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Effect of Magnesium and Iron on the Hydration and Hydrolysis of Guar Gum

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The effect that magnesium and iron have on the hydration and hydrolysis of guar gum at pH 12 was studied as a function of viscosity. It was found that small concentrations of magnesium do not affect the dissolution ratio of guar but significantly decrease hydrolysis at high temperatures. These results suggest that $Mg(OH)_2$ forms an adduct with the polysaccharide that prevents thermal hydrolysis of the guar. Viscosity measurements recorded in the presence of iron at pH 12 show that ferric iron inhibits hydration or dissolution of guar and may accelerate chain scission of fully hydrated guar when solutions are heated in an autoclave at 121 °C.

Introduction

Guar is a biopolymer similar to locust bean gum consisting of a 1,4-linked β-D-mannopyranose backbone with branches of 1,6-linked α-D-galactopyranose (Scheme 1). There are 1.5−2 mannose residues for each galactose residue. Industrial applications are numerous and require a detailed knowledge and control of the viscosity properties of aqueous solutions.[1−4] Gelling is an important property that is relevant to applications in the pharmaceutical and food industries. Thus, an understanding of the rate and degree of hydration or dissolution of these polymers is of considerable interest.[1,5,6] Viscosity is often used to monitor hydration and degradation of polysaccharides[7−10,11] and also to measure other interactions such as cross-linking.[3]

Applications that result from complex formation between metals and biopolymers can be found in the food, pharmaceutical, and agricultural industries.[12,13] Guar gum also finds important applications in oil field operations as a high-viscosity fracturing fluid.[14,15] This fluid forces a propping agent into the fractures to keep them from closing when the pumping pressure is released. After a short period of time, the viscosity of this fluid decreases, allowing both the injected water and the low-viscosity fluids to travel back through the man-made fracture to the well and up to the surface. Impurities that are present in the water during the fracturing process can alter the properties of the guar, leading to unfavorable results. Literature reports provide evidence that metal cations, such as Na^+, K^+, Ca^{2+}, and Mg^{2+}, can change the properties of polysaccharides by interacting with the hydroxyl groups. In this way, the degree of hydration and, consequently, the viscosity may be altered.[16−19] Magnesium is commonly present in water, and other metals that are absorbed from the soil where the plant grows are present in guar.

In this study, we describe how two elements, magnesium and iron, affect the hydration or dissolution of guar and their effect on thermal degradation at high pH. Viscosity was measured as a way to assess the development of these processes. According to the literature,[20] 1% solutions of guar gum are expected to have non-Newtonian viscosity and a pseudoplastic behavior. The pseudoplasticity decreases and the behavior approximates to Newtonian at concentrations <0.3%. In this study, the rheology of the solutions (at a concentration of 0.5 wt/vol %) was not studied, but they are expected to exhibit non-Newtonian behavior.

Experimental Section

Materials. Guar gum flour was provided by Halliburton Energy Services (Duncan, Oklahoma) and was used as received. NaOH, $FeCl_3 \cdot 6H_2O$, HCl, HNO_3, and ethanol (95%) were obtained from Fisher Scientific. EM Science provided the $MgSO_4$. Sodium chlorite ($NaClO_2$), from Alfa Aesar, was used as an oxidant and sodium thiosulfate ($Na_2S_2O_3$), used as a free radical scavenger, was obtained from Fisher Scientific. Yttrium as a 1000 μg/mL plasma standard solution and iron as a 1000 μg/mL atomic absorbance standard solution were obtained from Alfa Aesar.

Guar Hydration and Hydrolysis. Typical hydration and hydrolysis experiments were carried out using 0.5 wt % guar solutions. Solutions were prepared by the slow addition of guar gum (0.5 g) to 100 mL of distilled H_2O with stirring via a magnetic stirrer. This produces a rapid dispersion that prevents particle aggregation. Guar solutions were allowed to hydrate at room temperature with continuous stirring. Except where indicated, 0.5 mL of a 25 wt % NaOH solution was added after solutions were close to complete hydration (4 h). Solutions were then placed in a glass bottle and the cap sealed with Teflon tape. The samples were hydrolyzed in an autoclave (All American, Model No. 25X), to approximate the high temperature and pressure conditions found in oil wells, at 121 °C for 1 h, typically reaching pressures of 15 psi.

Measurements. Viscosity measurements were carried out at 300 rpm (5 1/s) using a Fann Instruments viscometer model 35A, equipped with R1 sleeve, B1 bob, and #1 spring. Measurements were taken at standard intervals during a 4-h period, at which time complete hydration has occurred. Degradation of the guar solutions was evaluated by comparing viscosity before and after heating at 121 °C for 1 h in the autoclave. Viscosity measurements were taken at room temperature. The time for the final viscosity measurement depended on heating and cooling rates for the autoclave, typically about 540 min, and this value is used in all of the plots for consistency. After thermal degradation, no further change in viscosity was observed within a 24-h period.

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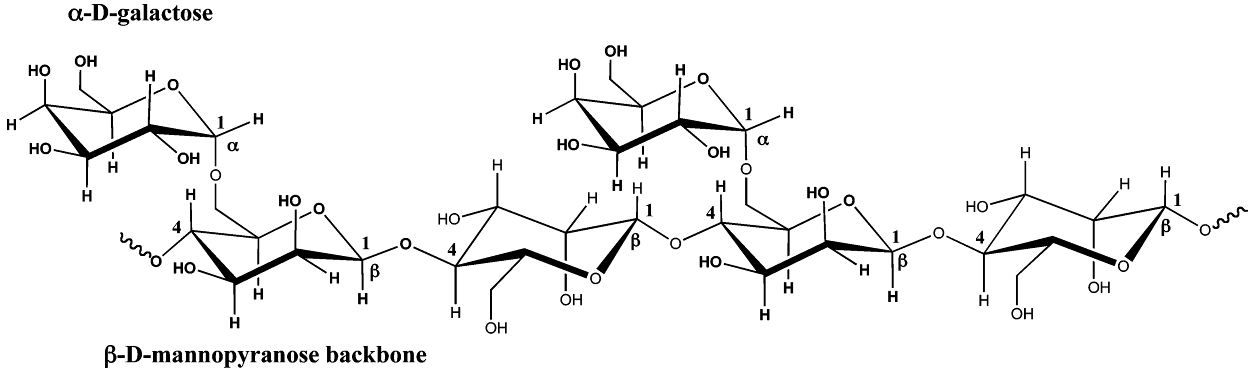
Scheme 1. Guar Gum Structure Consisting of a 1,4-Linked β-D-Mannopyranose Backbone with Random Branches of 1,6-Linked α-D-Galactopyranose



Thermogravimetric analyses were performed using a TA STD 2960 instrument. DTA−TGA data were collected simultaneously. Samples for iron analysis were prepared by dissolving the guar in hot aqua regia. A 1 ppm (11.2×10^{-6} M) yttrium solution was used as an internal standard, and samples were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP) using a Perkin-Elmer Optima 4300 DV optical emission spectrometer.

Results and Discussion

Effect of Mg^{2+} on Hydration and Hydrolysis of Guar. Magnesium salts were shown to inhibit the degradation of guar at pH 12. In these experiments, samples were allowed to hydrate until they equilibrated (4 h). The pH was then adjusted to 12 by the addition of sodium hydroxide. The viscosity was observed to increase upon heating as the Mg^{2+} concentration was increased (Figure 1), demonstrating that Mg^{2+} inhibits hydrolysis. Magnesium was found to have little effect on the dissolution rate of guar gum at neutral pH. Similar results were obtained when the oxidant $NaClO_2$ was added. These results are presented in Table 1 showing that the final viscosity increased with increasing magnesium concentration.

It has been reported previously that carbohydrates form complexes with hydroxides of alkaline-earth metals in aqueous and alcoholic solutions. Formation of these complexes, stabilized by chelation of the metal ion, affects the viscosity, the electrical conductivity, and the optical rotation of carbohydrate solutions.[20] In the following section, the formation of a complex between guar and magnesium hydroxide is examined.

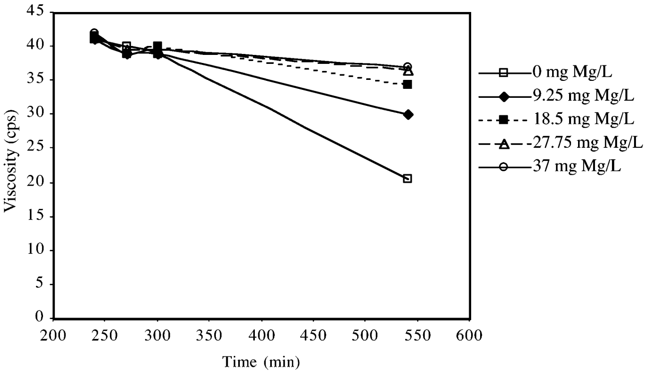


Figure 1. Guar hydration and hydrolysis study carried out in the presence of magnesium sulfate (1 ppm Mg = 41.1×10^{-6} M). Samples contain 0.5 wt % guar in water. The pH was adjusted to 12 after 270 min. The values after 540 min were recorded after the samples had been heated at 150 °C. Viscosity measurements were taken at room temperature.

Table 1. Variation of the Final Viscosity (after heating) of Guar Samples versus Mg^{2+} Concentration (1 ppm Mg = 41.1×10^{-6} M)

	viscosity (cP)			
	with NaOH, $NaClO_2$, and $Na_2S_2O_3$[a]		with NaOH only	
Mg^{2+} (ppm)	initial (before autoclaving)	final (after autoclaving)	initial (before autoclaving)	final (after autoclaving)
0	42.5	5	39	20.5
9.25	40.5	18	39	30
18.5	42	23	40	34.5
27.75	41.5	33	39.5	36.5
37	42.5	32	39.5	37

[a] NaOH, $NaClO_2$, and $Na_2S_2O_3$ added to samples.

$Mg(OH)_2$ Complex with Guar. Since all reactions were carried out at pH 12, the magnesium will be in the form of the hydroxide. UV analysis indicates that there is no interaction between the oxidizer $NaClO_2$ and $Mg(OH)_2$. Thus, the absorbance peak of ClO_2^- at 260 nm does not change as the Mg^{2+} concentration is increased. The observation that magnesium ions affect the degree of guar degradation in the absence of sodium chlorite suggests that $Mg(OH)_2$ forms a complex with the polysaccharide. Formation of an adduct might be expected to prevent the thermally induced hydrolysis by protection of the hydroxyl groups. A result that supports the formation of a complex comes from the observation that guar is partially hydrated in a concentrated solution of $MgSO_4$ (50% aqueous ethanol at neutral pH) without swelling. The product obtained from this procedure was shown by TGA analysis to have gained 50% more weight than the original sample. TGA analyses are presented in Figure 2.

These results demonstrate that when guar is stirred in aqueous ethanol, without magnesium, decomposition occurs above 500 °C. The product obtained from guar in a concentrated magnesium solution in 50% aqueous ethanol leaves a residue of about 20 wt % that is probably magnesium oxide. It has been reported that similar adducts are formed in water.[21] It is also known that metal ions, by cross-linking, can form complexes with more than one sugar unit in a polysaccharide chain.[12,22]

Effect of Fe^{3+} on Guar Hydration. The interactions of Fe^{3+} with biopolymers have been studied previously. Coe[23,24] and Jones[25] and their co-workers reported that $FeCl_3$ forms FeO(OH) upon addition of base. Surrounding layers of polysaccharides stabilize these species through octahedral structures. Other studies have shown that iron forms a similar complex with chitosan by Fe−OH and Fe−NH_2 ligation.[26,27]

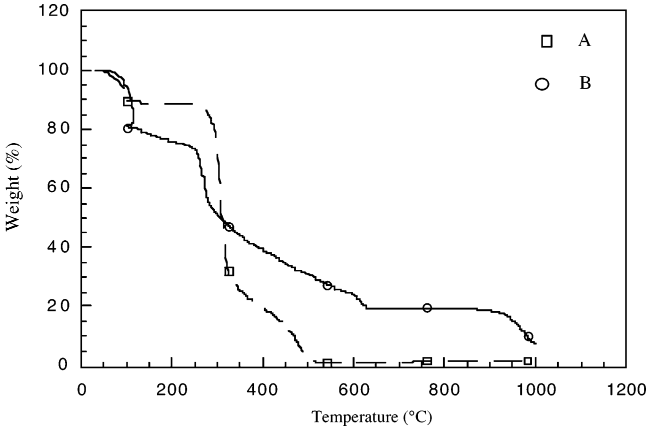


Figure 2. Thermal gravimetric analysis of guar in air: (A) 50% guar stirred in ethanol and (B) 50% guar stirred in a concentrated solution of $MgSO_4$ in ethanol.

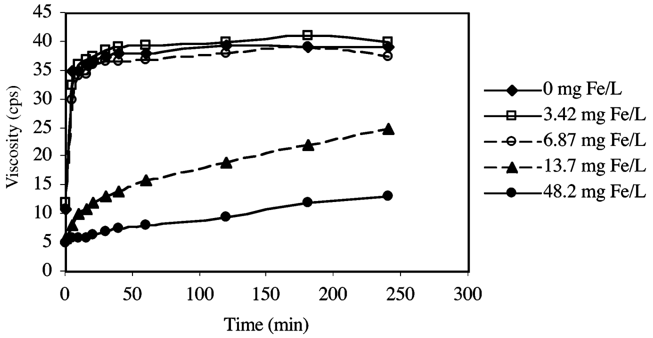


Figure 3. Guar hydration study in the presence of Fe^{3+} (1 ppm Fe = 17.9 × 10^{-6} M). Samples contain 0.5 wt % of guar in water. The pH was adjusted to 12 immediately after the addition of guar. The viscosity measurements were taken at room temperature.

The dissolution rate of guar versus Fe^{3+} concentration is presented in Figure 3. In these experiments, the iron chloride was added to water prior to the addition of guar. The pH was then adjusted to 12. The viscosity plots show clearly that a high concentration of iron significantly suppresses the dissolution rate of the guar (also observed in the next set of experiments). The absence of a precipitate suggests that ferric hydroxide and/or FeO(OH) particles aggregate on the surface of the guar, creating a coating that competes with the water molecules. This would prevent swelling of the polysaccharide chains.

Effect of Iron on Guar Hydrolysis. The effect that Fe^{2+} and Fe^{3+} have on the degradation of guar in the absence of an oxidant is presented in Figure 4. For these experiments, a measured amount of iron was added to the water prior to the addition of guar. Sodium hydroxide was added after the viscosity reached equilibrium (270 min). The final viscosity (after heating) was recorded after 540 min for consistency, as mentioned earlier. To significantly alter the final viscosity, it was necessary to add more than 0.5 ppm (8.95 × 10^{-6} M) of Fe^{3+}. Our analysis of iron shows that the natural concentration of Fe in guar is about 45 ppm (806 × 10^{-6} M). This would correspond to 0.225 ppm (4.03 × 10^{-6} M) in a 0.5 wt % solution.

The results presented in Figure 5 were recorded using samples prepared by adding guar to solutions containing various concentrations of Fe^{3+}. Sodium hydroxide was added after complete guar hydration (270 min). Upon addition of base, the viscosity was observed to increase significantly for those runs containing the highest concentration of iron. This suggests that precipitation of ferric hydroxide and/or FeO(OH) initially causes cross-linking between the polysaccharide chains, resulting in solutions with a gel-like appearance. One can also observe that iron promotes chain scission even in the absence of oxidizer when guar solutions are heated at 121 °C. This results in a final solution that is fluid. Although the molecular weight of guar was not determined, the dramatic decrease in viscosity suggests that degradation of the guar has occurred. We attribute this observation to the oxidizing power of ferric iron. It is known that ferric iron in aqueous solution is reduced readily by many reducing agents, such as iodide and sulfide. The observation that Fe^{2+} did not exhibit the same effect suggests that Fe^{3+} is participating in a redox process that leads to the concomitant cleavage of the guar and formation of Fe^{2+}.

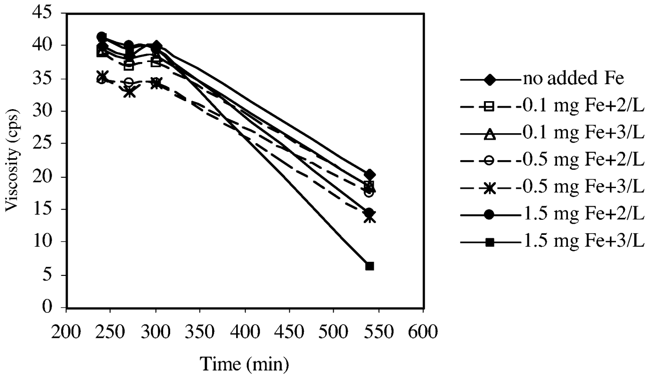


Figure 4. Guar hydration and hydrolysis study. Comparison of the effect of Fe^{3+} vs the effect of Fe^{2+}. Samples contain 0.5 wt % of guar in water. The pH was adjusted to 12 after 270 min. The value at 540 min indicates the viscosity after heating at 150 °C. The viscosity measurements were taken at room temperature.

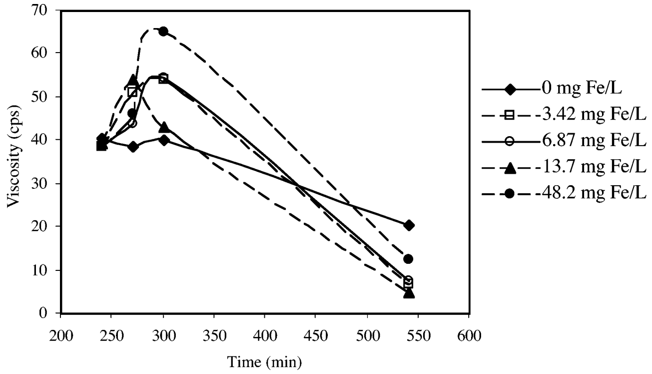


Figure 5. Guar hydration and hydrolysis study in the presence of Fe^{3+}. Samples contain 0.5 wt % guar in water. The pH was adjusted to 12 after 270 min. The values at 540 min indicate the viscosity after heating at 150 °C. The viscosity measurements were taken at room temperature.

Metal Combinations. Viscosity versus time measurements of solutions containing both magnesium and iron at pH 12 are presented in Figure 6. The presence of magnesium has no effect on hydration, whereas iron significantly retards dissolution of the guar. Curiously, when both are present, the magnesium seems to inhibit the effect of iron. Surface adsorption of the ferric iron on the magnesium hydroxide might result in deactivation of the iron.

The effect of Ca^{2+} is illustrated in Figure 7. In this experiment, the concentration of calcium and magnesium are similar to that found in hard water (47 ppm, 1170 × 10^{-6} M, of calcium and 18.5 ppm, 761 × 10^{-6} M, of magnesium in potable water was determined by a HATCH colorimeter using the HATCH method 8030). The concentration of iron in this experiment is much higher than is naturally present in guar. The high concentration of calcium leads to enhanced protection

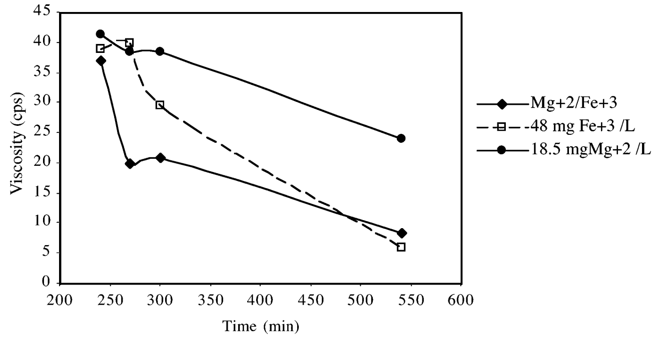


Figure 6. Guar hydration and hydrolysis study. Effect of Mg^{2+} and Fe^{3+}. Samples contain 0.5 wt % guar in water. The pH was adjusted to 12 after 270 min. The value at 540 min indicates the viscosity after heating at 150 °C. The viscosity measurements were taken at room temperature.

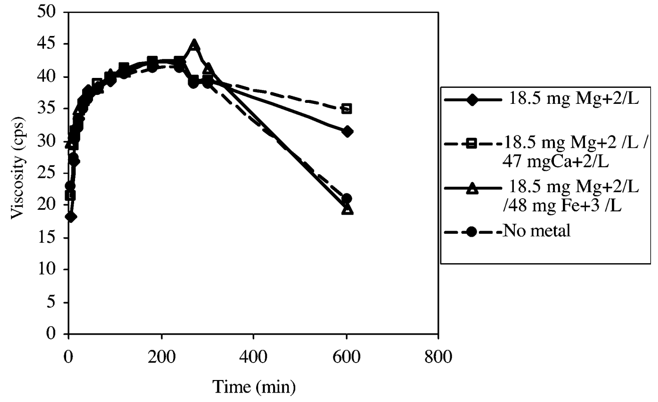


Figure 7. Guar hydration and hydrolysis study. Effect of Ca^{2+}, Mg^{2+}, and Fe^{3+}. Samples contain 0.5 wt % guar in water. The pH was adjusted to 12 after 270 min. The value at 540 min indicates the viscosity after heating at 150 °C. The viscosity measurements were taken at room temperature.

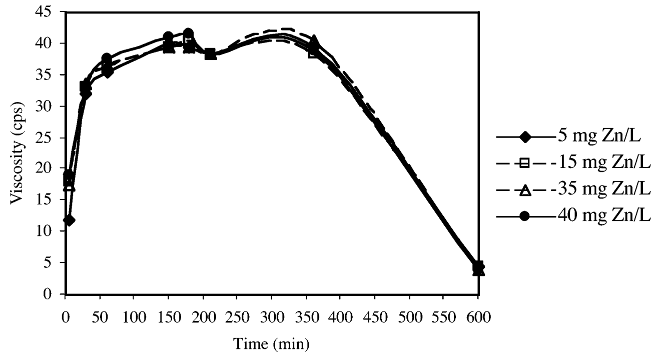


Figure 8. Guar hydration and hydrolysis study. Effect of Zn^{2+}. Samples contain 0.5 wt % guar in water. The pH was adjusted to 12 after 270 min. The value at 540 min indicates the viscosity after heating at 150 °C. The viscosity measurements were taken at room temperature.

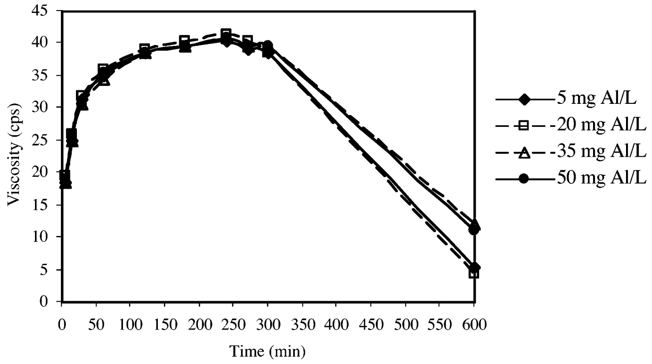


Figure 9. Guar hydration and hydrolysis study. Effect of Al^{3+}. Samples contain 0.5 wt % guar in water. The pH was adjusted to 12 after 270 min. The values at 540 min indicate the viscosity after heating at 150 °C. The viscosity measurements were taken at room temperature.

against degradation over that from magnesium alone, and the presence of a large concentration of Fe^{3+} appears to inhibit the effect of magnesium.

Although zinc (about 18 ppm, 275 × 10^{-6} M) and aluminum (about 150 ppm, 5,560 × 10^{-6} M) are present in high concentration in our samples of guar gum, they do not affect degradation rates (Figures 8 and 9) or accelerate hydrolysis. Although there are reports of complex formation between aluminum and zinc with saccharides, we did not observe any effect on the viscosity of the guar solutions used for this study. Experiments using simple sugars suggest that trivalent cations complex better than divalent ones and that smaller cations complex more weakly than larger ones. The most favorable ionic radius for complex formation was found to be 100−110 pm.[22] Related studies using polysaccharides have not been reported. Thus, it is difficult to find a correlation to ionic radius as Al and Zn have radii around 60−70 pm and iron and magnesium can have similar ionic radii depending on the coordination number of the cation.[28] A more plausible explanation for the activity of iron involves the ease with which ferric iron is reduced, probably by electron transfer from the polysacharride. The fact that zinc and aluminum do not participate in redox reactions may account for the lack of reactivity of these metals.

Conclusions

Magnesium ion at pH 12 inhibits degradation of guar gum at 121 °C. These results suggest that $Mg(OH)_2$ forms an adduct with the polysaccharide that prevents thermal hydrolysis of the guar. Viscosity measurements recorded in the presence of ferric iron at pH 12 show that iron inhibits hydration or dissolution of guar but accelerates chain scission of fully hydrated guar when solutions are heated in an autoclave at 121 °C. The observation that Fe^{2+} did not exhibit the same effect suggests that Fe^{3+}, a strong oxidant, is participating in a redox process that leads to the concomitant cleavage of the guar and formation of Fe^{2+}. Additional work will be required to confirm that the presence of iron leads to scission of the polysaccharide chains. When both iron and magnesium are present, the magnesium inhibits the effect of iron, suggesting that magnesium hydroxide provides an alternate surface for adsorption of the ferric hydroxide and/or FeO(OH) particles.

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References and Notes

(1) Goldstein, A. M.; Alter, E. N. In *Industrial Gums. Polysaccharides and Their Derivatives*; Whistler, R. L., Ed.; Academic Press: New York, 1959; p 321.
(2) Cheng, Y.; Brown, K. M.; Prud'homme, R. K. *Biomacromolecules* **2002**, *3*, 456.
(3) Goel, N.; Shah, S. N.; Yuan, W.-L.; O'Rear, E. A. *J Appl. Polym. Sci.* **2001**, *82*, 2978.
(4) Rayment, P.; Ross-Murphy, S. B.; Ellis, P. R. *Carbohydr. Polym.* **2000**, *43*, 1.
(5) Wang, Q.; Ellis, P. R.; Ross-Murphy, S. B. *Carbohydr. Polym.* **2002**, *49*, 131.
(6) Debon, S. J. J.; Tester, R. F. *Food Chem.* **2001**, *73*, 401.

(7) Picout, D. R.; Ross-Murphy, S. B.; Errington, N.; Harding, S. E. *Biomacromolecules* **2001**, *2*, 1301.

(8) Kök, M. S.; Hill, S. E.; Mitchell, J. R. *Food Hydrocolloids* **1999**, *13*, 535.

(9) Wang, Q.; Ellis, P. R.; Ross-Murphy, S. B. *Food Hydrocolloids* **2000**, *14*, 129.

(10) Wang, Q.; Wood, P. J.; Cui, W.; Ross-Murphy, S. B. *Carbohydr. Polym.* **2001**, *45*, 355.

(11) Bradley, T. D.; Ball, A.; Harding, S. E.; Mitchell, J. R. *Carbohydr. Polym.* **1989**, *10*, 205.

(12) Whitfield, D. M.; Stojkovski, S.; Sarkar, B. *Coord. Chem. Rev.* **1993**, *122*, 171.

(13) Lynn, J. D.; Nasr-El-Din, H. A. *J. Pet. Sci. Eng.* **1998**, *21*, 179.

(14) Nayak, B. R.; Singh, R. P. *Polym. Int.* **2001**, *50*, 875.

(15) Etemadi, O.; Petrisor, I. G.; Kim, D.; Wan, M.-W.; Yen, T. F. *Soil Sedimentation Contamination* **2003**, *12*, 647.

(16) Sudhakar, V.; Singhal, R. S.; Kulkarni, P. R. *Food Hydrocolloids* **1996**, *10*, 329.

(17) Miyoshi, E.; Nishinari, K. *Colloid Polym. Sci.* **1999**, *277*, 727.

(18) Gittings, M. R.; Cipelletti, L.; Trappe, V.; Weitz, D. A.; In, M.; Lal, J. *J. Phys. Chem. A* **2001**, *105*, 9310.

(19) Lai, L. S.; Chao, S. J. *J. Food Sci.* **2000**, *65*, 954.

(20) Dea, I. C. M.; Morrison, A. In *Advances in Carbohydrate Chemistry and Biochemistry*; Tipson, R. S., Horton, D., Eds.; Academic Press: New York, 1975; Vol. 31, p 241.

(21) Rendelman Jr., J. A. *Adv. Carbohydr. Chem.* **1966**, *21*, 209.

(22) Angyal, S. *Adv. Carbohydr. Chem. Biochem.* **1989**, *47*, 1.

(23) Coe, E. M.; Bereman, R. D.; Monte, W. T. *J. Inorg. Biochem.* **1995**, *60*, 149.

(24) Coe, E. M.; Bowen, L. H.; Speer, J. A.; Wang, Z.; Sayers, D. E.; Bereman, R. D. *J. Inorg. Biochem.* **1995**, *58*, 269.

(25) Jones, F.; Cölfen, H.; Antonietti, M. *Colloid Polym. Sci.* **2000**, *278*, 491.

(26) Bhatia, S. C.; Ravi, N. *Biomacromolecules* **2000**, *1*, 413.

(27) Bruke, A.; Yilmaz, E.; Hasirci, N.; Yilmaz, O. *J. Appl. Polym. Sci.* **2002**, *84*, 1185.

(28) Huheey, J. E. *Química Inorgánica*; 2nd ed.; Harla: Mexico, D. F., 1981; p 77.

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