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Barreto Alcoba, Morela; Buescher, Ronald
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Influence of viscosity on rutin crystallization in model brine solutions

Morela Barreto Alcoba[1], Ronald Buescher[2]

[1]Facultad de Ingenieria, Av Universidad, Bárbula Naguanagua 2005. Valencia. Edo Carabobo. Venezuela. Telfax: 58-241-867-5364. E-mail mialcoba@hotmail.com

[2] University or Arkansas, 2650 Young Ave, Fayetteville, AR. 72704 USA. 1-479-575-4775. E-mail buescher@uark.edu

RESUMEN

La rutina, flavonol abundante en espárragos, se deposita sobre los espárragos encurtidos. Información referente a la cristalización de la rutina en soluciones viscosas es limitada. En los alimentos la cristalización puede controlarse incrementando la viscosidad. Nosotros determinamos la influencia de la pectina y el xantano, modificadores de la viscosidad, sobre la cristalización de la rutina en buffer acetato. Se prepararon soluciones buffer acetato 0.1 M (pH 3.7 con 3% de NaCl) con diferentes concentraciones de gomas. Se prepararon soluciones diluidas de rutina y se pasteurizaron (74 ºC), enfriaron y almacenaron a 25 ºC. El contenido de rutina se determino periódicamente. La referencia utilizada fue buffer acetato supersaturado con 400 mg/L de rutina sin espesantes. La desupersaturación de la rutina paso de rápida a lenta al aumentar la viscosidad. La cristalización de la rutina fue retrasada aumentando la viscosidad con pectina en soluciones con menos de 240 mg/L de rutina.

Palabras clave: rutina, cristalización, desupersaturación, xantano, pectina

Influencia de la viscosidad sobre la cristalización de la rutin en salmueras utilizadas como sistemas modelo

ABSTRACT

Rutin, the main flavonol in asparagus, precipitates on pickled asparagus surfaces. Information about rutin crystallization at different viscosities is limited, but in food systems crystallization may be controlled by increasing the viscosity. We determined the influence of pectin and xanthan as viscosity modifiers on rutin crystallization in acetate buffer. Buffered acetate solutions (pH 3.7 with 3% NaCl) with different pectin and xanthan concentrations were made. Rutin stock solution was used to achieve different concentrations. Solutions were pasteurized to 74 °C, cooled, and stored at 25 °C. Samples were analyzed for rutin content periodically. The same treatment was made with acetate buffer solution with 400 mg/L rutin without thickening agent. Desupersaturation of rutin shifted from fast, in acetate buffer, to slow when the buffer solution viscosity was changed. Rutin crystallization was retarded by increasing the buffer viscosity with pectin in solutions where rutin concentration was lower than 240 mg/L.

Keywords: Rutin, crystallization, desupersaturation, xanthan, pectin

INTRODUCTION

Rutin (quercetin -3-0- rhamnoglucoside) is a flavonol compound with antioxidant capacity. However, rutin uses in foods are limited due to its low solubility in water systems. As a natural compound in asparagus (*Asparagus officinalis*), rutin has produced some discolorations in commercial canned asparagus [1] and crystallization on the surface of pickled asparagus [2]. Nevertheless, rutin does not form crystals in commercial canned asparagus, which differs from pickled asparagus in the higher content of pectin in the brine. During the sterilization, commercial canned asparagus releases pectin into the brine as a consequence of tissue disruption.

Pectins and other hydrocolloids are used in the food industry, generally in proportion lower than 1%, with different purposes such as prevention of crystallization of ice and sugar [3]. Klahorst [4] reported the use of gums to retard or minimize ice crystallization in ice cream. Hartel [5] pointed out that increases in the food viscosity reduce molecular mobility, preventing in this way the crystallization in food systems. High molecular weight compounds such

as proteins and gums are used to inhibit or retard the crystallization in sugar.

Gums are selected depending on their functional properties and the characteristics of the product in which the gum will be used [3, 6]. Voragen [7] reported pectins as a compound with good thickening properties, having the advantage of being stable at pH between 3 to 4. Morris [8] said that xanthan forms viscous solutions stable at wide pH range, ionic strength, and temperature. As a consequence, xanthan has broad applications in food industry.

The primary purpose of this research was to determine the influence of the solution viscosity, increased with pectin and xanthan, on rutin crystallization in buffer acetate as a model system.

MATERIALS AND METHODS

Chemicals.

Rutin and pectin were acquired from Sigma Chemical Co., (St Louis, MO). Methanol was from EMD Chemicals Inc (Gibbstown, NJ). Sodium acetate and acetic acid (reagent grade) were obtained from Fisher Scientific Co (Fairlawn, NJ). Sodium chloride was USP grade reagents. Xanthan was obtained from TIC-gums (Belcamp, MD).

Stock solution preparation

Because of the problems associated with the gum precipitation in methanol, the methanolic stock solution of rutin used was of 20 g/L, so that the amount of methanol added to the test samples was very small. No gum precipitation occurred in this way. In the stock solution, rutin was dissolved by sonication (Ultrasonic cleaner 8891R-MT, Cole Parmer Instrument Co. Vernon Hills ILL US). The solution was refrigerated, and when used, it was warmed to 25 °C and sonicated again.

Gum solutions preparation

Water solutions of pectin (0.25%, 0.5%, 0.75%, 1%, and 2%) and xanthan (0.025%, 0.05%, 0.075%, 0.1%, 0.2%, and 0.3%) were prepared. With these viscous solutions, acetate buffers 0.1 M (pH 3.7 with 3% NaCl) were made to obtain viscous acetate buffers solutions. Additionally 3% NaCl was added. Rutin stock methanolic solution was added to reach the desired final concentrations in the buffer. The final rutin concentrations in the pectic solutions were approximately 150 mg/L, 250 mg/L, 350 mg/L, and 450 mg/L. The final rutin concentrations in the xanthan solutions were 90 mg/L, 250 mg/L, and 340 mg/L of rutin. The solutions were pasteurized at 74 °C for 15 min, cooled to 25 °C, stored at the same temperature, and analyzed for rutin content over time.

The control solution was acetate buffer 0.1 M (pH 3.7 with 3% NaCl) supersaturated with 400 mg/L of rutin from a stock solution. Supersaturation was completed by heating the simulated brine at 74 °C, cooling it to 25 °C, and letting it stand at this temperature. Changes in rutin concentration of these solutions and the solutions with the pectin and xanthan at different viscosities were monitored from day 0 to day 25 by a spectrophotometer (UV-Visible Varian Model Cary 50 Bio, Varian Australia). The concentrations were calculated from absorbance versus rutin concentration (mg/L) calibration curve made at 260 nm and 25 ºC with Win UV- software. The rutin standard solutions were prepared in the same acetate buffer. The samples were diluted with acetate buffer. In the blank the relative amount of pectin or xanthan in the samples were included.

The specific viscosities of these solutions were determined by the method described by [9]. Viscosities were measured at 30 °C by submerging the Cannon-Fenske capillary viscometers in a thermostatic glass water bath (thermostat was a Haake type E-52. Berlin, Germany).

Statistical analysis

Three replications of each treatment were made. Therefore each value in the graph and viscosity values represent the mean of the triplicate analyses. Statistical analysis was performed by JMP IN version 5.1 (SAS Institute, INC).

RESULTS AND DISCUSSION

Variation of the acetate buffer viscosity

Figure 1 shows the changes in the viscosity of the acetate buffer by increasing the xanthan concentration (Figure 1a) and pectin concentration (Figure 1b). The solution viscosity increased with increasing gum concentration, but as pointed by Bourne [10] no exact linear relationship existed between the viscosity and the xanthan or pectin concentration at 25 °C. Lower amounts of xanthan compared to pectin were needed to reach the desired viscosities in the solutions.

Pectins in the prevention of rutin crystallization

The viscosity was substantially increased to values higher than 0.02, which was the viscosity in the

acetate buffer. Rutin behavior in the buffer containing pectin was different than in the control without pectin (Figure 2). In the control, rutin crystals were formed in 3 h and the rutin concentration decreased fast and reached equilibrium at 18 d, after which no significant variations in the concentration were detected in the rutin concentration. A similar result was found by Lueck [11], who was working at higher pH. In that case, rutin solutions in 0.2 M acetate buffer at pH 5.44 reached equilibrium at 77 d.

In general, about 150 mg/L of rutin was held by all the solutions containing pectin which was much higher than the control (Figure 2). Particularly, solution with pectin and 150 mg/L of rutin did not demonstrate desupersaturation within the study time and did not form crystals in any of the solutions. Desupersaturation was very slow in the pectin solutions containing about 250 mg/L of rutin. These results indicated that by adding little amounts of pectin, rutin crystallization can be prevented in buffer solutions with rutin content about 250 mg/L or less. In general, desupersaturation was slower with the use of pectins than in the control. Solutions with 0.25 %, 0.5%, 0.75%, and 1% pectins and more than 300 mg/L of rutin showed faster desupersaturation than the ones with lower rutin content (Figure 2).

In solutions around 250 mg/L rutin, crystallization was observed at 17 d except for the solution with 9.43 viscosity that crystallized at 25 d. In solutions containing 350 mg/L rutin the crystallization started at 5 d except for the solution with 9.43 viscosity that crystallized at 8 d. Solutions around 450 mg/L rutin crystallized at 2 d except for the solution with 9.43 viscosity that crystallized at 8 d.

In general, all the pectin solutions were able to hold rutin concentrations close to 250 mg/L for at least 7 d. Perhaps due to the entanglement of the rutin particles with the increase in the viscosity [10]. In solutions with 2% (9.43 specific viscosity) pectin, desupersaturation was substantially slower for all the rutin concentrations than in the control.

All the solutions with 2% pectin (Figure 2) and more than 300 mg/L of rutin showed slower desupersaturation than in acetate buffer only, but they equilibrated to rutin concentrations lower than 150 mg/L rutin which was the minimal amount retained for the solutions without desupersaturation. The solutions with about 250 mg/L of rutin had slower desupersaturation than the ones with higher rutin content. The shift in rutin desupersaturation from fast in the brine to slow in the viscous brine showed that rutin crystallization in more viscous solutions will be slower than in acetate buffer alone. Comparing the minimum amount of rutin held in the solution having 0.25% pectin with rutin solubility in water at 25 °C (54 mg/L), it was observed that more rutin was held in solution when the viscosity increased due to the presence of pectins. Adapa [12] reported prevention in crystal formation in ice cream but with significant increases in hydrocolloids concentration to reduce the molecular mobility. Hartel [5] pointed out that the prevention of sugar crystallization in candies was caused by reducing the molecular mobility. The reduction of molecular mobility can be reach by increasing the viscosity.

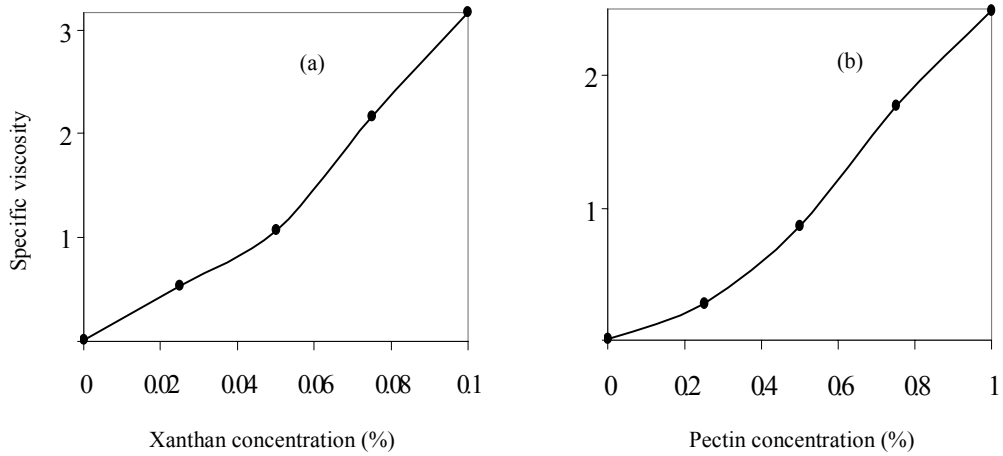

Figure 1. Specific viscosities of xanthan and pectin solutions prepared in acetate buffer 0.1 M (pH 3.7, 30 °C (a) by increasing xanthan concentration and (b) by increasing pectin concentration. Each data point represents the mean of triplicate values

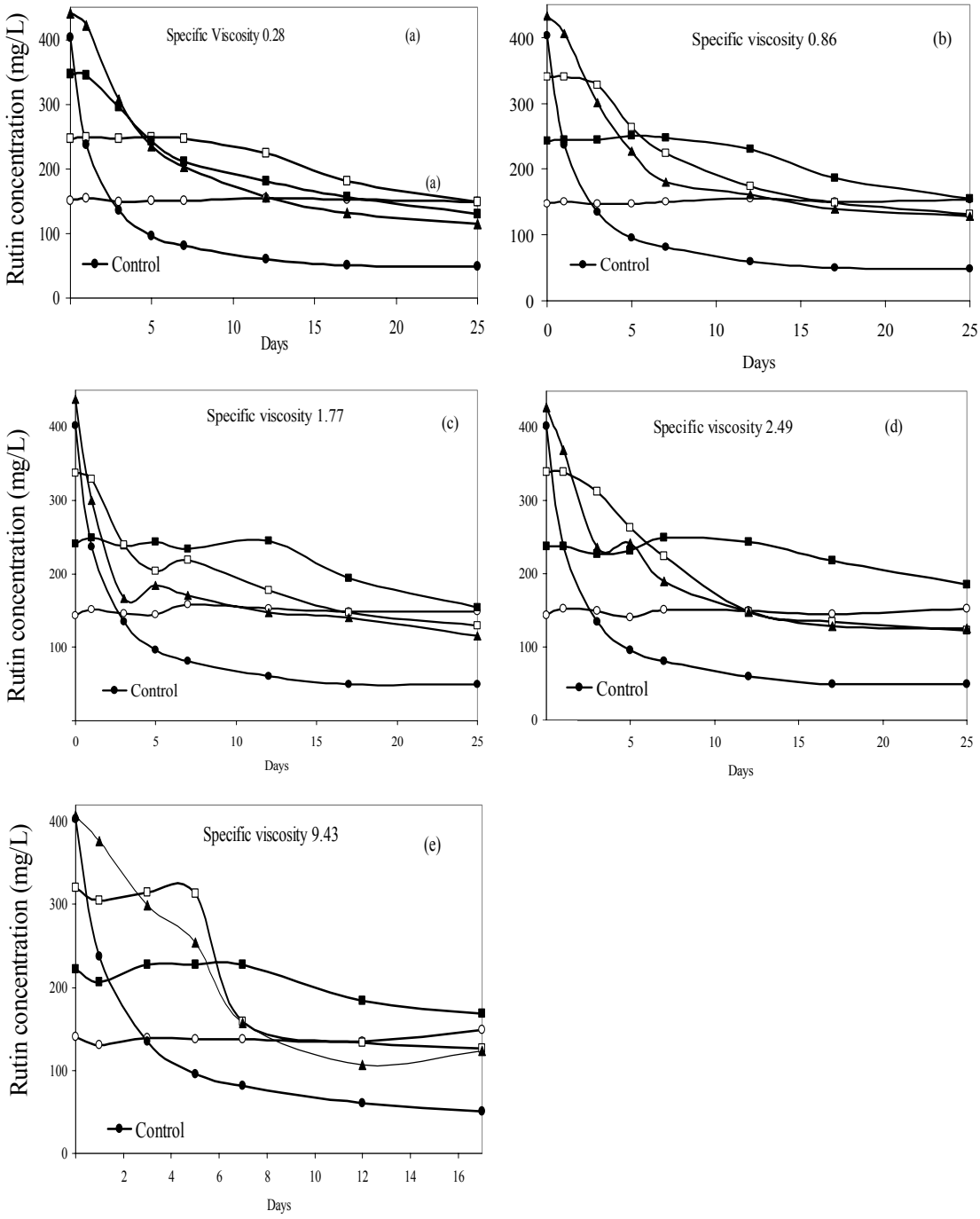

Figure 2. Effect of specific viscosity (pectin) on maintaining rutin in solution. (a) 0.25% pectin. (b) 0.50% pectin. (c) 0.75% pectin. (d) 1% pectin. (e) 2% pectin. Each line except for the control represents different rutin concentration in the pectin solution and the solution desupersaturation. Each data point represents the mean of triplicate values.

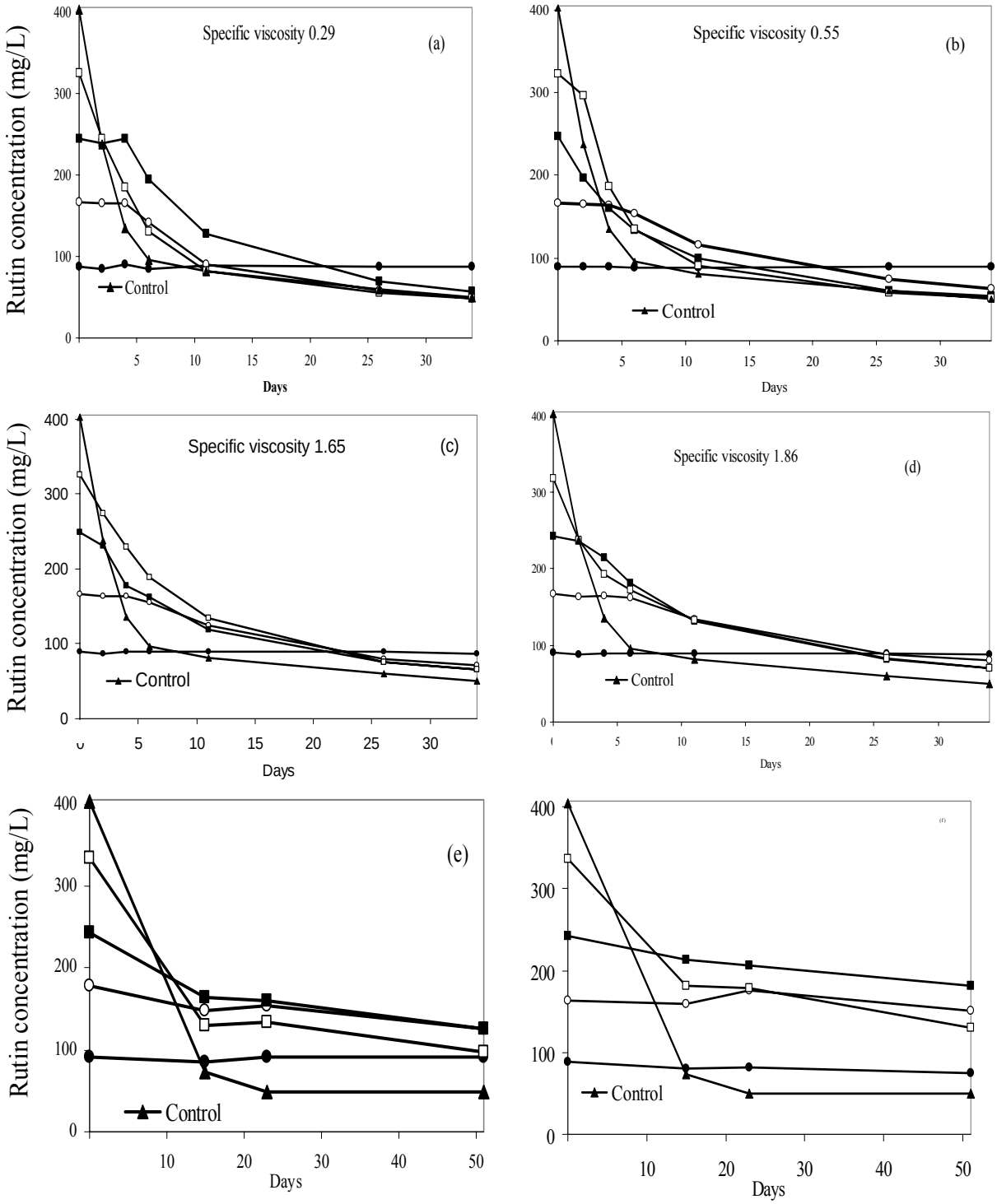

Figure 3. Effect of specific viscosity (xanthan) on maintaining rutin in solution (a) 0.025% xanthan. (b) 0.050% xanthan. (c) 0.075% xanthan. (d) 0.1% xanthan. (e) 0.2% xanthan. (f) Buffer containing 0.3% xanthan. Each line, except for the control, represents different rutin concentration in the pectin solution and the solution desupersaturation. Each data point represents the mean of triplicate values.

Pectin solutions were cloudy. This characteristic could limit its application in the brine solution for pickled vegetables or other food products where transparency of the solution is a favorable sensory attribute.

In general, desupersaturation and so the crystallization was prevented at low rutin concentrations (150 mg/L to 250 mg/L) and delayed at rutin concentrations above 250 mg/L rutin.

Xanthan in the prevention of rutin crystallization

To determine differences in rutin crystallization with another gum the same experiment as the previous one was performed with xanthan, which is one of the gums used in pickles [13]. Xanthan is one of the gums with more versatile applications because of its solubility in cold and hot water, the wide pH range of application and the solutions stability [8].

At different viscosities, no desupersaturation was observed in solution containing 90 mg/L (Figure 3) of rutin during the study time. In these cases, desupersaturation was slightly slower than the control at viscosities between 0.29 and 1.86, and the rutin solution concentration went to values very close to the control solution. In Figurea 3e and 3f with higher viscosities than the ones presented in Figure 3a, 3b, 3c, and 3d rutin desupersaturation was slow.

In these solutions rutin crystal formation was delayed compared with the time at with the crystals were observed in the solutions with lower viscosity (Table 1).
In general, desupersaturation (Figure 3) in solutions with 170 mg/L of rutin or more were faster than in solutions with pectins. Solutions with 0.2% and 0.3% xanthan (Figure 3) the desupersaturation was faster (15 d crystal precipitation) than in the 2% pectin (25 d crystal precipitation). The exception was the solution with 170 mg/L rutin and 0.3% of xanthan where the crystallization was delayed 51 d.

In solutions with 0.2% and 0.3% xanthan no viscosity was taken because these fluids were extremely viscous and the method used was for mobile fluids [10]. All the solutions with xanthan gum were crystalline and the crystals were deposited in the bottom.

Table 1. Time (days) for appearance of rutin crystals in buffer* affected by xanthan amd rutin concentrations.

Rutin concentration (mg/L)	***Xanthan concentration (%)***					
	0.025	0.05	0.075	0.1	0.2	0.3
170	2	4	4	26	15	51
250	2	1	1	2	15	15
330	1	1	1	1	15	15

* acetate buffers 0.1 M (pH 3.7 with 3% NaCl).

The times in which the crystals were formed in the xanthan solutions are shown in Table 1. Rutin crystallization was faster than in the control samples where the crystals were formed at 3 h. The solution with rutin concentration around 90 mg/L never showed desupersaturation and did not formed crystals in the study time. In the samples with rutin concentrations around 170 mg/L the crystals formation was considerably delayed at 0.1% and 0.3% xanthan. However, rutin precipitation was faster than for the solutions with pectin. The the xanthan solutions were transparent.

CONCLUSIONS

The amount of rutin held in solution increased by 100 mg/L when pectin (0.25%) or xanthan (0.025%) was added in the buffer solution. In general, desupersaturation of rutin changed from fast to slow when the viscosity of the buffer solution was increased by pectin or xanthan. This produced a delay in the rutin crystal formation in solution compared with the control (no gums). No rutin crystallization was observed in solutions containing low rutin concentration (about 150 mg/L rutin in pectins solutions and about 90 mg/L rutin in xanthan solutions). In solutions where rutin concentration was higher than 250 mg/L the crystallization was delayed in respect to the control. In general, pectin was more effective in retarding the rutin desupersaturation in its solutions than in xanthan.

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