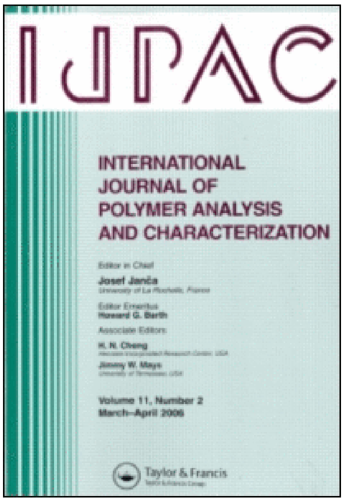

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^{1}H NMR Relaxation Time, T_2, Distribution of HP Am/Cr(III) Acetate Gels in Glass Beads

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SHORT COMMUNICATION

^{1}H NMR Relaxation Time, T_2, Distribution of HPAm/Cr(III) Acetate Gels in Glass Beads

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Abstract: ^{1}H nuclear magnetic resonance (^{1}H NMR) was used to monitor changes in the transverse relaxation time (T_2) of solutions formulated at 40°C with partly hydrolyzed polyacrylamide (HPAm) and Cr(III) acetate 50% active in bulk and in the presence of glass beads. ^{1}H NMR detected changes in T_2 that may be related to the distribution and changes in the gel's H species mobility within the porous medium.

Keywords: ^{1}H NMR; HPAm; Cr(III) acetate; Polymer gels; T_2 distribution; Porous media

INTRODUCTION

Nuclear magnetic resonance (NMR) tools are noninvasive and nondestructive and can be applied in porous media.[1,2] Vargas-Vasquez et al. are currently investigating the use of ^{1}H NMR to characterize gels formulated with hydrolyzed polyacrylamide (HPAm) and Cr(III) acetate 50% active.[3,4] They found that although Cr(III) is paramagnetic, ^{1}H NMR

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detects T_2 changes in solutions with a concentration of Cr(III) acetate 50% active lower than 2000 mg/L placed in glass beads.[3] The objective of this work is to monitor HPAm/Cr(III) acetate solutions in bulk and in a porous medium at 40°C using ^{1}H NMR. The T_2 relaxation rate of H species within porous media can be described as the combination of T_2 from H species with restricted motion, in small pore spaces or bound to the pore walls, and T_2 from more mobile H species in large pore spaces. Hence, $1/T_{2\ \mathit{observed}} = (1 - P_b)/(T_{2\ \mathit{more\ mobile\ H}}) + P_b/T_{2\ \mathit{H\ with\ restricted\ motion}}$ where P_b is the proton fraction of H species with restricted motion. The ^{1}H NMR signal decays following a multi-exponential (distributed exponential or DXP) model.[3] Thus, the hypothesis of this study is that ^{1}H NMR detects T_2 changes in HPAm/Cr(III) acetate gels formulated with less than 2000 mg/L of Cr(III) acetate 50% active in the presence of glass beads.

EXPERIMENTAL SECTION

A polymer solution of 7500 mg/L concentration of a commercial HPAm (Alcoflood 935 with degree of hydrolysis of about 10% and manufacturer-reported molar mass of 8×10^6–10×10^6 g/mol) prepared in distilled water was used. A concentration of 100 mg/L of Na_2SO_3 was added as oxygen scavenger. The HPAm solutions were cross-linked with commercial Cr(III) acetate ($Cr(OOCCH_3)_3$) 50% active in water supplied by McGean-Rohco, Inc. The cross-linker concentrations were 750 mg/L and 1500 mg/L, which correspond to HPAm to Cr(III) acetate 50% active weight ratios of 20/1 and 10/1. A mass of 0.8 g of glass beads (0.4 mm diameter) and 0.2 g of HPAm/Cr(III) acetate solution was placed in NMR vials. Samples were vacuumed and Teflon plugs were placed at the sample surface inside the vials. Teflon tape was applied around the vials' caps to avoid evaporation. Three sister samples of each formulation were tested using a Bruker Minispec model mq10 NMR Analyzer and a CPMG (Carr, Purcell, Meiboon, and Gill) pulse sequence to measure T_2. A distributed exponential (DXP) routine based on the Butler-Reeds-Dawson algorithm[5] was used to generate a spectrum of the T_2 values present in the samples. ^{1}H NMR measurements were also conducted on bulk samples and their T_2 decays fitted a mono-exponential model. To observe changes in the gel-strength codes at 40°C, bottle testing using Sydansk's gel-strength code[6] was conducted.

RESULTS AND DISCUSSION

Figure 1 depicts the DXP fitting of the HPAm/Cr(III) acetate samples 1.5 and 24 h after formulation. Each solution is characterized by two

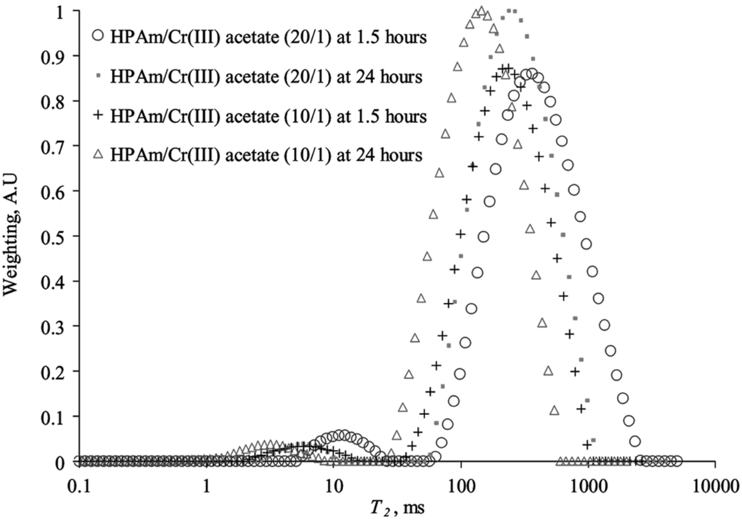

Figure 1. T_2 distribution of HPAm/Cr(III) acetate solutions in glass beads at 40°C. CPMG parameters: echo time = 0.25 ms, recycle delay = 9 s, echoes = 12500, scans = 258, and measuring time = 55 min.

distinct peaks. The first peak represents the gel-forming solution located in the smallest pore spaces and the second peak corresponds to the solution in the biggest pore spaces. Even though the HPAm/Cr(III) acetate (10/1) and the HPAm/Cr(III) acetate (20/1) solutions have the same fluidity at 1.5 h (Table 1), the T_2 distribution of the 10/1 system is

Table 1. Changes in the gel-strength codes[6] of HPAm/Cr(III) acetate gels formulated at 40°C

	HPAm to Cr(III) acetate 50% active weight ratio	
Time (hours)	10/1	20/1
0	A	A
1.5	A	A
4.1	B	A
8	C	B
13	D	B
24	E	C
48	F	D
72	G	D

A, no detectable gel formed; B, highly flowing gel; C, flowing gel; D, moderately flowing gel; E, barely flowing gel; F, highly deformable non-flowing gel; G, moderately deformable non-flowing gel.

represented by a spectrum with shorter T_2 values than those of the 20/1 system because the concentration of Cr(III) acetate is inversely related to T_2.[3] The T_2 values are higher at 1.5 h than at 24 h for both formulations, and no changes were observed after 24 h. T_2 of bulk samples also decreased with time, and the lowest values were detected at 24 h. T_2 remained stable from 24 to 72 h (data not shown). As the solutions aged, the reduction in the T_2 values might be caused by a decrease in the mobility of the H species due to the gelation reaction. The complex viscosity of HPAm/Cr(III) acetate formulations that form a continuous gel network increases as the gelation reaction proceeds, restricting the motion of H species.[4] The HPAm/Cr(III) acetate systems studied experienced changes in the gel-strength code and fluidity (Table I). During the first 24 h, the solutions changed from highly flowing gel to flowing gel, for the 20/1 system, and to barely flowing gel for the 10/1 system. Although changes in the gel fluidity contribute to the reduction of the T_2 values, it has been found that the Cr(III) acetate complex in solution undergoes chemical changes that contribute to T_2 reduction as well.[4] Hence, the combined effect of complex viscosity changes, Cr(III) acetate chemistry, and Cr(III) paramagnetism reduces the T_2 values of HPAm/Cr(III) acetate solutions in bulk. In glass beads, T_2 is also affected by surface relaxation. In reservoir sandstone containing paramagnetic minerals, T_2 will be further reduced.[3] Therefore, the CPMG sequence used here to measure T_2 may not be applicable for the characterization of HPAm/Cr(III) acetate in reservoir rocks. Allen et al.[2] reported a new multi-wait CPMG to improve the short T_2 measurement at reservoir conditions.

CONCLUSION

^{1}H NMR detected reduction in the T_2 values of HPAm/Cr(III) acetate samples in bulk and in glass beads during the first 24 h after formulation. Two distinct peaks were observed in the spectra of the samples in glass beads representing the distribution of the gel's H species within the porous medium. These results support the stated hypothesis, yet more research is needed to better understand the effects of gel complex viscosity and Cr(III) acetate chemistry on T_2 changes. Although gel-strength code changes were observed during 72 h, T_2 remained stable after 24 h.

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