Influence of Pressure on Boron Cross-Linked Polymer Gels

Michael D. Parris,[†] Bruce A. MacKay,[†] Jerome W. Rathke,*[,‡] Robert J. Klingler,[‡] and Rex E. Gerald II[‡]

Schlumberger Technology Corporation, Stimulation Fluids Engineering, 110 Schlumberger Drive, Sugar Land, Texas 77478, and Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

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ABSTRACT: Using steady-shear rheometry in combination with high-pressure ^{11}B nuclear magnetic resonance spectroscopy (^{11}B NMR), we have found that gels formed from water-soluble polymers containing vicinal hydroxyl groups cross-linked with various boron-containing compounds undergo significant structural changes that result in a pronounced loss of viscosity when placed under pressure. Importantly, gels from other cross-linking agents tested, including Ti(IV) and Zr(IV), did not show this loss in viscosity. The experimental study probed pressure-induced changes to both galactomannan and polyvinyl alcohol (PVA) gels cross-linked with either aryl boronic acids or alkali metal boron-containing salts using pressure conditions that ranged from atmospheric to 680 bar and temperatures that ranged from 20 to 65 °C. Significantly, the pressure-induced losses in viscosity and, to a somewhat lesser extent, the concomitant pressure-induced ^{11}B NMR spectral changes were found to be reversed upon lowering the pressure.

Introduction

Guar is a high-molecular weight, water-soluble galactomannan polysaccharide widely used in the petroleum and gas industries to thicken aqueous solutions for hydraulically fracturing hydrocarbon bearing rock formations.[1,2] To achieve the required thickening with a minimal amount of guar, a cross-linking agent (frequently, borax) is added to greatly increase the viscosity of the fluid. The cross-linking process for galactomannans and a similarly binding polymer, PVA, with boron compounds has been extensively studied and involves intermolecular binding of vicinal hydroxyl groups on the polymers via boronic ester formation.[3−8] Similar chemical approaches with much higher boron content have been used to design porous solids,[9,10] some of which exhibit the self-repairing behavior[11] characteristic of the relatively shear-insensitive borate−guar system.

In the hydraulic fracturing process, the gel formed with guar, cross-linking agent, and water is used to suspend a proppant (typically smaller mesh sand and man-made ceramics) while it is pumped at high pressure into the hydrocarbon bearing zone of an oil or gas well. The pressure must be sufficient to fracture the rock and thereby allow penetration of the proppant and gel mixture into the fracture and propagate the fracture for a distance away from the drilled wellbore into the hydrocarbon-bearing formation. After the guar is degraded chemically or thermally and flushed from the proppant-packed area, the pathway connecting the treated formation and the wellbore is much improved, which allows increased hydrocarbon production at higher flow rates as compared to untreated areas. Additionally, the productive face of the fracture is well beyond the near-wellbore area, which is often “damaged” or flow-impaired with drilling fluids and fine particles of rock and clay.

Of key importance in the hydraulic fracturing process, the cross-linked guar must have sufficient viscosity during the high-pressure pumping step to create, propagate, and maintain adequate fracture width as well as to suspend the proppant and prevent it from settling prior to and while penetrating the fractured rock formation.

In this Article, we report the surprising result that guar and related vicinal-diol model compounds can lose a substantial portion of the viscosity increase afforded by boron cross-linking agents, when pressurized near the kilobar region that is used in the hydraulic fracturing process. Importantly, the large changes in viscosity reported here are distinct from the much smaller changes in viscosity that occur as a result of the weakening of hydrogen bonds under pressure in aqueous systems and have been measured for uncross-linked PVA gels at pressures comparable to and, in some cases, considerably higher than those used here.[12]

Experimental Section

Materials. Two high molecular weight PVAs manufactured by Celanese were used: Celvol 165SF, >99.3% hydrolyzed and Celvol 540S, 87% hydrolyzed, approximate molecular weight, 125 000.

Guar and the guar derivatives, hydroxypropyl guar (HPG) and carboxymethylhydroxypropyl guar (CMHPG), were supplied by Economy Polymers, Hercules, and Rhodia.

Sodium tetraborate decahydrate (borax) was supplied by Rio-Tinto/US Borax, and 1,4-benzenediboronic acid was supplied by Sigma-Aldrich. The titanium and zirconium-containing cross-linker complexes were supplied by Benchmark Research and Technology, Inc.

Rheometry. Steady-shear measurements were largely carried out on a Grace M7500 high pressure rheometer. This instrument, designed for pressures to 2380 bar and temperatures to 260 °C, employs a narrow-gap, Couette geometry using a bob that has a diameter of 3.45 cm and a height of 3.80 cm, with the rotating cup having an internal diameter of 3.68 cm.

A second, capillary-tube, rheometer was constructed using stainless steel tubing connected between two ISCO 500D syringe pumps. The tubing inner diameter was nominally 1.75 mm, and the pressure drop over 3.05 m was measured using a Rosemount transducer with a digital readout. During measurements, the controller maintained the delivery pump in constant rate mode and the receiving pump in constant pressure mode.

Guar solutions for rheometry were prepared by adding guar powder to 500 mL of water (or water + salt), which is being stirred in a 1 L Waring blender cup at approximately 2000 rpm. This mixture is allowed to remain stirring at that rate for approximately 30 min, at which point the polymer is fully hydrated. Similarly, PVA solutions for rheometric measurements were prepared by

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* Corresponding author. E-mail: rathke@anl.gov.
[†] Schlumberger Technology Corp.
[‡] Argonne National Laboratory.

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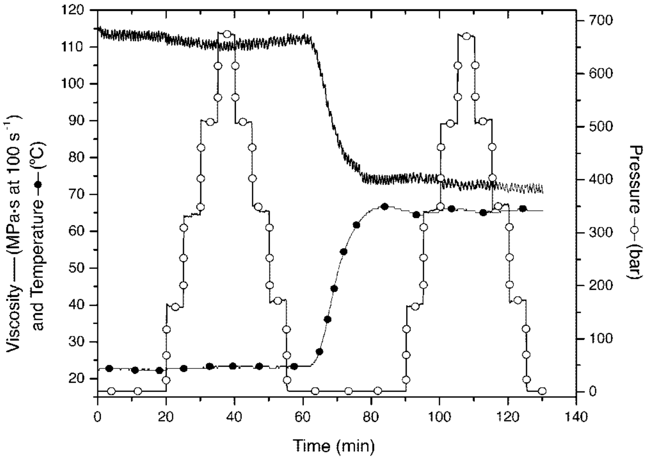

Figure 1. Viscosity of 0.6% (wt) guar solution in deionized water at neutral pH. Pressure stepped from atmospheric to 680 bar and back to atmospheric at both 21 °C (left side) and 65 °C (right side).

adding the powdered or granular polymer to 400 mL of water being stirred at approximately 1000 rpm with an overhead mixer with a three-blade impeller. After the polymer was dispersed, the solution with unhydrated polymer was transferred to a 1 L plastic jar, and placed horizontally and rotated in a roller oven at ambient temperature overnight, which provided a clear viscous solution.

^{11}B NMR Spectroscopy. High-pressure ^{11}B NMR spectra of borax in water and boron containing cross-linked PVA gels were measured at 96.4 MHz using a General Electric model GN 300/89 NMR spectrometer equipped with a toroid cavity pressure probe built in-house.[13,14] The pressure vessel portion of the probe was machined from Be−Cu alloy (Brush-Wellman alloy 25) and had an internal volume of 10 mL. The cylindrical toroid cavity used in the experiments was machined from copper and had an internal diameter and height of 12 mm. Pressures were monitored using a strain-gauge pressure transducer (Omega, model PX302-10KGV) and are believed to be accurate to within 1%. Pressures were controlled by means of an ISCO model 100DM high-pressure syringe pump.

Borate cross-linked PVA solutions for NMR spectral analysis were prepared by mixing equal volumes of two aqueous solutions, one containing Celvol 165SF (>99.3% hydrolyzed) (2.00 g in 50.0 mL of distilled water) and the other containing sodium tetraborate decahydrate (0.1024 g in 50.0 mL of distilled water). Preparation of the Celvol 165SF solution required heating with stirring at 100 °C for 15 min to form a clear liquid. Equal volumes of these solutions when mixed yield a viscous but pourable fluid having the approximate composition: boron, 116 ppm, Celvol 165SF, 2.0%.

The NMR pressure vessel was loaded with 3.5 mL of each solution and shaken to ensure complete mixing. With this amount of liquid, the detector within the pressure vessel was completely submerged in cross-linked polymer to a depth of about 6 mm. The vessel was pressurized using nitrogen gas delivered from the high-pressure syringe pump. ^{11}B NMR data, 20 000 pulses at 96.4 MHz, were acquired at various pressures using spectral window size, 5000 Hz, acquisition time, 0.1024 s, and pulse width, 26 μs. ^{11}B NMR chemical shifts are relative to $Et_2O \cdot BF_3 = 0.0$ ppm, with positive shifts at higher frequencies.

Results and Discusssion

Rheology. The viscosity measurements were carried out between 20 and 65 °C, and at atmospheric and higher pressures up to 680 bar. To establish a baseline, tests were conducted with a polymer solution prepared in deionized water. Figure 1 shows the expected thermal thinning with increasing temperature, and the small change in viscosity (leading to slight curvature in the plots) probably stemming from the small pressure dependence of viscosity for hydrogen-bonded materials in water.[12,15] Similarly, uncross-linked polymer solutions of PVA and the derivatized guars HPG and CMHPG showed, at most, only this slight hydrogen-bonding-related viscosity change with applied pressure.

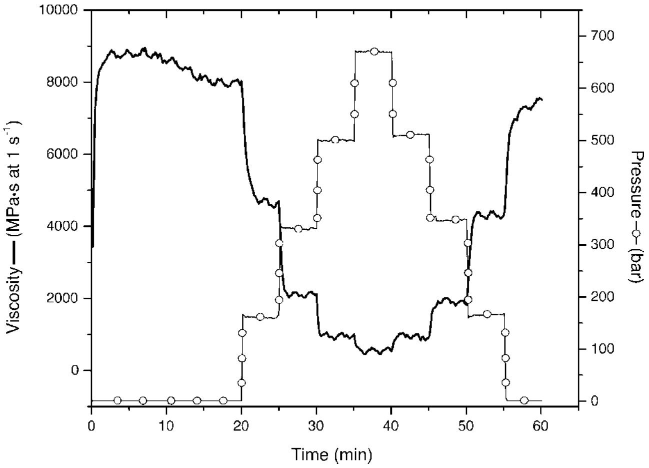

Figure 2. Viscosity of 0.3% (wt) guar solution cross-linked with a 5% (wt) solution of borax decahydrate at 30 °C and pH 9.0. Boron concentration in gel is 60 ppm.

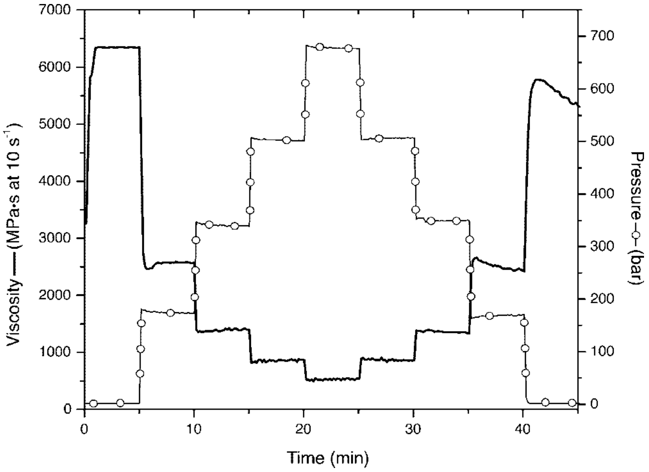

Figure 3. Viscosity of 2% (wt) PVA solution (Celvol 540S) cross-linked with a 5% (wt) solution of borax decahydrate at 22 °C and pH 8.8. Boron concentration in gel is 116 ppm.

However, when a guar solution was cross-linked with monoborate, a rapid viscosity loss was observed with increasing pressure, which was subsequently regained when the pressure was removed (Figure 2).

Figure 3 illustrates that this response to pressure also occurred when PVA was cross-linked with boron.

The pressure effect observed with monoborate also occurs with the related boronic ester, 1,4-benzenediboronic acid. Figure 4 shows large and reversible pressure-induced viscosity losses on gels that are formed by cross-linking guar with 1,4-benzenediboronic acid in which the initial extent of cross-linking was varied by means of pH (making use of the fact that boronic ester formation increases with pH).[7] Large viscosity losses occurred for both the more extensively cross-linked solution at pH 11.2 and the less extensively cross-linked solution at pH 9.5.

Because guar and guar derivatives are known to cross-link with group IV metals,[16] the viscosity of several such gels was tested while changing pressure. As shown in Figures 5 (titanium cross-linker) and Figure 6 (zirconium cross-linker), neither the titanium- nor the zirconium-cross-linked gel showed large

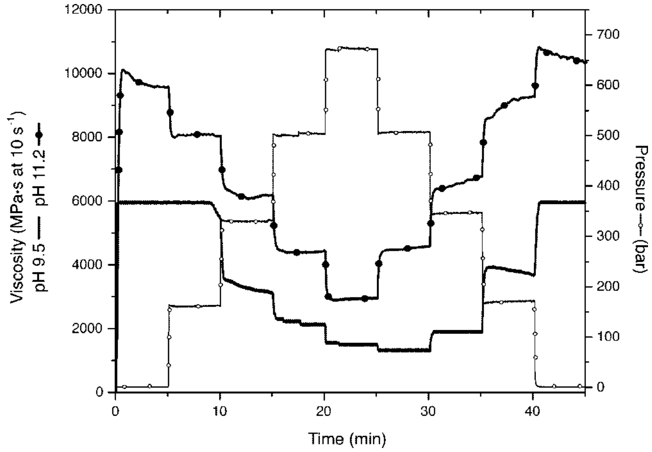

Figure 4. Viscosity of 0.36% (wt) guar solution cross-linked with 1,4-benzenediboronic acid at 25 °C at pH 9.5 and pH 11.2 while pressure is stepped from atmospheric to 680 bar and back to atmospheric. Boron concentration in gel is 67 ppm.

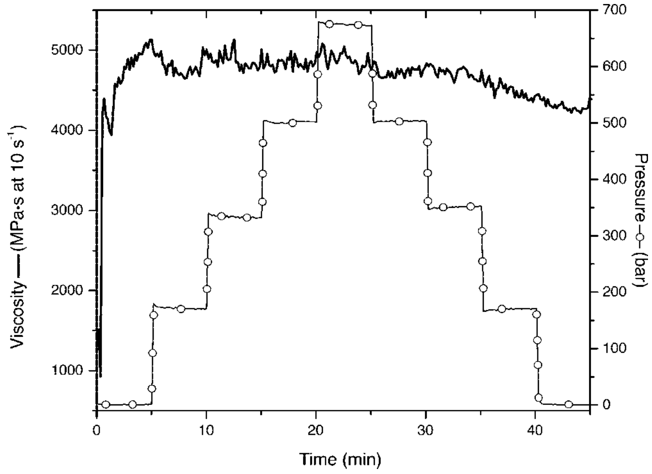

Figure 5. Viscosity of 0.3% (wt) hydroxypropylguar solution cross-linked with a Ti−isopropoxide complex in aqueous 2% KCl at 21 °C at pH 5.4 while pressure is stepped from atmospheric to 680 bar and back to atmospheric. Titanium concentration in gel is 53 ppm.

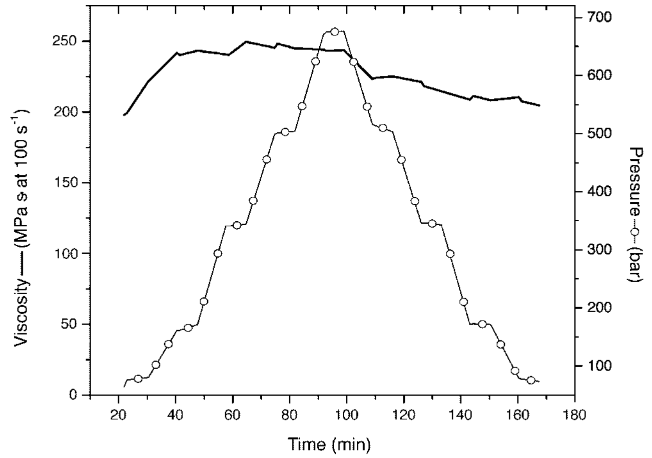

Figure 6. Viscosity of 0.3% (wt) carboxymethylhydroxypropylguar (CMHPG) solution cross-linked with a Zr−lactate complex in deionized water at 65 °C and pH 9.3 while pressure is stepped from atmospheric to 680 bar and back to atmospheric. Zirconium concentration in gel is 34 ppm.

responses to pressure. Note that the difference in viscosity between these two experiments is a result of elevated experimental temperature and shear rate in the case of the zirconium-cross-linked fluid.

^{11}B NMR Spectroscopy. To determine if the pressure-induced viscosity changes stem from structural variations large enough to be detected spectroscopically, ^{11}B NMR spectra were recorded at pressures varied from 1.0 to 667 bar at 25 °C. A typical boron spectrum measured in the pressure probe is shown in Figure 7. Consistent with the earlier work of Sinton[3] and Pezron and Liebler et al.,[4] the spectrum consists of a “free borate” resonance near 18 ppm comprising rapidly interconverted signals from $B(OH)_4^-$ and $B(OH)_3$, and two partially overlapping signals near 1.0 ppm, one sharper and one broader, with the broader signal at slightly higher frequency. Our ambient pressure results using least-squares fitting with Lorentzian lines to deconvolute the overlapped resonances, as shown in Figure 7, are comparable to those of the earlier workers. Although Sinton suggested that the two signals near 1.0 ppm might arise from intra- and intermolecular coordination of the PVA chains with borate, the later paper by Pezron and Liebler et al.[4] showed that the narrow signal is due to borate with four organic groups attached, while the broad signal is due to borate with two attached organic groups. Thus, the measured areas of the three observable ^{11}B NMR resonances can be used as an important method to monitor the breakage of the B−O−C bonds that are involved in cross-linking the PVA.

A stacked plot of the ^{11}B NMR spectra at varied pressure is shown in Figure 8. As can be seen from this figure, the pressure-induced changes are not large. The free borate signal sharpens and shifts to lower frequency at increased pressure, while the signals from borate with two- and four-attached organic groups remain at nearly constant frequency as the pressure is increased.

To quantify spectral changes occurring during the pressurization process, areas, chemical shifts, and linewidths of the ^{11}B NMR signals were determined by least-squares Lorentzian line-fitting analysis and are shown in Table 1.

Figure 9 shows a plot of relative signal intensity (in area %) versus pressure for the sharp resonance near 1.0 ppm stemming from borate with four organic groups attached. This plot shows a nearly linear decrease of the borate signal stemming from borate with four attached organic groups and indicates that B−O−C bonds are broken as a result of pressurization. The plot also indicates that to a considerable extent, at least, the process is reversed when the pressure is lowered.

An important issue concerning the breakage of B−O−C bonds in borate with four organic groups attached is whether the product ends up as “free borate” or borate with only two organic groups attached. We note here that extensive prior work involving esterification of borates in aqueous systems shows that these choices are the only thermodynamically favorable ones at atmospheric pressure.[3,4] In the interpretation of our results, in view of the fact that we do not see new ^{11}B NMR signals in the spectra, we assume that pressure does not greatly favor other coordination types that differ from what has been observed at ambient pressure. Perhaps stemming from the considerable broadness of the unsymmetrically substituted borate signal for two attached organic groups, the data of Table 1 are too scattered to determine whether the diorganic-substituted species is increasing with pressure at the expense of the four organic group containing species. To avoid problems associated with Lorentzian fitting of the broad signal, the NMR standard integration method was used to integrate the “free borate” signal and the combined signal for the di- and tetra-organic-substituted borate. Figure 10 shows the result of this integration, demonstrating that the “free borate signal” remains essentially constant at elevated pressure. Thus, with the aforementioned assumption that ambient pressure species are also the only ones favored at high pressure, the result indicates that borate with four organic

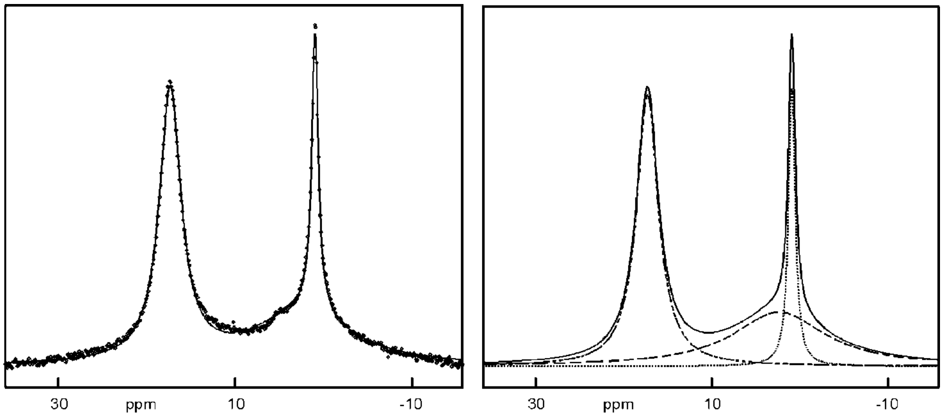

Figure 7. A typical 96.4 MHz ^{11}B NMR spectrum for the PVA gel containing boron, 116 ppm, Celvol 165SF, 2.0% at ambient conditions showing partially overlapped signals from "free borate" and borate bound to two and four alkoxy groups. Also shown is the least-squares fit of the experimental data to three overlapping Lorentzian lines (left) whose composition is shown (right); free borate (— - - —), borate bound to two alkoxy groups (— — —), borate bound to four alkoxy groups (• • •).

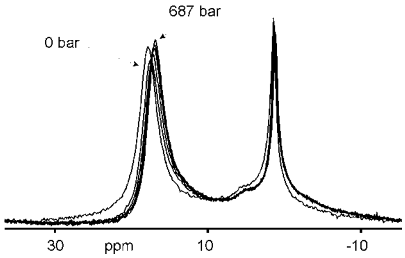

Figure 8. Stacked plot of 96.4 MHz ^{11}B NMR spectra of the cross-linked PVA gel containing boron, 116 ppm, Celvol 165SF, 2.0% at varied pressure (0, 137, 268, 401, 525, and 659 bar).

groups is converted mainly to borate with two organic groups while "free borate" remains relatively constant. This observation seems chemically reasonable in that the more sterically constrained borate with four attached organic groups (formed by esterification with either vicinal hydroxyl groups from the same polymeric chain or from a second polymeric chain) seems far more likely to be affected by pressure than the relatively less sterically constrained borate bound by esterification to vicinal hydroxyl groups attached to one chain.

We also note here that the shift of the "free borate" signal to lower frequencies at higher pressures evident in the stacked plot in Figure 8 and quantified in Table 1 is consistent with a small increase in the ratio of $B(OH)_4^-/B(OH)_3$.[3] This amount can be estimated by Sinton's data,[3] which showed that the chemical shift of the "free boron" signal, δ_f, and the chemical shifts for pure $B(OH)_3$, $\delta_B = 19.3$ ppm, and pure $B(OH)_4^-$, $\delta_{B^-} = 1.6$ ppm, are related to the mole fractions of these species, X_B and X_{B^-}, by eq 1.

$$\delta_f = X_B\delta_B + X_{B^-}\delta_{B^-} \tag{1}$$

Using this equation (and noting that $X_{B^-} = 1 - X_B$), it can be shown that the "free boron" chemical shifts in Table 1 of 17.90 ppm at ambient pressure and 17.13 ppm at 659 bar correspond to an increase in $[B(OH)_4^-]$ by about 4%.

There are two possible explanations for this change. First, there could be an increase in the equilibrium constant for the dissociation of boric acid in eq 2.

$$B(OH)_3 + H_2O = H^+ + B(OH)_4^- \tag{2}$$

Atkinson et al. showed that boric acid does become more acidic and the equilibrium in eq 2 shifts to the right at higher pressures.[17] However, the predicted change in the equilibrium in eq 1 is too small to account for the change in the "free boron" resonance in Table 1 for the reasons indicated below. Thus, interpolation of Atkinson's data shows that for aqueous solutions of boric acid the equilibrium constant for eq 1 at 25 °C increases from 5.6×10^{-10} at 1.0 ambient pressure to 11×10^{-10} at 659 bar, the highest pressure used in Table 1. For solutions with pH near 9.0 and total boron concentrations near 0.01−0.4 M used here, this small, less than a factor of 2, increase in acid dissociation constant would lead to an extremely small increase, on the order of 10^{-9} M, in $[B(OH)_4^-]$ and a correspondingly small decrease in $[B(OH)_3)]$. These amounts are much smaller than the amount predicted from the pressure-induced chemical shift changes for the "free boron" signal in Table 1. Consistent with these calculations, pressurization of a borate solution in pure water (i.e., in the absence of PVA) showed no significant ^{11}B NMR spectral changes at the highest pressures used in this research. Thus, Figure 11 shows the superposition of 11 ^{11}B NMR spectra measured at 1000 psi increments from 0 to 10 000 psig pressure (i.e., from 0 to 680 bar gauge) for a solution of borax (0.1 M) in pure water. This figure shows no significant pressure-induced change in chemical shift for the monoborate/boric acid signal near 9 ppm or, for that matter, in the signals for the polyborate species near 13 and 2 ppm. Comparison of Figures 8 and 10 indicates that a pressure-induced change in the chemical shift for the "free borate" resonance in Figure 8 must be associated with an interaction with the PVA complexing agent. It should be noted that Sinton has shown[3] that the polyborate signals present at the high concentration used in Figure 11 are completely hydrolyzed to the monomeric species (monoborate and boric acid) at boron concentrations below about 0.02 M used in our cross-linking experiments. In addition, he showed that the relatively sharp monoborate/boric acid signal seen at high concentrations of boron near 0.4 M broadens and shifts to higher frequencies, at lower concentrations, consistent with the "free boron" signal in our cross-linked PVA solutions.

A second explanation for an increase in the $B(OH)_4^-$ concentration as evidenced by the change in the ^{11}B NMR chemical shift for the "free borate" resonance is that a small amount of the coordinated boron ester could be completely hydrolyzed, resulting in free $B(OH)_4^-$. The predicted 4% change in $B(OH)_4^-$ concentration is too small to be reliably detected by the NMR integration method, Figure 10. The ^{11}B NMR chemical shift is apparently a more sensitive measure of the $[B(OH)_4^-]$.

Conclusions

This research shows that gels formed from guar, other galactomannans, and PVA by cross-linking with various boron-

Table 1. Relative Areas of the "Free Borate" Signal and the Two Overlapping Borate Signals Due to Coordination of Two and Four Organic Groups as a Function of Pressure, Measured with (a) Increasing Pressure and (b) Decreasing Pressure[a]

pressure, bar (guage)	"free borate" with 0 alkoxy groups area, %	chemical shift, ppm	linewidth, Hz	borate with 4 alkoxygroups area, %	chemical shift, ppm	linewidth, Hz	borate with 2 alkoxygroups area,%	chemical shift, ppm	linewidth, Hz
0	46.2	17.90	287	14.4	1.52	87	39.4	2.97	1224
137 (a)	48.1	17.72	286	13.7	1.47	81	38.2	2.69	1136
268 (a)	48.5	17.45	281	13.0	1.36	80	38.4	2.53	1123
401 (a)	49.3	17.28	275	12.8	1.31	80	37.9	2.65	1100
525 (a)	48.5	17.25	267	12.3	1.41	80	39.2	2.69	1148
659 (a)	48.7	17.13	261	12.0	1.40	80	39.3	2.73	1130
153 (b)	48.3	18.01	253	13.1	1.38	82	38.7	3.10	1244
0 (b)	48.6	17.07	273	14.8	2.06	104	36.6	4.24	1238

[a] The areas were determined using least-squares Lorentzian fits for the 96.4 MHz ^{11}B NMR spectra. The data are for the cross-linked PVA gel containing boron, 116 ppm, Celvol 165SF, 2.0%.

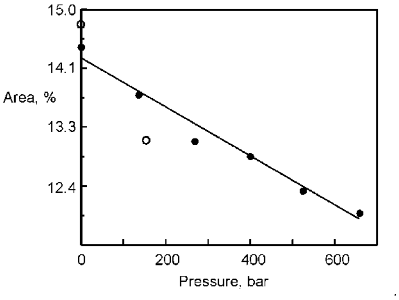

Figure 9. Plot showing the decrease in relative signal intensity (area %) as a function pressure for the sharp ^{11}B NMR resonance near 1.0 ppm stemming from borate with four organic groups attached using least-squares Lorentzian line-fitting analysis. The data are for the cross-linked PVA gel containing boron, 116 ppm, Celvol 165SF, 2.0%, and were recorded at increasing (●) and decreasing (○) pressure.

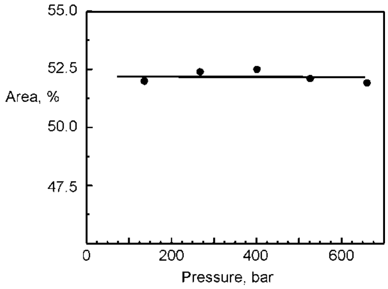

Figure 10. Signal intensity (area %) of the "free borate" ^{11}B NMR signal versus the total signal at elevated pressures obtained by standard NMR signal integration methods. The data are for the cross-linked PVA gel containing boron, 116 ppm, Celvol 165SF, 2.0%.

containing compounds undergo a pronounced loss of viscosity when placed under pressure. The viscosity loss at pressures below 1 kbar is essentially all of that afforded by addition of the boron containing cross-linking agent and is reversed upon lowering the pressure. Concomitant structural changes that occur in these systems are large enough to be probed by high-pressure ^{11}B NMR spectroscopy and result in changes (albeit small) in line width, chemical shift, and relative signal intensities in the spectra. The ^{11}B NMR signal integration and Lorentzian line fitting analysis show that at high pressure, B−O−C bond breakage occurs, and borate coordinated to four organic groups is converted mainly to borate binding only two organic groups.

In addition, the pressure-induced ^{11}B NMR chemical shift changes for the "free boron" signal in the cross-linked PVA solutions suggest that a small amount, approximately 4%, of the borate ester is completely hydrolyzed, resulting in an increase in the $B(OH)_4^-$ concentration. An alternative explanation based on the previously known pressure-induced increase in the acidity of boric acid in pure water[14] was ruled out due the small magnitude in the calculated and observed change in the ^{11}B NMR chemical shift with pressure in the absence of the PVA complexing agent.

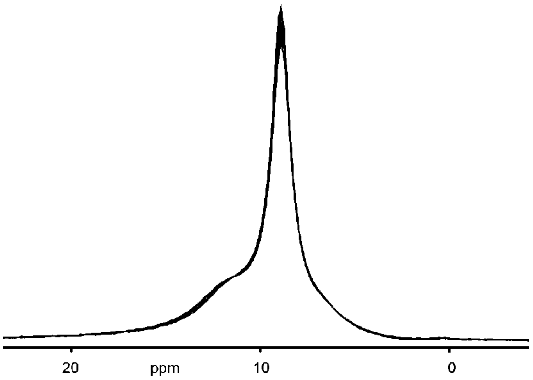

Figure 11. Superposition of 11 96.4 MHz ^{11}B NMR spectra measured at 1000 psi increments from 0 to 10 000 psig (0−680 bar, gauge) for an aqueous solution of borax, 0.1 M.

Pressure effects on the ^{11}B NMR spectra were observed to be, to a considerable extent, reversible. However, we note here that due to the possibility of slow chemical changes occurring in the pressurization and depressurization processes, accurate determinations of true reversibly for the NMR spectra would require time-dependent studies that were not performed in this work. In addition, in the absence of such studies, it is not possible to state in this work that we have captured the full extent of the changes that might occur in the spectra after longer times at pressure.

Significantly, gels from other cross-linking agents tested, including Ti(IV) and Zr(IV), did not show this major loss in viscosity. It seems relevant that borate cross-links are considerably more labile than those produced from Ti(IV) and Zr(IV). In addition, unlike these other two systems, borate imparts a negative charge to the chains on which it is bound. Because of the presence of charged polymer chains, borate cross-linked galactomannan and PVA polymer gels belong to a class of materials known as polyelectrolyte hydrogels.[18] The viscosities of these materials depend not only on the extent of cross-linking, but also upon complex interactions involving both hydrogen bonding and electrostatic forces, including screening effects, associated with charged species (in the boron system, the bound borate anion and its counterion).[18]

It should also be noted that borate cross-linked polymers are unusual in their response to mechanical shear. Unlike polymers cross-linked with Al, Sb, Cr, and the Ti (IV) and Zr(IV) cross-linking agents tested here, polymers that are cross-linked with borate yield solutions with high viscosity dependence on mechanical shear.[1,19] We suspect that this viscosity dependence on mechanical shear is probably related to the pressure dependence observed here for borate, and the lack of such a pressure effect for Ti(IV) and Zr(IV).

Importantly, the large changes in viscosity reported here are distinct from the much smaller changes in viscosity that occur as a result of the weakening of hydrogen bonds under pressure in aqueous systems and have been measured for uncross-linked PVA gels at pressures comparable to and, in some cases, considerably higher than those used here.[12] The small change in viscosity stemming from the pressure effect on hydrogen bonds in the uncross-linked PVA system (typically 5% or 10% of the viscosity of the uncross-linked PVA gel at 1 kbar) might only be evident in our viscosity plots as small changes in the baseline or lost entirely in the noise.

In future research on borate cross-linked systems, we hope to determine the root cause of B−O−C bond breakage in the system and to determine if this factor alone or perhaps more likely in combination with other factors, including hydrogen bonding and electrostatic forces, is responsible for the large pressure-dependent deviscosification.

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