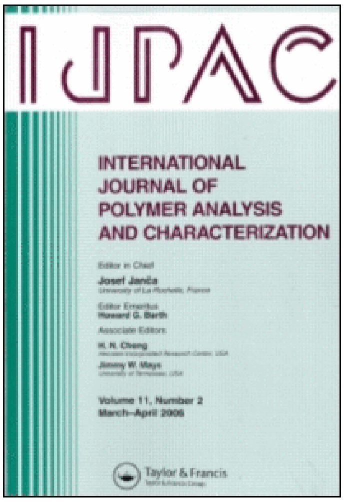

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Monitoring the Cross-Linking of a HPAm/Cr(III) Acetate Polymer Gel Using ^{1}H NMR, UV Spectrophotometry, Bottle Testing, and Rheology

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Abstract: The gelation of a polymer gel formulated at 40°C with 7500 mg/L of partly hydrolyzed polyacrylamide (HPAm) and 3000 mg/L of Cr(III) acetate 50% active was monitored for 72 h using ^{1}H nuclear magnetic resonance (NMR) techniques, oscillatory rheology, bottle testing, and UV spectrophotometry.

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During the first 5 h, ^{1}H NMR techniques detected changes in the polymer gel signal intensity and transverse relaxation that may be related to the rheological properties of the HPAm/Cr(III) acetate polymer gels. Bottle testing and UV spectrophotometry detected additional changes during 30 and 72 h respectively. Monitoring of the gelation process using these techniques is presented here.

Keywords: Bottle testing; Cr(III) acetate; HPAm; MRI; ^{1}H NMR; Oscillatory rheology; Polymer gels; UV spectrophotometry

INTRODUCTION

Nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) techniques have been used for material characterization.[1–7] Polymers such as polypropylene, nylon, rubber,[4] polyethylene, polyvinyl chloride,[5] and acrylamide[7] have been studied using NMR techniques. However, limited information is available regarding the NMR properties of partly hydrolyzed polyacrylamide chromium(III) acetate (HPAm/Cr(III) acetate) polymer gels.[8–10] HPAm/Cr(III) acetate polymer gels are commonly used in enhanced oil recovery (EOR) and conformance-improvement (sweep-improvement and water-shutoff) methods, and their application has become more important as oil reserves become depleted worldwide.[8,11] Oscillatory rheology and bottle testing[9,12–14] are conventional methods to characterize HPAm/Cr(III) acetate polymer gels. A new approach to characterize these polymer gels using NMR techniques has been proposed by the EOR Laboratory at the University of New Brunswick (UNB).[10] This approach aims to relate the gelation time and storage modulus (obtained from rheological measurements) to the transverse relaxation time (T_2) changes of HPAm/Cr(III) acetate polymer gels obtained from NMR measurements using CPMG (Carr, Purcell, Meiboom, and Gill) sequences. HPAm/Cr(III) acetate polymer gels are suitable for ^{1}H NMR studies because they have high water concentrations (up to 99.7 wt%). Thus, the objectives of this work are (1) to obtain the gelation time using oscillatory rheology; (2) to monitor the cross-linking of a polymer gel using bottle testing; (3) to observe the changes that the polymer gel undergoes as a function of time using UV spectrophotometry; (4) to evaluate the applicability of 1-D and 2-D spin-echo MRI techniques to characterize HPAm/Cr(III) acetate polymer gels; (5) to assess the applicability of conventional ^{1}H NMR to characterize HPAm/Cr(III) acetate polymer gels; and (6) to determine ^{1}H NMR T_2 relaxation times during the cross-linking of HPAm/Cr(III) acetate polymer gel. For these purposes, a polymer gel was formed at 40°C using 7500 mg/L of HPAm and 3000 mg/L of Cr(III) acetate 50% active. The following hypotheses were tested: (1) UV spectrophotometry traces the gelation process as a function of time; (2) the spin-echo MRI technique detects changes in the signal intensity as the cross-linking reaction proceeds; and (3) ^{1}H NMR detects changes in T_2 as Cr(III) acetate cross-links HPAm. The UNB's EOR Laboratory has determined the baseline behavior of the ^{1}H NMR T_2 of Cr(III) acetate 50% active in polymer-free solutions. Hence, the results from this study allow for comparison between the behavior of the baseline and the polymer gel at 40°C and set the preliminary bases for developing an NMR-based methodology for characterizing HPAm/Cr(III) acetate polymer gels.

Oscillatory rheology tests (also referred to as dynamic mechanical analysis)[15] are used to quantitatively study the viscoelastic properties of HPAm/Cr(III) acetate polymer gels. Yet oscillatory rheology testing is an invasive method that has been reported to cause some disruption of the polymer gel network and cannot characterize polymer gels inside porous media.[9,16–18] Oscillatory shear tests using small amplitude and constant frequency are recommended to monitor the cross-linking reaction of HPAm/Cr(III) acetate.[19,20] For these polymer gel systems, the viscoelastic properties are studied via the elastic response (storage modulus or G'), which increases as the polymer concentration and aging time increase, and the viscous response (loss modulus or G''), which remains almost constant. Additionally, oscillatory rheology tests provide information on complex viscosity ($|\eta^*| = (G'^2 + G''^2)/\text{angular frequency}^2)^{1/2}$ that can be used to characterize polymer gel systems.[8,9,12] More details on oscillatory rheology measurements can be found in the work of Ferry[21] and Winter.[22] Bottle testing using Sydansk's gel-strength code[14] is a noninvasive and nondestructive method that has been used effectively in the oil industry to monitor the gelation process of HPAm/Cr(III) acetate.[9,13,14,19] Bottle testing is a cost-effective and straightforward technique to measure gelation rate and gel strength semi-quantitatively, and it allows for screening a large number of samples faster than rheological techniques.[14] However, bottle testing is measured by the naked eye, and the results could be inconsistent and mistakenly interpreted; thus, the data obtained cannot be used for numerical modeling of polymer gels. NMR techniques have the potential to provide accurate information on the gelation processes because they combine the exacting quantitative feature of rheology with the noninvasive and nondestructive features of bottle testing. Furthermore, NMR techniques allow for screening numerous samples concurrently and can be applied in many porous media.[4,23,24] In the oil industry, there are two important parameters in using HPAm/Cr(III) acetate polymer gels: gelation time and gel strength. Overestimation of the gelation time can cause premature gelation at the well bore, while underestimation can lead to insufficient shut-in times.[25] Gel strength is an indication of the maximum drawdown that polymer gels can sustain. Therefore, accurate characterization of HPAm/Cr(III) acetate provides the oil industry with the information needed to properly assess the performance of the polymer gel treatment.[8,9,26,27] Eriksen et al.[28] define the gelation time as the time needed for the gel-forming solution to reach twice its initial viscosity, and Al-Muntasheri et al.[25] define gelation time as the inflection point on the viscosity-versus-time curve. Another definition is the time at which the G' and G'' curves intersect.[8,9,15,20] This last definition of gelation time is used in this work.

EXPERIMENTAL SECTION

Materials

Solvent

A solution of distilled water and Na_2SO_3 (oxygen scavenger)[29] with a concentration of 10 mg/L was used to prepare polymer and cross-linker solutions. The pH of the solvent was 7.4 at 25°C and the density was 0.9924 g/cc at 40°C.

Polymer

Partially hydrolyzed polyacrylamide (HPAm), commercially known as Alcoflood 935, was the polymer used in this study. Alcoflood 935 was supplied by Ciba Specialty Canada Inc. It has a degree of hydrolysis of about 10% and manufacturer-reported molar mass of 8×10^6–10×10^6 g/mol. The polymer solution used had an HPAm concentration of 7500 mg/L, a pH of 5.8 at 25°C, and a density of 0.9955 g/cc at 40°C.

Cross-Linker

Cr(III)acetate solution 50% active in water ($pH = 2.6$) supplied by McGean-Rohco, Inc. was the cross-linker used. The certificate of analysis reports less than 0.0001% of Cr(VI) in the Cr(III) acetate solution 50% active. A 3000 mg/L (0.3 wt% or 3000 ppm) solution of Cr(III) acetate 50% active was used to formulate the cross-linker solution, which had a pH of 3.4 at 25°C, and a density of 0.9937 g/cc at 40°C. The density of the solutions was measured using an Anton Paar density meter, model DMA 35 N.

Polymer Gel Forming Solution

The 7500 mg/L polymer solution was cross-linked using 3000 mg/L of Cr(III) acetate 50% active, which means that there were 1500 mg/L

(1500 ppm) of Cr(III) acetate, so the polymer-to-cross-linker weight ratio was 5/1. The resulting solution was referred to as HPAm/Cr(III) acetate (5/1) and had a pH of 4.6 at 25°C.

Experimental Procedures

Rheology

An Anton Paar Physica MCR 301 rheometer with concentric cylinder geometry (CC27) was used to test the polymer gel solution. The MCR 301 rheometer has a minimum torque of 0.1 microNm and a torque resolution of 0.001 microNm and applies oscillatory shear. The CC27 concentric cylinder has a cup diameter of 28.92 mm and a bob diameter of 26.66 mm. A Peltier chamber (C-PTD 200) coupled with a cover and a solvent trap was used to prevent vertical temperature gradients, reduce the influence of environmental conditions, and avoid evaporation. Time sweeps were conducted on the polymer gel forming solution at 40°C, with frequency of 1 Hz and amplitude of 5%. Inertia calibration and motor adjustment were performed before measurement. Each sample was tested three times, and the average data were plotted to observe the changes in the sample's G' and G'' as a function of time.

Bottle Testing

Characterization of the polymer gel was carried out using Sydansk's code.[14] A 30 mL amount of each sample was placed in a 60 mL flint glass widemouthed bottle with a polyvinyl-liner cap seal, Teflon tape was used to cover the bottle cap (as an additional way to prevent evaporation), and the bottle was then placed in a water bath at 40°C. Samples were monitored periodically by inverting the bottle, and according to the observation a gel code was assigned to the sample.

UV Spectrophotometry

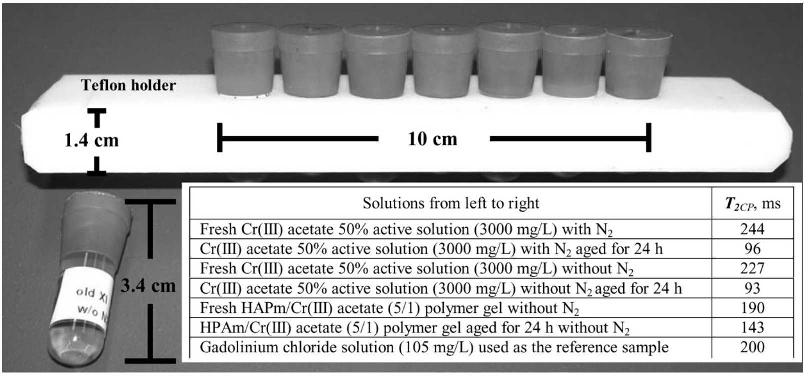
Measurements were conducted using a Spectronic GENESYS 6 UV-visible Spectrophotometer from the Thermo Electron Corporation. The spectrophotometer has an accuracy of ±1.0 nm and a repeatability of ±0.5 nm. Samples of the polymer gel were prepared and placed in 5 mL glass vials under a nitrogen atmosphere. The vials were completely filled, Teflon tape was applied around their caps to prevent evaporation, and they were kept in an oven at 40°C. A sample of solvent was used to calibrate the spectrophotometer before every set of tests. The samples were placed in cuvettes (UV grade CS-500) using disposable syringes. To prevent cross-contamination, the samples, vials, and cuvettes were not reused. Once prepared, the samples were monitored at 3 min, 5 h, 24 h, 48 h, and 72 h. Each sample was tested five times, and the average data were plotted to observe the changes in the sample's wavelength and absorbance as a function of time. In all cases, the standard deviation was small and ranged from 0 to 0.008.

Spin-Echo Magnetic Resonance Imaging

Spin-echo is an NMR technique whose maximum amplitude is a function of the transverse relaxation time (T_2) and is stimulated by the pulse sequence $90°\text{-}TE/2\text{-}180°$ (TE is the time to echo).[31] One-dimensional (1-D) and two-dimensional (2-D) spin-echo techniques were used to determine if they detect changes in signal intensity during the gelation reaction. More details on spin-echo MRI can be found in the work of Fukushima.[31] Spin-echo MRI was used to acquire 1-D spin-echo profiles (z-axis) of polymer gel and cross-linker solutions simultaneously. The measurements were conducted in a 2.4 tesla horizontal board magnet made by Nalorac Cryogenics using a Tecmag (NTNMR) Apollo MRI electronics console. Seven customized NMR vials (1.4 mL) were used. Two vials were each filled with samples of polymer gel forming solution and cross-linker solution. A third vial was filled with cross-linker solution and nitrogen was bubbled for 10 min. During this procedure, solution evaporation was not observed. These three vials were covered with a plastic cap and Teflon tape and aged for 24 h in a water bath at 40°C. After 24 h, three more vials were filled following the same procedure (except for the aging). The last vial was filled with a solution of gadolinium chloride ($GdCl_3$), which was used as the reference sample ($GdCl_3$ is commonly used as an MRI standard).

Prior to 1-D and 2-D spin-echo MRI, T_{2CP} of each sample was measured using a CP (Carr-Purcell) sequence.[31] This T_2 is referred to as T_{2CP} and governs the mono-exponential decay of the signal intensity. Figure 1 presents the T_{2CP} values of each sample. The equation that describes the signal decay of each sample is $S = S_0 e^{-t/T_{2CP}}$, where S = signal intensity (A.U), t = measuring time, and S_0 = signal at $t = 0$. The T_{2CP} values were used to select a $GdCl_3$ solution with T_{2CP} (and therefore signal intensity) within the range of the samples studied (93 to 244 ms). Thus, a solution with a $GdCl_3$ concentration of 105 mg/L was used.

The seven vials were placed in a Teflon holder (Figure 1) and then introduced in a 100 MHz birdcage probe, which has an ID of 4.6 cm and a coil length of 10 cm and is H free. The 1-D spin-echo tests were performed at 40°C using a dwell time of 12 μs, an acquisition time of 3.072 ms, a receiver gain of 150 dB, a last delay of 1 s, 256 acquisition points, and four scans. The Tau time (τ), which is the time between



Solutions from left to right	T_{2CP}, ms
Fresh Cr(III) acetate 50% active solution (3000 mg/L) with N_2	244
Cr(III) acetate 50% active solution (3000 mg/L) with N_2 aged for 24 h	96
Fresh Cr(III) acetate 50% active solution (3000 mg/L) without N_2	227
Cr(III) acetate 50% active solution (3000 mg/L) without N_2 aged for 24 h	93
Fresh HAPm/Cr(III) acetate (5/1) polymer gel without N_2	190
HPAm/Cr(III) acetate (5/1) polymer gel aged for 24 h without N_2	143
Gadolinium chloride solution (105 mg/L) used as the reference sample	200

Figure 1. Sample setup for spin-echo measurements.

the 90° and 180° pulses or $TE/2$, was 84 ms. At this Tau time, the echo signal amplitude of the polymer gel at 0.3 h and 24 h after formulation had the maximum difference and therefore the maximum contrast. The best contrast condition allows for observing changes in the amplitude profiles with time. The procedure described above was repeated to acquire 2-D spin-echo images (y-axis and z-axis), and the image data were Fourier transformed (no filter) and displayed using NTNMR software.

^{1}H Nuclear Magnetic Resonance (^{1}H NMR)

Low-field ^{1}H NMR was used to monitor the changes that the transverse relaxation times of the polymer gel undergo with time. This transverse relaxation is described by the time constant T_2, which was measured using a Bruker Minispec model mq10 NMR Analyzer and CPMG (Carr, Purcell, Meiboom, and Gill) pulse sequences.[4,31] All samples were tested using the following CPMG parameters: echo time = 0.25 ms, ms, recycle delay = 15 s, gain = 80 dB, number of scans = 64, and a number of echoes = 7000. A sample of mineral oil in a 10 mL NMR vial was used to update the Minispec settings and to run the daily check, which validates the instrument for 24 h. Furthermore, a sample of distilled water (used as a quality control sample) was tested using a CPMG sequence at the beginning of every test program to check the stability of the T_2 measurement. The temperature of the NMR probe was kept constant at 40°C by connecting a water bath to the Minispec. NMR vials were filled under a nitrogen atmosphere with fresh samples, and their caps were covered with Teflon tape. The vials were kept in a water bath at 40°C. The samples were tested several times during the first 10 h and monitored for 72 h. This procedure was performed on three sister samples of each sample, and the average data were plotted as function of time. The signal intensity of the polymer gel decreased following an exponential function governed by T_2, and the data obtained were fitted to mono-exponential decay using SigmaPlot 8.02 (from SYST Software Inc.). Thus, the equation that characterizes the signal decay of the HPAm/Cr(III) acetate is $S = S_0 e^{-t/T_2}$, where S = signal intensity (%), t = measuring time (ms), S_0 = signal at $t = 0$ of the polymer gel forming solution, and $T_2 = T_{2\text{polymer gel}}$ (ms).

RESULTS AND DISCUSSION

Rheology

Changes in G' and G'' with time were used to monitor the cross-linking reaction of the polymer gel over 5 h. It was observed that the loss modulus (G'') remained stable (experienced only minor changes from 0.76 to 0.77 Pa), while the storage modulus (G') and the complex viscosity (η^*) increased from 0.31 to 0.88 Pa and from 0.13 to 0.18 Pa · s respectively (Figure 2). The relation between G' and G'' (referred to

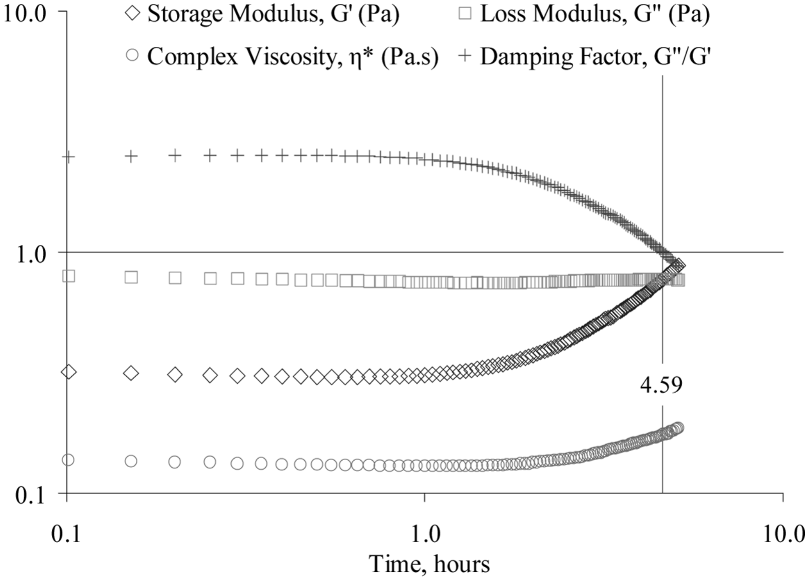


Figure 2. Rheology of a polymer gel formulated with 7500 mg/L of HPAm and 3000 mg/L of Cr(III) acetate 50% active at 40°C.

as the ratio of liquid to solid) is also presented in Figure 3 as the dumping factor ($\tan\delta = G''/G'$), also known as shift angle, phase angle, or loss factor.[9,15,19,20,22] The time at which the G' curve intersects the G'' ($\tan\delta = 1$) was used as the cross-linking time, which for the polymer solution studied is 4.59 h. At cross-linking time, G' and G'' are 0.77 Pa and η^* is 0.17 Pa · s. At times lower than 4.59 h, G'' is greater than G' ($\tan\delta > 1$) and the polymer gel behaves more like a viscous liquid. Afterwards, G' is greater than G'' ($\tan\delta < 1$) and the elastic component begins to dominate. Figure 2 depicts the average data of the three polymer gel sister samples. In all cases the standard deviation was low; it ranged from 0.009 to 0.013 for G', 0.007 to 0.013 for G'', 0.001 to 00.2 for η^*, and 0.001 to 0.005 for $\tan\delta$. From Figure 2 it is evident that the polymer gel continues to experience changes in G' after 5 h. This work focuses only on the interval from 0 to 5 h because this is the time at which the NMR curves show major changes. Nonetheless, more rheological research is currently taking place to characterize these polymer gels over longer periods.

Bottle Testing

Table I presents the results of bottle testing. It is shown that at 4.59 h (cross-linking time from rheological testing) the gel-strength code is C, which corresponds to a flowing gel: most of the obvious gel flows upon bottle inversion. Bottle testing indicated that the polymer gel undergoes changes over 30 h, when the gel-strength code is H. No further changes were observed after 30 h.

Table I. Bottle testing characterization using Sydansk's code[14] of a polymer gel forming solution formulated with 7500 mg/L of HPAm and 3000 mg/L of Cr(III) acetate 50% active at 40°C

Time, hours	Gel strength code	Time, hours	Gel strength code
0	A No detectable gel formed	7	D Moderately flowing gel
1	A	10	E Barely flowing gel
3	A	13	E
3.5	B Highly flowing gel	18	F Highly deformable non-flowing gel
4	B	22	G Moderately deformable non-flowing gel
4.6	C Flowing gel	24	
5	C	30	H Slightly deformable non-flowing gel
5.4	C	72	H

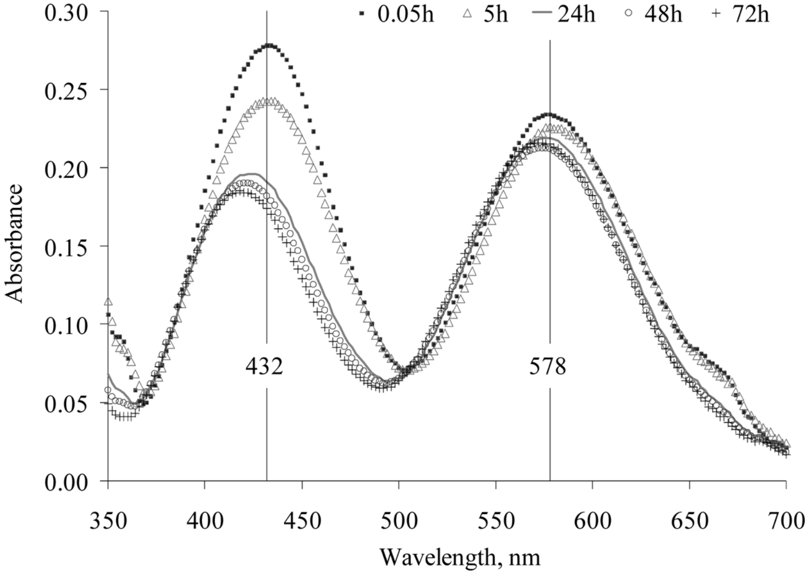


Figure 3. Changes in the spectra of the cross-linker solution formulated with 3000 mg/L of Cr(III) acetate 50% active at 40°C.

UV Spectrophotometry

The spectra of fresh cross-linker solution and polymer gel are characterized by two well-defined peaks. The broad absorptions are at 432 nm (first peak) and 578 nm (second peak) respectively (Figures 3 and 4). Both solutions are initially green due to the presence of chromium acetate cyclic structure. Aqueous solutions of Cr(III) acetate contain green cyclic chromium trimer, but depending on the source of Cr(III) acetate and the pH of the solution, oxalates and other conformations of chromium(III) acetate complexes may be present.[30] These results are in agreement with previous UV spectrophotometry studies conducted on Cr(III) acetate solutions[32] and HPAm/Cr(III) acetate polymer gels.[33] According to Tackett, aqueous solutions of Cr(III) acetate experience hydrolysis and hydroxyl groups replace the central oxygen (in the green cyclic structure) and some of the acetates and form a blue linear structure.[33] The solution with 3000 mg/L of Cr(III) acetate 50% active became blue after 24 h.

Figure 3 shows how the wavelength and the absorbance of the first peak rapidly decreased during the first 24 h from 432 to 418 nm and from 0.278 to 0.191 respectively. For the second peak the wavelength decreases from 578 to 572 nm and the absorbance from 0.234 to 0.219. Afterwards, the spectra continued changing slowly. Tackett[33] reported that the

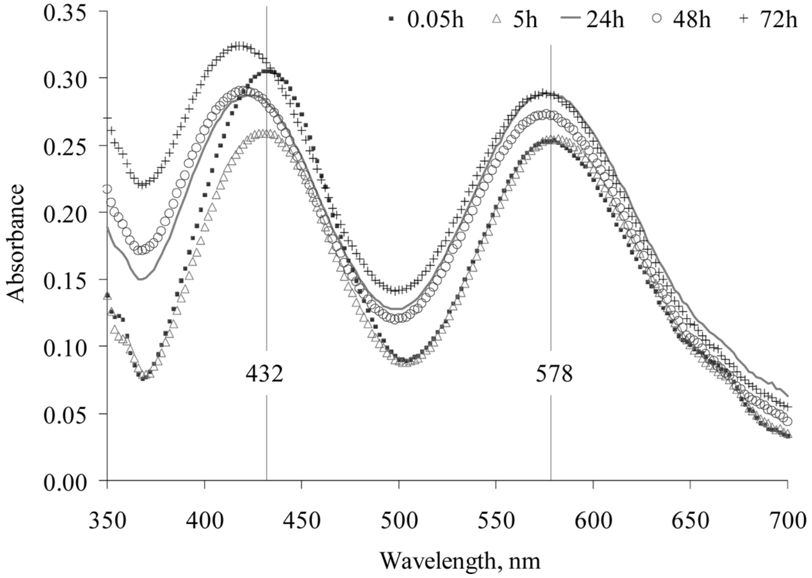


Figure 4. Changes in the spectra of the polymer gel formulated with 7500 mg/L of HPAm and 3000 mg/L of Cr(III) Ac 50% active at 40°C.

reaction of HPAm and Cr(III) acetate inhibits the Cr(III) acetate hydrolysis, and the original green color of Cr(III) acetate is retained when the HPAm has a degree of hydrolysis greater than 5%. However, the HPAm used in this work reportedly has a degree of hydrolysis of 10% and the polymer gel turned blue after 72 h. Figure 4 shows that the absorbance of the first peak of the polymer gel decreased during the first 5 h while the wavelength remained constant. After 24 h, the absorbance progressively increased while the wavelength decreased. UV spectrophotometry traced the progression of the gelation of HPAm/Cr(III) acetate (5/1) as stated in hypothesis 1. These results show that UV spectrometry continued to detect changes in the polymer gel after gelation time and support hypothesis 1. More experimental evidence is being acquired at the EOR Laboratory to characterize cross-linker and polymer gel solutions using UV spectrophotometry over longer periods.

Spin-Echo Magnetic Resonance Imaging

1-D Spin-Echo

Figure 5 presents the normalized signal intensity as a function of z-axis position and yields information about the changes that solutions

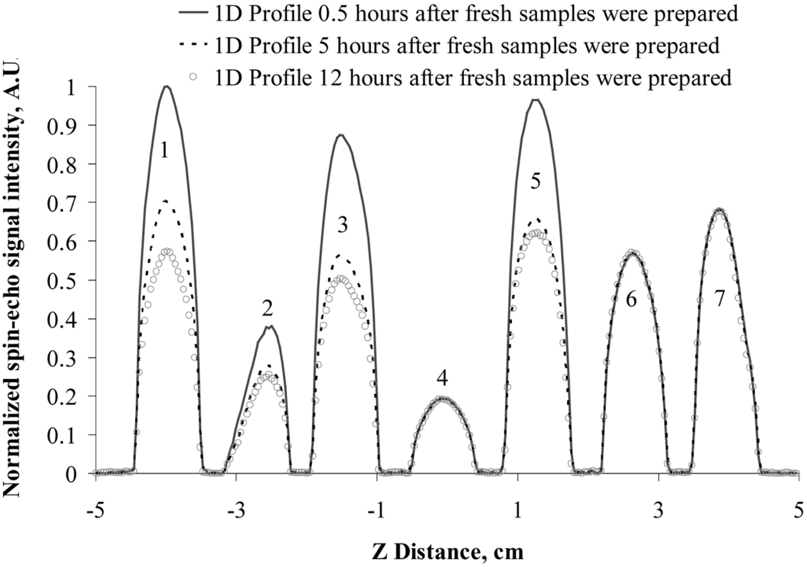


Figure 5. 1-D spin-echo profiles: 1, fresh Cr(III) acetate 50% active solution with N_2; 2, Cr(III) acetate 50% active solution with N_2 aged for 24 h; 3, fresh Cr(III) acetate 50% active solution without N_2; 4, Cr(III) acetate 50% active solution without N_2 aged for 24 h; 5, fresh HPAm/Cr(III) acetate (5/1) solution without N_2; 6, HPAm/Cr(III) acetate (5/1) solution aged for 24 h without N_2; 7, gadolinium chloride used as the reference sample.

experience. Although the signal intensity of the fresh Cr(III) acetate solutions decreased as time progressed, the presence of N_2 reduced the rate at which the intensity decreased. Several mechanisms could be involved in the N_2 effect on the cross-linker solutions. One possible reason is that N_2 inhibits reactions that take place in the presence of O_2. However, these observations were not further investigated in this study. Figure 5 shows that the Cr(III) acetate solution without N_2 always has a lower signal intensity than that of the cross-linker solution bubbled with N_2 prior to spin-echo imaging. In fact, after 5 h the maximum intensity of the cross-linker solution without N_2 is 0.56, while that of the cross-linker solution with N_2 is 0.69. Furthermore, the aged Cr(III) acetate solution without N_2 does not experience changes in intensity after 24 h (maximum intensity remained constant at 0.19), while the aged cross-linker solution bubbled with N_2 does (maximum intensity is further reduced from 0.37 to 0.25). It has been reported that Cr(III) acetate solutions experience chemical changes such as hydrolysis.[30] These results suggest that even under the N_2, Cr(III) acetate solutions experience chemical changes, but based on the Cr(III) acetate 1-D profiles, N_2 appears to delay them. Figure 5 also depicts the changes in the signal intensity of the polymer gel, which also decreases with time. The most significant reduction in the signal intensity of the fresh polymer gel was observed during the first 5 h, when the maximum value of the intensity decreased by a factor of 1.47 (from 0.96 to 0.65). After 5 and up to 12 h, the maximum intensity was reduced only by a factor of 1.05 (from 0.65 to 0.62). In contrast, the aged polymer gel did not experience any changes in signal intensity because the maximum intensity remained constant at 0.57. The changes in signal intensity may be related to the cross-linking reaction between HPAm and Cr(III) acetate. According to the rheology data, the gelation time of the HPAm/Cr(III) acetate (5/1) is 4.59 h at 40°C. Thus, the results indicate that the greatest change in signal intensity occurs before gelation time. However, bottle testing indicates that the gel strength of HPAm/Cr(III) acetate (5/1) polymer gel at 40°C experienced changes during the 30 h after formulation, and it is observed that after 5 h the signal intensity of the polymer gel experiences only minor changes (Figure 5). There are no changes after 24 h as determined by spin-echo signal intensity.

2-D Spin-Echo

Figure 6 presents the 2-D spin-echo images of the cross-linker and polymer gel. Fresh Cr(III) acetate 50% active and HPAm/Cr(III) acetate (5/1) solutions have a brighter intensity than aged solutions and become darker as time passes. The 2-D spin-echo images detected changes in the polymer gel only during the first 5 h, the stage at which the gelation time (4.59 h) was rheologicaly measured. After 5 h, the fresh solution signals have the same intensity as that of the aged solutions. No changes were observed in the 2-D spin-echo images after 5 h. Similar to the 1-D profile, the 2-D spin-echo images of the aged solutions remained stable. Differences in bulk magnetic susceptibility within the sample cause imaging artifacts known as susceptibility artifacts.[34] In this case, susceptibility artifacts occurred, as pointed out by the arrows in Figure 6, due to variation in the magnetic field strength near the interfaces of the vials and the Teflon holder. Figures 5 and 6 show that the signal intensity of the gadolinium chloride (reference sample) remained constant (in both 1-D and 2-D profiles), which confirms that the changes detected by spin-echo are due to the changes experienced by the cross-linker and polymer gel.

Spin-echo detected changes in the signal intensity of the HPAm/Cr(III) acetate (5/1) polymer as stated in hypothesis 2; hence, this hypothesis is supported. Based on the results obtained from 1-D and 2-D spin-echo, the changes in the signal intensity of the polymer gel detected by spin-echo MRI may be related only to the early stage of the cross-linking reaction between HPAm and Cr(III) acetate (in this

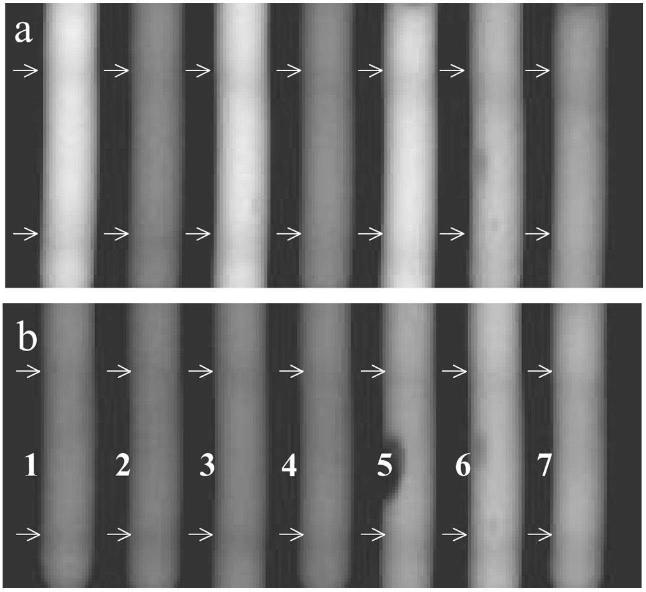


Figure 6. (a) 2-D spin-echo images 0.5 h after fresh samples were formulated and (b) 2-D profile 5 h after fresh samples were formulated: 1, fresh Cr(III) acetate 50% active solution with N_2; 2, Cr(III) acetate 50% active solution with N_2 aged for 24 h; 3, fresh Cr(III) acetate 50% active solution without N_2; 4, Cr(III) acetate 50% active solution without N_2 aged for 24 h; 5, fresh HPAm/Cr(III) acetate (5/1) solution without N_2; 6, HPAm/Cr(III) acetate (5/1) solution aged for 24 h without N_2; 7, gadolinium chloride used as the reference sample.

case, during the first 5 h), as no significant changes are observed afterwards, and the signal intensity remains constant after 24 h. Nonetheless, further work is required using other polymer gel formulations before generalizing this tendency.

^{1}H Nuclear Magnetic Resonance (^{1}H NMR)

Previous studies of the components of HPAm/Cr(III) acetate polymer gels conducted at the UNB EOR laboratory yielded T_2 values greater than 3200 ms for the solvent and the polymer solution (7500 mg/L of HPAm) at 40°C. These T_2 values remain constant with time.[10] Eighteen minutes after formulation, a solution with 3000 mg/L of Cr(III) acetate 50% active at 40°C has a T_2 of 281 ms. However, T_2 of Cr(III) acetate changes with time.[10] Figure 7 depicts how T_2 of

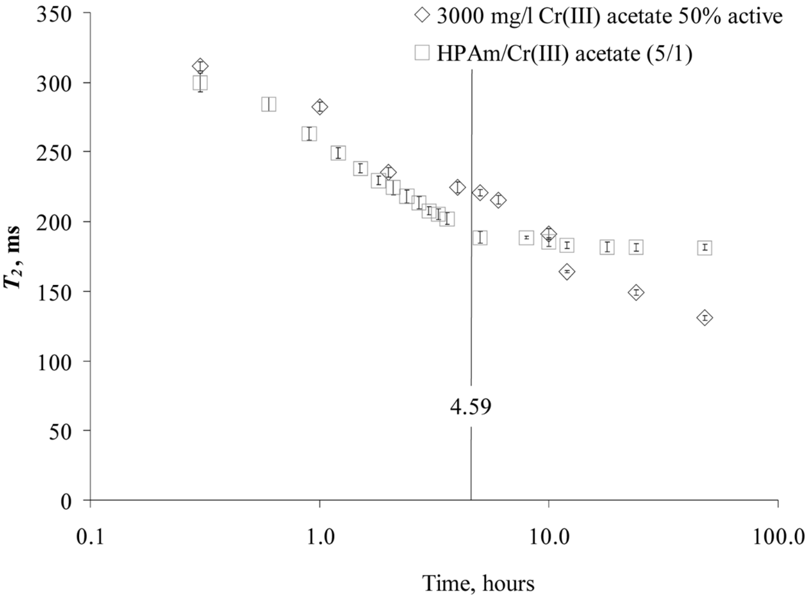


Figure 7. T_2 of Cr(III) acetate 50% active and a polymer gel formulated with 7500 mg/L of HPAm and 3000 mg/L of Cr(III) acetate at 40°C.

the 3000 mg/L Cr(III) acetate 50% active solution continuously decreases over 72 h. Similarly, T_2 of the HPAm/Cr(III) acetate (5/1) decreases during the first 5 h, but levels off thereafter. T_2 of the polymer gel is lower than T_2 of the cross-linker solution during the first 10 h, and afterwards the opposite is true. This may be due to increases in the complex viscosity of the polymer gel that restrict the movement of the H species and therefore reduces the T_2. Figure 8 depicts the η^* and $1/T_2$ changes as a function of time before cross-linking time, and it can be observed that both curves have similar trends. These results suggest that ^{1}H NMR detects changes in the polymer gel before gelation time (4.59 h for the polymer gel studied here) and the time at which T_2 stabilizes may be related to the gelation time. These results support hypothesis 3. Although ^{1}H NMR does not detect changes in gel strength after gelation time (as opposed to bottle testing, which detected changes during 30 h), this technique provides quantitative information that can be related to rheological properties without disrupting the polymer gel network. More ^{1}H NMR studies are being conducted using other polymer gel formulations to confirm the results that are reported here and to fully develop an NMR-based methodology to characterize polymer gels in oil fields.

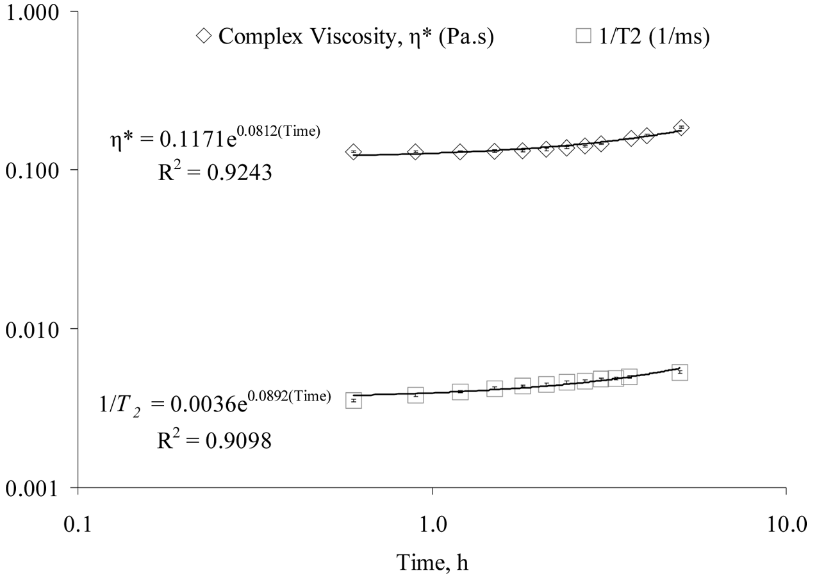


Figure 8. Comparison between complex viscosity and T_2 values from 0.6 to 5 h after polymer gel formulation at 40°C.

CONCLUSIONS

HPAm/Cr(III) acetate (5/1) polymer gel has a rheological gelation time of 4.59 h and corresponds to a gel strength code of C, flowing gel, according to bottle testing. At times lower than 4.59 h, the polymer gel behaves more like a viscous liquid. Afterwards, elastic behavior begins to dominate. The changes in the 3000 mg/L Cr(III) acetate 50% active solution detected by UV spectrophotometry may be related to the hydrolysis (characterized by a blue color) that the solution undergoes while aging. Both cross-linker and polymer solutions experience wavelength changes (as the solutions change from green to blue). However, the cross-linker solution changes faster than the polymer solution. These results could suggest that the HPAm used in this work does not stop the hydrolysis of Cr(III) acetate but delays it.

The 1-D and 2-D spin-echo profiles indicated that the most significant changes in the signal intensity of the polymer gel occurred during the first 5 h, that is, the stage at which the gelation time (4.59 h) was rheologicaly measured. Similarly, ^{1}H NMR detected changes in the T_2 of HPAm/Cr(III) acetate (5/1) during the first 5 h of the gelation reaction. Although the curves of T_2 as a function of time of the cross-linker solution and the polymer gel have similar trends prior to gelation time, the T_2 values of the HPAm/Cr(III) acetate (5/1) are lower, which may be due to the increase in complex viscosity. Bottle testing detected changes in the gel strength of the HPAm/Cr(III) acetate (5/1) during the 30 h after formulation, and UV spectrophotometry detected changes during 72 h. Compared to NMR techniques, bottle testing was a better and more practical indicator of the gel strength changes experienced by the polymer gel used in this study after the gelation time. Yet NMR and MRI techniques allow for quantitative studies of HPAm/Cr(III) acetate (5/1) in a noninvasive and nondestructive manner, and the data obtained can be correlated to rheological data prior to gelation time. These results indicate that an NMR-based methodology can be implemented as a new technique to characterize HPAm/Cr(III) acetate (5/1) in oil fields. The chemistry of HPAm/Cr(III) acetate is complex, and further work is required to accurately characterize these polymer gels using NMR techniques. Currently, more ^{1}H NMR studies using different formulations are being conducted to find a correlation between T_2 and the rheological properties of HPAm/Cr(III) acetate gels.

The 1-D and 2-D spin-echo techniques detected changes in signal intensity as the Cr(III) acetate 50% active solution aged. The maximum signal intensity decreased faster when the Cr(III) acetate 50% active was not bubbled with N_2 prior to imaging than when the Cr(III) acetate was bubbled with N_2 before imaging. These results indicate that in the absence of N_2 other effects that affect the spin-echo signal intensity are taking place. Although more research is needed to explain these observations, ^{1}H NMR and MRI techniques coupled with spectroscopy techniques can be used to study the structural changes of cross-linker solutions.

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