same viscosities. This observation might be due to the increase in pectin concentration would increase the number of carboxyl groups, which in turn could contribute to hydrogen bonding and so the effectiveness of added hydrogen bonding agents increased and hence, less sugar was needed to form jellies. Similar explanation was mentioned by SOlms (1960) and Sarhan (1975). It could be concluded

Table (3)

The effect of sucrose concentration on relative viscosities of pectins

Conc. of sucrose g/100ml	Orange peel pectin		Prickly pear pectin "A"		Prickly pear pectin "B"	
	η_r (Conc.0.1%)	η_r (Conc.0.2%)	η_r (Conc.0.1%)	η_r (Conc.0.2%)	η_r (Conc.0.1%)	η_r (Conc. o.2%)
0	1.357	2.349	1.318	1.923	1.365	2.229
1	1.383	2.716	1.362	1.925	1.550	2.654
5	1.429	3.016	1.430	2.050	1.950	3.150
10	1.590	3.381	1.500	2.300	2.250	3.450
15	1.863	3.801	1.520	2.450	2.620	3.950
20	2.040	4.091	1.620	2.760	2.950	4.650
25	2.340	4.360	1.680	2.800	3.650	4.850
30	3.250	4.850	1.760	2.950	4.090	5.360
35	5.250	5.850	1.880	3.080	4.850	8.250
40	6.050	8.450	2.040	3.260	7.530	jel
45	7.800	jel	2.450	3.530	jel	"
50	jel	"	2.780	3.880	"	"
55	"	"	3.430	4.360	"	"
60	"	"	3.780	5.010	"	"
65	"	"	5.100	6.680	"	"
70	"	"	jel	jel	"	"

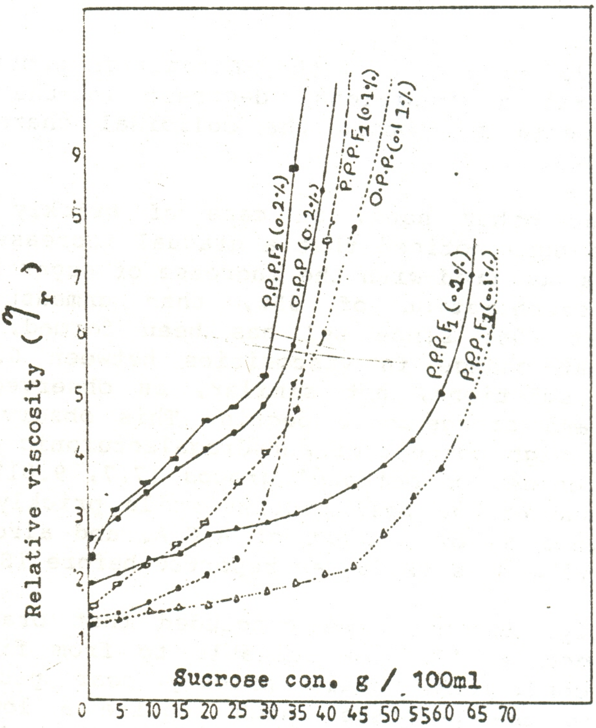

Fig.(IV) , The effect of sucrose concentration on the relative viscosities of 0.1 and 0.2% solutions of orange peel (O.P.P.) , prickly pear "A"(P.P.P.F_1)and prickly pear "B"(P.P.P.F_2) pectins that at a definite volume, the increase in pectin concentration requires a poportional decrease in the added sugar and vice versa to obtain the colloidal character of the resulting gel.

On the other hand, in case of prickly pear pectin "A" it has been noticed that a gradual increase in relative viscosities occurred with the increase of sugar concentration till a concentration of 65%, then unmeasured increase occurred at 70%, since gel has been formed. Also, there is no great change in viscosities between 0.1% and 0.2% of pectin solutions, not similar, as observed in prickly pear "B" and orange peel pectin. This observation may be due to the high content of anhydrogalacturonic acid (A.G.A.) and high contnet of methoxyl groups (7.7, 9.01%) of prickly pear "B" and orange peel pectins while prickly pear pectin "A" contained a low content of A.G.A. and also low content of methyoxyl groups (2.06) as reported before (Saad, 1985).

Finally, it could be concluded that orange peel and prickly pectins "B" are suitable to from firm gel under suitable conditions. While prickly pear pectin "A" can be used in the purposes which require a low content of A.G.A. and methoxyl content such as some medical purposes.

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تأثير تركيز أيون الايدروجين ـ الكالسيوم والسكروزعلى لزوجة محاليل بكتين قشر البرتقال والتين الشوكى المصرى

صلاح مصطفى محمود سـعد

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جامعة الزقازيق

أستخلصت المواد البكتينية من قشور البرتقال والسيقان المحورة للتين الشوكى المصرى ودرس تأثير درجة الحموضة وتركيز كل من ايون الكالسيوم ـ والسكروز على اللزوجه النسبية ومن ثم قابلية هذه الانواع لتكوين جل لما لهذه الخاصية من أهمية تكنولوجية .

وقد وجد أن اضافة ايونات الكالسيوم لمحاليل بكتين قشور البرتقال والتين الشوكى "ب" يوءدى الى زيادة اللزوجه النسبية الى ان يتكون جل ثابت دون الحاجة الى أضافة سكر وهذه الخاصية هامة لانتاج جل لمرضى السكر .

أما بكتين التين الشوكى "أ" لوحظ عدم تكون جل رغم اضافة تركيزات عالية من الكالسيوم . وجد أن درجة الحموضة المثلى تساوى ٢٫٥٥ لكلا من بكتين قشر البرتقال وبكتين التين الشوكى وقد أوضحت النتائج أنه بزيادة تركيز السكروزتزداد اللزوجة النسبية وكذلك بزيادة تركيز البكتين (قشر البرتقال والتين الشوكى"ب") أدى الى زيادة ملحوظة فى اللزوجه النسبية لنفس التركيز من السكر .

أما النوع "أ" فكانت الزيادة تدريجية حتى مع التركيزات العالية من السكر.
ومن هذه النتائج اتضح أنه يمكن استخدام بكتين قشر البرتقال والتين الشوكى "ب" فى الاغراض التى تتطلب تكوين جل قوى اما بكتين التين الشوكى "أ" فيمكن استخدامه فى الاغراض التى تتطلب جل ضعيف مثل الاغراض الطبية .