¹H NMR Characterization of HPAm/Cr(III) Acetate Polymer Gel Components

Silvia Magnolia Vargas-Vasquez[a]; Laura Beatriz Romero-Zerón[a]; Bryce MacMillan[b]

[a] Department of Chemical Engineering, University of New Brunswick, Fredericton, New Brunswick, Canada [b] Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

^{1}H NMR Characterization of HPAm/Cr(III) Acetate Polymer Gel Components

Silvia Magnolia Vargas-Vasquez and Laura Beatriz Romero-Zerón
Department of Chemical Engineering, University of New Brunswick,
Fredericton, New Brunswick, Canada

Bryce MacMillan
Department of Physics, University of New Brunswick, Fredericton,
New Brunswick, Canada

Abstract: Low-field ^{1}H nuclear magnetic resonance (NMR) was used to characterize the components of polymer gels formulated with partly hydrolyzed polyacrylamide (HPAm) and Cr(III) acetate. Changes in the NMR relaxation times were used to characterize samples of polymer, cross-linker, polymer solutions, and cross-linker solutions in bulk and in porous media. The results obtained indicated that changes of HPAm concentration do not have a significant effect on the relaxation times, while changes in Cr(III) acetate concentration do. Therefore, the concentration of cross-linker is the most critical variable in the process of characterizing HPAm/Cr(III) acetate polymer gels using low-field ^{1}H NMR.

INTRODUCTION

Polymer flooding is a chemical enhanced oil recovery (EOR) process that consists of using water-soluble polymers of high molecular weight as water flooding additives in order to control displacing fluid mobility in reservoirs, to improve sweep efficiencies, and to increase oil production. Polymer flooding is intended to improve water flood mobility control primarily by increasing the viscosity of the displacing fluid (not by reducing permeability). In most situations, polymer flooding is implemented as a tertiary process near the end of a water flood. Polymer gel treatment is also a chemical EOR process in which water-soluble high-molecular-weight polymers are dissolved in water or brine and subsequently chemically cross-linked so as to impart elastic and solid-like properties to the aqueous gels via the resultant chemically cross-linked three-dimensional polymer network. These gels are cost-effective materials for use as plugging (permeability-reducing) agents in conformance-improvement treatments. These gels do not increase the viscosity of the flood water. Conformance improvement includes sweep improvement and water shutoff.[1] A polymer gel frequently used in the oil and gas industry is formulated with hydrolyzed polyacrylamide (HPAm) and Cr(III) acetate.[2]

The production of conventional light oil in Canada is in continuous decline. According to the National Energy Board, current production levels ($115300 \, m^3$ per day)[3] are expected to decrease by 50% by 2015, while demand is expected to increase by 230%.[4] For this reason, the implementation of new technology and methodologies for EOR is important to the Canadian oil industry. It has been proposed that an aggressive approach to research and technological modernization should be maintained in order to supply the demand for conventional oil. This is possible only with significant advances in EOR techniques.[5] Polymer gel treatment is an important chemical method within EOR processes and plays a significant role in the mitigation of conventional oil production decline. The oil industry does not have a standardized procedure that can be implemented in the field to accurately determine the gelation time and gel strength of the polymer gel. These are critical factors for the proper design of polymer gel treatments. The EOR laboratory at the University of New Brunswick aims to develop and validate a ^1H nuclear magnetic resonance (NMR) methodology that allows for the practical and accurate characterization of HPAm/Cr(III) acetate polymer gels in the oil field. This new methodology is based on relating the gelation time and rheological storage modulus to the transverse relaxation time (T_2) changes of HPAm/Cr(III) acetate polymer gels. NMR is noninvasive; hence, this technique will not disrupt the polymer gel network. The development of an NMR-based methodology

to characterize HPAm/Cr(III) acetate polymer gels requires separate study of the four components present in a polymer gel forming solution: polymer (HPAm), cross-linker (Cr(III) acetate), Na_2SO_3 (used as an oxygen scavenger to prevent polymer degradation), and distilled water (DIW). Separate characterization of these components allows for their ¹H NMR bulk relaxation times (T_2) to be determined in pure form as well as in solution and provides information about the effect that each component has on T_2.

In the presence of porous media, ¹H NMR T_2 measurements have been shown to be strongly dependent on the surface area, pore size distribution, type of porous medium, and details of the T_2 experiments, particularly the echo time.[5] Thus, studies of the polymer solutions in the presence of porous media are also required to observe the effect that the type of porous medium has on the T_2 values of the HPAm solutions. This information is also needed to select the porous media and parameters to conduct future experiments. The same approach is used to characterize the cross-linking solutions. In this case, the paramagnetic properties of Cr(III) add to the complexity of the correlation between the NMR relaxation times and the type of porous medium. As a result of these factors, there are five objectives in this study: (1) to select proper parameters to characterize HPAm/Cr(III) acetate polymer gels with ¹H NMR; (2) to find the ¹H T_2 NMR relaxation time of as-received HPAm, as-received Cr(III) acetate (50% active in water), distilled water (DIW), and a solution of 0.01 wt% Na_2SO_3 in DIW (which is the solvent of the polymer gel forming solution); (3) to measure the ¹H T_2 NMR relaxation time of the polymer solvent in bulk and in the presence of unconsolidated porous media; (4) to determine the ¹H T_2 NMR relaxation times of the polymer solutions with HPAm concentrations ranging from 0.25 to 2 wt% in bulk and porous media; and (5) to obtain the relaxation times of the cross-linker solutions with Cr(III) acetate concentrations ranging from 0.0083 to 0.3 wt% in bulk and porous media. The four hypotheses of this study are that (1) the addition of 0.01 wt% of Na_2SO_3 to DIW does not significantly affect the ¹HNMR bulk relaxation time (T_2) values of DIW; (2) solutions of HPAm at different concentrations ranging from 0.25 to 2 wt% do produce similar T_2 values; (3) the presence of Berea sandstone and Stoney Creek sandstone greatly reduces the T_2 values of the HPAm solutions compared to those T_2 values obtained from measurements performed using glass beads as porous media; and (4) in the presence of porous media, the paramagnetic properties of Cr(III) acetate at concentrations greater than or equal to 0.3 wt% dominate pore surface induced relaxation as this relates to the relaxation time responses of Cr(III) acetate solutions.

LITERATURE REVIEW

[1]H Nuclear Magnetic Resonance

[1]H nuclear magnetic resonance is based on the interaction between the magnetic moments of hydrogen nuclei in a static magnetic field and a radio frequency magnetic field. The spin-spin relaxation is described by the time constant T_2 and is referred to as transverse relaxation.[6–9] T_2 is related to the mobility of the hydrogen species within the test medium. H species that have restricted motion, such as those that are bound to a surface or inside the smaller void spaces, generally have shorter T_2 values. Conversely, more mobile or free hydrogen species, such as those in larger void spaces, have longer T_2 values. Furthermore, there is a rapid exchange between bound and free hydrogen protons.[10,11] Thus, in the presence of porous media, the observable T_2 of the hydrogen species can be described as a combination of the T_2 values of the bound and free solution as $1/T_{2\text{-}observed} = ((1 - P_b)/T_{2\text{-}free}) + P_b/T_{2b}$, where P_b = pro-proton fraction of bound hydrogen species, $T_{2b} = T_2$ of the bound hydrogen species, and $T_{2\text{-}free} = T_2$ of the free hydrogen species.[10,12] HPAm/Cr(III) acetate polymer gels have very high water concentrations (up to 99.7 wt%), which make them suitable for ^{1}H NMR studies. The measurement of T_2 yields information about the reaction between HPAm and Cr(III) acetate and allows characterization of the components of this polymer gel in their pure form as well as in solution.

HPAm/Cr(III) Acetate Polymer Gels

The successful placement of an HPAm/Cr(III) acetate polymer gel in a specific location within the reservoir depends on the ability to predict and to modify the gelation time and the final strength of the gel. For the oil field operators, these two parameters are the most important because they provide information concerning the time during which the HPAm/Cr(III) acetate gelant solution is pumpable and the maximum differential pressure that this polymer gel can sustain.[13–15] The gelation time and gel strength are obtained from rheological monitoring[13,15–21] or bottle testing.[15,22,23] Although rheology provides consistent polymer gel descriptions, it is not practical because it is time consuming, expensive, and invasive (it ultimately disrupts the polymer gel network). Bottle testing, on the other hand, is practical and not time and equipment intensive, but it can lead to inconsistent gel description because of its qualitative nature. Thus, there is not a practical, accurate methodology available in the oil field for determining the gelation time and gel strength of HPAm/Cr(III) acetate polymer gels. Moreover, the gelation process of

HPAm/Cr(III) is affected by temperature, salinity, and polymer as well as cross-linker concentrations and quality. As a result, the operational constraints are delicate. Therefore, the information obtained from this study helps to understand how low-field NMR can be applied to monitor the gelation reaction of HPAm/Cr(III) acetate, how transverse relaxation time (T_2) relates to polymer and cross-linker concentrations, and the effect of the presence of porous media on the relaxation time.

EXPERIMENTAL SECTION

Materials

Polymer Gel Solvent

A solution of DIW and 0.01 wt% of Na_2SO_3 (pH = 7.4) was used to prepare the polymer and cross-linker solutions. The density of the polymer gel solvent is 0.9924 g/cc at 40°C and 0.9881 g/cc at 50°C. Na_2SO_3 was used to prevent polymer degradation.

Polymer

Alcoflood 935, which is a partially hydrolyzed polyacrylamide (HPAm), is the polymer used in this study. This anionic acrylamide copolymer has been supplied by Ciba Specialty Canada Inc., which classifies Alcoflood 935 as a conformance control polymer. Alcoflood 935 has a degree of hydrolysis of about 10% and manufacturer-reported molecular mass of 8×10^6–10×10^6 g/mol. Four polymer solutions were prepared dissolving 0.25, 0.5, 0.75, and 2 wt% of HPAm in the polymer gel solvent. Table I presents the density and viscosity of the polymer solutions at 40°C and 50°C respectively. A density meter, Anton Paar model DMA 35 N, was

Table I. Density and viscosity of the polymer solutions

| Polymer concentration, wt% | pH | 40°C | | | 50°C | | |
| | | Density, g/cc | Viscosity, cP | | Density g/cc | Viscosity, cP | |
			6 rpm	60 rpm		6 rpm	60 rpm
0.25	6.1	0.9935	119	79	0.9890	108	67
0.50	5.9	0.9943	288	174	0.9896	254	165
0.75	5.8	0.9955	825	383	0.9909	723	350
2.00	5.6	1.0004	10467	3488	0.9968	8667	3048

used to obtain the density, and a Brookfield Syncro-electric viscometer was employed to measure the viscosity of the polymer solutions.

Cross-Linker

Cr(III) acetate solution 50% active in water (pH = 2.6) supplied by McGean-Rohco, Inc. is the cross-linker used in this study. Five cross-linker solutions were prepared using 0.0083, 0.05, 0.1, 0.2, and 0.3 wt% of Cr(III) acetate in the polymer gel solvent. The pH of the solutions ranged from 6.5 to 3.5 and the densities ranged from 0.9924 to 0.9941 g/cc at 40°C and 0.9881 to 0.9895 g/cc at 50°C correspondingly.

Porous Media

The polymer solutions were tested using three types of porous media: glass beads, Berea sandstone purchased from Temco Inc. (Tulsa, Okla.), and Stoney Creek sandstone provided by the Department of Natural Resources (Fredericton, Canada). The unconsolidated porous media have an average particle size diameter of 0.4 mm (35 mesh). X-ray diffraction (XRD) tests were conducted on samples of Berea sandstone and Stoney Creek sandstone for mineral identification. The step size and step time used for the XRD test were 0.020 deg/step and 0.50 s respectively. Thin section analyses were also performed to estimate the composition of the sandstones (Table II). Although Berea sandstone and Stoney Creek sandstone have an NMR signal, it is not detectable with the CPMG parameters used to test the solutions in the presence of porous media. The glass beads, on the other hand, do not have an NMR signal.

Table II. Composition of Berea sandstone and Stoney Creek sandstone

Minerals	Estimated amount, %	
	Berea	Stoney Creek
Quartz (SiO_2)	70	55
Rock fragments	17	39
Feldspar: Albite ($NaSi_3AlO_8$) and microcline ($KAlSi_3O_8$)	8	—
Feldspar: Albite ($NaSi_3AlO_8$)	—	3
Muscovite $(K \cdot Na)(Al \cdot Mg \cdot Fe)_2(Si_3AlO_{10})(OH_2)$	1	2
Clinochlore $(MgFe)_6(SiAl)_4O_{10}(OH)_8$	1	—
Chlorite $(Mg \cdot Fe)_5(Al \cdot Si)_5O_{10}(OH)_8$	—	1
Carbonate ($CaCO_3$)	3	—

Experimental Procedures

T_2 measurements were carried out using a Bruker Minispec spectrometer model mq10 NMR Analyzer, which employs a 10 MHz benchtop permanent magnet. A water bath with a temperature controller set at 40°C or 50°C, as needed, was connected to the Minispec to maintain the NMR probe at a constant temperature. In order to measure bulk T_2, 1 mL of fresh sample was placed in NMR vials, and nitrogen was circulated inside the vials to displace the excess of oxygen and avoid oxidation. The samples used to perform T_2 measurements of each solution in the presence of porous media were prepared placing 0.8 g of the porous media inside the NMR vials and adding 0.2 g of the solution. A vacuum line was connected to the NMR vials to de-gas the porous media samples and allow homogeneous distribution of the solution within the porous media. Teflon plugs were placed at the surface of every sample inside the NMR vials, and Teflon tape was applied around the vials' caps to avoid evaporation. CPMG (Carr, Purcell, Meiboom, and Gill) pulse sequences were employed to measure T_2. The CPMG sequence consists of applying a 90° radio frequency pulse and a series of 180° radio frequency pulses that have twice the duration of the 90° pulse in order to acquire the spin echoes. The peak signal intensity of each sequential echo decreases following an exponential function governed by T_2.[24] Each sample was tested five times, and the data obtained were fitted to mono-exponential, bi-exponential, or tri-exponential decay, as appropriate, using SigmaPlot 8.02 A (from SYSTA Software Inc., Point Richmond, Calif.). For instance, the equation that characterizes the signal decay of Cr(III) acetate is $S = S_o e^{-t/T_2}$, where S = signal intensity (%), t = measuring time (ms), S_o = signal at $t = 0$, and $T_2 = T_{2Cr(III)\ acetate}$. Likewise, the bi-exponential decay of HPAm (Alcoflood 935) can be expressed by the equation $S = S_a e^{-t/T_{2a}} + S_b e^{-t/T_{2b}}$, where S = signal intensity (%), t = measuring time (ms), S_a = fractional size at the HPAm signal (S_{HPAm}), $T_{2a} = T_{2\text{-HPAm}}$(ms), S_b = fractional size of the signal from the impurities ($S_{impurity}$), and $T_{2b} = T_{2\text{-unknown component}}$ ($T_{2\text{-impurtiy}}$). Additionally, a distributed exponential (DXP) routine based on the Butler-Reeds-Dawson algorithm[25] was used to generate a spectrum of the T_2 values present in the sample.

RESULTS AND DISCUSSION

HPAm (Alcoflood 935)

The CPMG ^{1}H T_2 NMR decay curves obtained from testing a bulk sample of HPAm are bi-exponential. The analysis of the T_2 data indicates that 97%

of the NMR signal provided by Alcoflood 935 corresponds to the HPAm material itself (fast relaxing components). The remaining 3% of the NMR signal corresponds to an unidentified component (referred to here as impurity). In commercial production, the maximum conversion rates of HPAm range from 96 to 97%.[26] Thus, results provided by the ^{1}HNMR test are within the range. The values of S_{HPAm} and $T_{2\text{-}HPAm}$ are 46.8 and 0.13 ms at 40°C and 41.14 and 0.15 ms at 50°C. Correspondingly, the values of $S_{impurity}$ and $T_{2\text{-}impurity}$ are 1.66 and 3.83 ms at 40°C and 1.48 and 4.43 ms at 50°C.

Cr(III) Acetate

The T_2 measurements performed on a sample of Cr(III) acetate at 40°C and 50°C yield single exponential decay curves with an average T_2 of 0.185 ms at 40°C and 0.189 ms at 50°C. The values of S_o are 92.42 and 87.58 at 40°C and 50°C respectively.

Polymer Gel Solvent (0.01 wt% Na$_2$SO$_3$ in DIW)

The bulk T_2 measurements, conducted under the same conditions, yield very similar T_2 values for the samples of DIW alone (3147.0 ms) and the polymer gel solvent (3215.7 ms). Thus, Na$_2$SO$_3$ (at the concentration studied) does not have a significant effect on the T_2 relaxation time of DIW, and the first hypothesis of our study is valid. It should be noted that the T_2 measurement performed on a solid sample of Na$_2$SO$_3$ did not give any signal.

Polymer Solutions

Oil field application of polymer flooding and gelling agents is limited to low-concentration solutions because polymers are expensive and concentrated polymer solutions possess high viscosities that cannot be easily pumped. Yet a concentration of 2 wt% was used here as the upper limit of polymer concentration in order to obtain the maximum variation of T_2. Concentrations equal to or greater than 2 wt% of Alcoflood 935 are not used in the field; therefore, solutions with concentrations above this level were not tested. All the CPMG ^{1}H NMR T_2 decay curves of the polymer solutions are mono-exponential. After performing the fitting routine, it was found that as the concentration of polymer increases, the T_2 values of the polymer solutions slightly decrease from 3560 ms (0.25 wt% polymer) to 3226 ms (2 wt% polymer) at 40°C, and from 3744 ms (0.25 wt% polymer) to 3243 ms (2 wt% polymer) at 50°C. Hence, the changes in polymer concentration have a minor effect on T_2. These results support hypothesis number 2 of this study.

The T_2 components of measurements performed on fluids in porous media are governed by the fluid distribution within the porous media. T_2 from bound fluid to the pore walls will be short, and that from the more free fluid in the bulk of the pore space will be long.[27] This is the case with the polymer solutions in the presence of glass beads. The T_2 measurements yield bi-exponential decay curves, and the values of $T_{2\text{-}short}$ and $T_{2\text{-}long}$ are quite close in all cases at 40° and 50°C. $T_{2\text{-}short}$ varies from 191 to 296 ms and $T_{2\text{-}long}$ ranges from 711 to 887 ms. The T_2 distribution of the polymer solutions at 50°C in the presence of porous media is shown in Figure 1. The DXP fitting provides two distinct peaks: the first peak, which represents the polymer solution that is located in the smallest pore spaces, and the second peak, which corresponds to the free polymer solution located inside the bulk of the biggest pore spaces. Similar trends were obtained from the T_2 measurements conducted using unconsolidated Berea sandstone. However, the presence and/or interaction among paramagnetic ions such as Mn_2^+ and Fe_3^+ and ferroan phases (Fe-rich minerals such as clinochlore and chlorita; refer to Table II) significantly reduced the T_2 values of the polymer solution (Figure 2) compared to those obtained when glass beads were used. Furthermore, Figure 2 shows one peak spectrum, which indicates that the T_2 distribution is convoluted. The exponential fitting using a bi-exponential decay model provides two T_2 values. In sandstones,
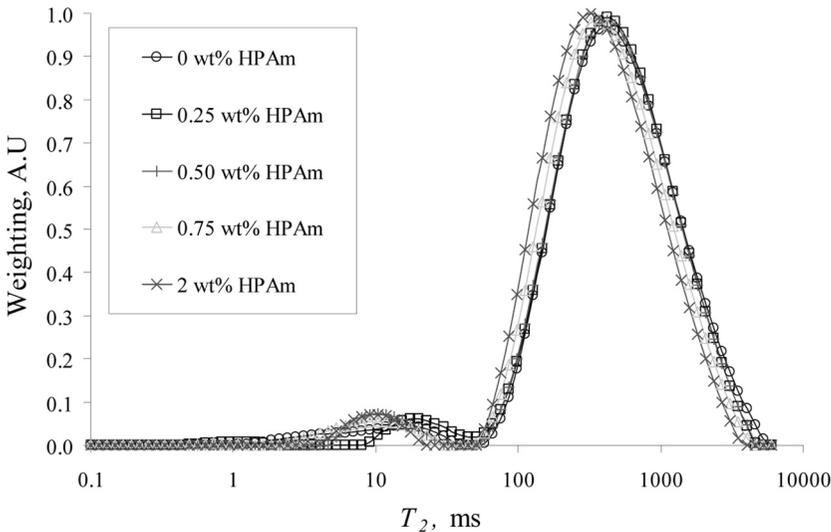
Figure 1. T_2 distribution of polymer solutions in the presence of glass beads at 50°C; CPMG parameters: echo time = 0.5 ms, recycle delay = 9 s, number of echoes = 8192, number of scans = 258.
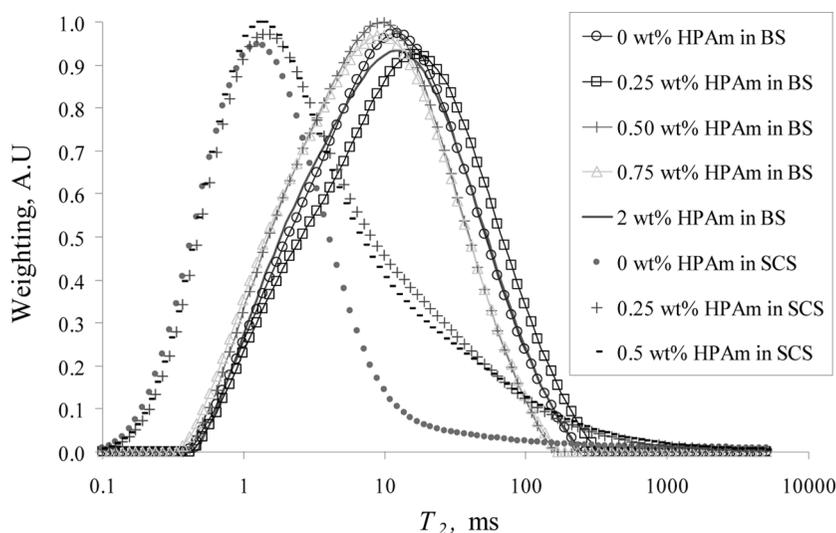
Figure 2. T_2 distribution of polymer solutions in the presence of Berea sandstone (BS) and Stoney Creek sandstone (SCS) at 40°C; CPMG parameters: echo time $= 0.5$ ms, recycle delay $= 2.5$ s, number of echoes $= 550$, number of scans $= 516$.

the bound fluid is characterized by relaxation times lower than 33 ms.[28] The $T_{2\text{-}short}$ values obtained using Berea sandstone are lower than 33 ms, suggesting that this T_2 component is related to the polymer solution bound to the Berea sandstone, while $T_{2\text{-}long}$ corresponds to the free fluid.

A tri-exponential model was used to fit the T_2 decay curves obtained from the measurements performed on the polymer solution in the presence of unconsolidated Stoney Creek sandstone. Thus, the T_2 constants are represented by $T_{2\text{-}1}$ (which ranges from 1.16 to 1.56 ms), $T_{2\text{-}2}$ (which ranges from 8.04 to 14.58 ms), and $T_{2\text{-}3}$ (which varies from 128.1 to 320.2 ms). $T_{2\text{-}1}$ and $T_{2\text{-}2}$ correspond to the polymer solution distributed in the smaller pores or closer to the pore walls, and $T_{2\text{-}3}$ represents the solution in the bulk of the pores. In this case, only the polymer solutions with concentrations of 0.25 and 0.5 wt% HPAm were tested because at greater concentrations, the polymer solutions tend to form clusters with the Stoney Creek sandstone grains, and therefore they are not well distributed in the porous media. Additionally, compared to Berea sandstone, more paramagnetic ions and ferran phases exist in the minerals composing the Stoney Creek sandstone (Table II), causing a more complex distribution of T_2, as shown in Figure 2, which depicts the convoluted one-peak spectrum. The behavior of the polymer solution in the porous media suggests that the concentration of Alcoflood 935 does not have a major effect on T_2. A comparison of the results obtained

from the measurements conducted using glass beads, Berea sandstone, and Stoney Creek sandstone indicates that T_2 relaxation times of the polymer solutions in the presence of the sandstones are drastically reduced by the combined effect of the paramagnetic ions, ferran phases, and surface area. These factors also cause the T_2 distribution of the polymer solution in sandstones to be more complex than that in glass beads. These observations support the third hypothesis of this study.

Cross-Linker Solutions

The rate of ¹H nuclear magnetic T_2 relaxation of the cross-linker solutions decreases as the concentration of Cr(III) acetate increases because of the paramagnetic properties of Cr(III). Thus, there is an inverse relationship between the concentration of Cr(III) acetate and T_2. This effect is known as NMR paramagnetic relaxation enhancement, and it consists of interaction between the magnetic moments of an electron and a nucleus.[9] Figure 3 shows the T_2 distribution of the cross-linker solutions in comparison to that of the polymer gel solvent (without cross-linker). It also illustrates that the changes in cross-linker concentration have a major effect on T_2 and that as the concentration of Cr(III) acetate increases the peaks become narrower. The decay curves of the cross-linker solutions in bulk
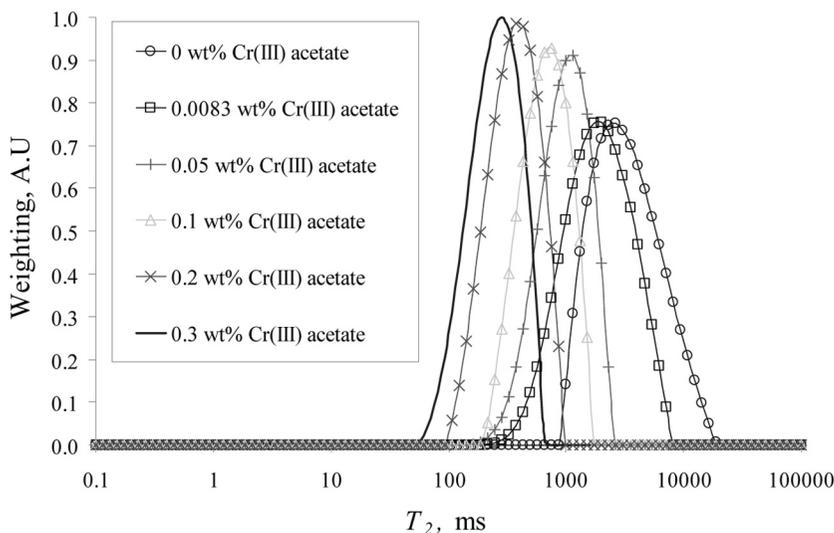
Figure 3. Bulk T_2 distribution of fresh cross-linker solutions at 40°C; CPMG parameters: echo time = 1.1 ms, recycle delay = 15 s, number of echoes = 16384 (0 wt% Cr(III) acetate) and 1024 (0.3 wt% Cr(III) acetate), number of scans = 64.

are mono-exponential in all cases. The changes in T_2 values were corre-lated with changes in the cross-linker concentration. The resulting correla-tions are linear, and temperature does not have a significant effect on T_2. The T_2 measurements performed in the presence of glass beads yielded bi-exponential decay curves for the cross-linker solutions with a concen-tration of Cr(III) acetate lower than or equal to 0.2 wt%. The changes in cross-linker concentration also have a significant effect on the T_2 of the cross-linker solution. $T_{2-short}$ ranges from 198.9 to 98.5 ms at 40°C and 202.8 to 123.5 ms at 50°C, and T_{2-long} ranges from 670 to 250 ms at 40°C and 680.9 to 411.8 ms at 50°C. The first peak shown in Figure 4 represents the cross-linker solution (with 0 to 0.2 wt% of Cr(III) acetate) that is located in the smallest pore spaces. The second peak corresponds to the free cross-linker solution located inside the biggest pore spaces. At a cross-linker concentration of 0.3 wt%, the decay curve is single exponen-tial, which indicates that the effect of the paramagnetic properties of Cr(III) acetate becomes dominant over the effect of surface relaxation on T_2 (at 40°C, T_2 is 158.0 ms, and at 50°C T_2 is 208.2 ms). This effect is also shown in Figure 4, where at a concentration of 0.3 wt% the T_2 distribution of the Cr(III) acetate solutions is represented by only one narrow peak. These results support hypothesis number four of our study.
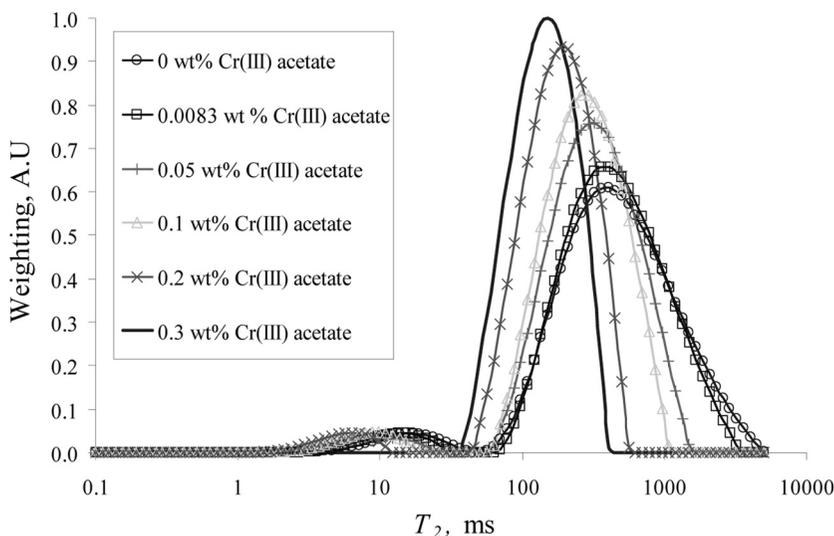
Figure 4. T_2 distribution of fresh cross-linker solutions in glass beads at 40°C; CPMG parameters: echo time = 0.5 ms, recycle delay = 9 s, number of echoes = 8192 (0 wt% Cr(III) acetate) and 2048 (0.3 wt% Cr(III) acetate), num-ber of scans = 258.

CONCLUSIONS

Low-field NMR has successfully been employed to characterize bulk samples of the components of HPAm/Cr(III) acetate polymer gels in as-received form as well as in solution. Appropriate experimental parameters were found and selected for use during future experiments to monitor the cross-linking reaction between HPAm and Cr(III) acetate. These parameters are strongly dependent on the concentration of cross-linker. Therefore, the concentration of Cr(III) acetate is the most critical variable in the process of characterizing HPAm/Cr(III) acetate polymer gels using ^{1}H NMR. This study also indicated that low-field NMR provides useful information about the distribution of HPAm solutions and Cr(III) acetate solutions when placed within porous media such as glass beads, unconsolidated Berea sandstone, and unconsolidated Stoney Creek sandstone.

It was demonstrated that the oxygen scavenger (Na_2SO_3), at a concentration of 0.01 wt%, does not have a significant effect on the [1]H T_2 relaxation time of DIW. Likewise, at Alcoflood 935 concentrations lower than or equal to 2 wt%, the polymer solutions exhibit similar T_2 in the presence of glass beads. Although the bulk T_2 values of polymer solutions were also similar, they tend to slightly decrease as the polymer concentration increased.

Despite the paramagnetic properties of Cr(III) acetate, the NMR spectrometer of this study was capable of detecting changes in bulk T_2 values of cross-linker solutions when the concentration of Cr(III) acetate was lower than or equal to 0.3 wt%. However, in the presence of glass beads and at a concentration of 0.3 wt%, the effect of the Cr(III) paramagnetism dominated the effect of pore wall surface relaxation.

The presence of paramagnetic ions and ferroan phases in Berea sandstone and Stoney Creek sandstone greatly reduced the T_2 values of the polymer solutions. Therefore, further work is required because of the complex composition of these sandstones. In particular, it is important to isolate each sandstone component to determine the effect that each mineral has on the T_2 values.

REFERENCES

[1] Sydansk, R. (2006). Polymers, gels, foams, and resins. In *SPE Petroleum Engineering Handbook*. Richardson, Tex.: Society of Petroleum Engineers. Submitted.

[2] Lake, L. W. (1989). *Enhanced Oil Recovery*. Englewood Cliffs, N.J.: Prentice Hall.

[3] Canada. National Energy Board. (2005). Estimated supply of Canadian crude oil and equivalent. Available at http://www.neb.gc.ca/Statistics/CrudeOil_PetroleumProducts/2005/esccoe05.xls.

[4] Canada. National Energy Board. (1999). *Canadian Energy Supply and Demand to 2025*. Calgary: The Publication Office of the National Energy Board.

[5] Canada. National Energy Board. (2004). *Canada's Oil Sands: Opportunities and Challenges to 2015*. Calgary: The Publication Office of the National Energy Board.

[6] Van As, H. and D. Van Dusschoten. (1997). NMR methods for imaging of transport processes in micro-porous systems. *Geoderma* **80**, 389–403.

[7] Hommans, S. W. (1992). *A Dictionary of Concepts in NMR*. Oxford: Clarendon Press.

[8] Coates, G., L. Xiao, and M. Prammer. (1999). *NMR Logging Principles and Applications*. Houston: Halliburton Energy Services.

[9] Bakmutuv, V. I. (2004). *Practical NMR Relaxation for Chemists*. Hoboken, N.J.: John Wiley.

[10] Zimmerman, J. R. and W. E. Brittin. (1957). Nuclear magnetic resonance studies in multiple phase systems: Lifetime of a water molecule in adsorbing phase on silica gel. *J. Phys. Chem.* **61**, 1328–1333.

[11] Wang, X., S. Ghoi, and W. Kerr. (2004). Effect of gluten content on recrystallisation kinetics and water mobility in wheat starch gels. *J. Sci. Food Agric.* **84**, 371–379.

[12] Lees, T. J. and B. Balcom. (2003). Magnetic resonance imaging of spatially resolved acrylamide photopolymerization. *Magn. Reson. Chem.* **41**, 229–236.

[13] Lockhart, T. P. (1991). Chemical and structural studies on $Cr+3$/polyacrylamide gels. SPE paper no. 20998 presented at SPE International Symposium on Oilfield Chemistry, Anaheim, Calif.

[14] Broseta, D., O. Marquer, N. Blin, and A. Zaiton. (2000). Rheological screening of low-molecular-weight polyacrylamide/Cr (III) acetate water shutoff gels. SPE paper no. 59319 presented at SPE/DEO Improved Oil Recovery Symposium, Tulsa, Okla.

[15] Romero-Zerón, L. B. (2004). Characterization of crosslinked gel kinetics and gel strength using NMR. SPE paper no. 86548 presented at SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, La.

[16] Prud'homme, R. B., J. T. Uhl, J. P. Poinsatte, and F. Halverston. (1983). Rheological monitoring of the formation of polyacrylamide/$Cr+3$ gels. *Soc. Pet. Eng. J.* **24**, 804–808.

[17] Liu, J. and R. S. Seright. (2001). Rheology of gels used for conformance control in fractures. *SPE J.* **6**(2), 120–125.

[18] Grattoni, C. A., H. H. Al-Sharji, C. Yang, A. H. Muggeridge, and R. W. Zimmerman. (2001). Rheology and permeability of crosslinked polyacrylamide gel. *J. Colloid Interface Sci.* **240**, 601–607.

[19] Nijenhuis, K. (2001). Crosslink nature in Cr(III)-polyacrylamide gels. *Macromol. Symp.* **171**, 189–200.

[20] Reddy, B. R., L. Eoff, D. Dalrymple, K. Black, D. Brown, and M. Rietjens. (2003). A natural polymer-based cross-linker system for conformance gel systems. *SPE J.* **8**(2), 99–106.

[21] Bani, E. S., B. Tremblay, M. Polikar, B. Wiwchar, and H. Huang. (2003). Rheology of sandy polyacrylamide gels: Application to conformance. Paper no. 2003-190 presented at the Petroleum Society Canadian International Petroleum Conference, Calgary, Alberta.

[22] Sydansk, R. (1988). A new conformance-improvement-treatment chromium (III) gel technology. SPE/DOE paper no. 17329 presented at SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, Okla.

[23] Sydansk, R. A. (1990). Newly developed chromium (III) technology. *SPE Reserv. Eng.* **5**(3), 346–351.

[24] Blumich, B. (2005). *Essential NMR*. Berlin: Springer.

[25] Butler, J. P., J. A. Reeds, and S. V. Dawson. (1981). Estimating solutions of first kind integral equations with nonnegative constrains and optimal smoothing. *SIAM J. Numer. Anal.* **18**, 381–397.

[26] Malachosky, E. (1997). Status report: Oil field copolymers. *Pet. Eng. Int.* **70**, 50–53.

[27] Allen, D., C. Flaum, T. S. Ramakrishan, J. Bedford, K. Castelijns, D. Fairhurst, G. Gubelin, C. C. Minh, M. A. Norville, M. Seim, T. Pritchard, and R. Ramamoorthy. (2000). Trends in NMR logging. *Oil Field Rev.* **12**(3), 2–12.

[28] Schlumberger. (2006). Bound-fluid log. Available at http://www.glossary.oilfield.slb.com/search.cfm.