Slow-Gelling Cr^{+3}/Polyacrylamide Solutions for Reservoir Profile Modification: Dependence of the Gelation Time on pH

THOMAS P. LOCKHART,* PAOLA ALBONICO, and GIOVANNI BURRAFATO

Eniricerche S.p.A., 20097 San Donato Milanese, Italy

SYNOPSIS

Systematic studies of the gelation of both buffered and unbuffered aqueous Cr^{+3}/polyacrylamide solutions show that the gelation time is a strong function of pH, increasing by about one order of magnitude per unit decrease in pH for polyacrylamides less than about 7.5% hydrolyzed. The gelation rate also depends strongly on the Cr^{+3} concentration, the degree of polymer hydrolysis, and temperature. At 25°C, gelation delays of more than 10 months have been obtained; the maximum delay observed at 60°C is about 1 month and at 90°C 1 d. The resistance of buffered gel solutions to change in pH results in significantly longer gelation times at 90°C and low pH than for identical unbuffered solutions; at lower temperatures, however, the differences are insignificant. Most importantly, the use of low pH to control the gelation time of Cr^{+3}/polymer solutions provides an attractive, inexpensive substitute for the environmentally unacceptable Cr^{+6}/reductant method currently employed for profile modification treatments.

INTRODUCTION

Fluids injected into heterogeneous reservoirs flood selectively the strata of higher permeability, bypassing substantially or completely the mobile oil-containing zones of lower permeability. This behavior imposes major constraints on the total recovery of oil from such reservoirs using water or chemical flooding techniques. For these reservoirs, there is a strong incentive to develop profile modification technologies by which flow of the injected fluids can be directed toward the lower permeability strata. One important profile modification procedure of demonstrated effectiveness involves the formation of aqueous polymeric gels within the watered-out, high-permeability zones of a reservoir.[1] Once in place, such gels greatly reduce the permeability of the treated zones toward fluids injected subsequently.

The gels most frequently employed are composed of a dilute aqueous solution of either partially hydrolyzed polyacrylamide or the biopolymer Xantham gum, and a crosslinking agent.[1] Systems crosslinked with Cr^{+3} have received particular attention not only because of their good physical properties but also because of a convenient redox chemistry involving Cr^{+6}, by means of which the crosslink-forming Cr^{+3} ion can be produced at a slow and predictable rate.[2,3]

Unfortunately, the negative health effects of chromium in its +6 oxidation state[4-6] is a serious environmental issue that places in doubt the continued use of the Cr^{+6}-reductant chemistry in profile modification treatments. Although the Cr^{+3} ion is of relatively low toxicity,[4-6] the rapid gelation of Cr^{+3}/polymer solutions under most conditions renders them unsuitable for profile modification applications. Considerable effort has therefore been devoted to the search for techniques that can provide slow-gelling aqueous Cr^{+3}/polymer solutions.[7,8] While results for chromium(III) triacetate/polyacrylamide solutions give good gel delays at low to moderate temperatures,[8] to date no Cr^{+3}/polymer systems have been described that provide sufficient control over gel time to permit their complete sub-

stitution for the Cr^{+6}-reductant system.

We are engaged in studies on the chemistry and physical properties of Cr^{+3} crosslinked polymer gels,[9-12] one goal of which is to identify new methods that can provide for slow gelation of Cr^{+3}/polymer solutions even at elevated temperature. Our studies[9,12] of the influence of pH on the gelation of aqueous Cr^{+3}/polyacrylamide solutions have revealed that gelation occurs as low as pH 2, significantly below the lower limit (pH 3–4.5) reported in the patent and technical literature.[13-15] Further, we have found a strong inverse dependence of the rate of gelation on pH. In the present article, we describe systematic studies of the influence of pH on the gelation rate as a function of the polymer hydrolysis level, concentration of Cr^{+3}, and temperature. The results demonstrate that the solution pH provides a particularly simple and effective parameter by which technologically useful gelation delays of Cr^{+3}/polymer solutions can be obtained at temperatures up to 90°C.

EXPERIMENTAL

Materials

Three commercial polyacrylamide samples have been employed, one obtained from Aldrich (cat. 18,127-7, lot. 80266MP) of nominal M_w 5–6 $\times$ 10^6, and two different samples of Lamberti Lamflood 0175 (produced by Allied Colloids) of M_w 6 $\times$ 10^6 as estimated from rheological measurements. ^{13}C NMR was employed to determine the degree of hydrolysis of the polymers[16] and showed the Aldrich polymer to be 0.7% hydrolyzed and the Lamflood polymers to be 4.2 and 7.5% hydrolyzed, respectively. Cr^{+3} solutions were prepared from either $CrCl_3$ or $Cr(NO_3)_3$. Aqueous solutions of the former were allowed to age for several days, until the $Cr(H_2O)_6^{+3}$ had formed, prior to use. Buffers were obtained from commercial sources and used without further purification.

Sample Preparation

Appropriate concentrations of a freshly prepared polymer stock solution (either 10,000 or 12,000 ppm) filtered through a 5-μm Millipore filter, a stock Cr^{+3} solution (1,000 ppm), and deionized water were combined in small vials (12 cm in height $\times$ 1.8 cm diameter) to give 10 mL final gel solution containing 50–400 ppm Cr^{+3} and 8,000 ppm polyacrylamide. Buffered gel solutions were prepared in the same manner, with the addition of an appropriate amount

of stock buffer solution whose pH had been adjusted previously with aqueous HCl, $HClO_4$, or NaOH solutions. The concentration of buffer in the final gel solutions ranged between 0.06–0.015M; the higher concentrations were necessary to prevent pH change in the solutions at 90°C. Measurements of pH made with a standard pH electrode were found to be unreliable after the onset of gelation. Accurate pH determinations on partially and even fully formed gels could be made, however, by using a microelectrode (Metrohm EA 125).

Vials containing the Cr^{+3}/polymer solutions were aged in either a circulating water bath at 25°C or a forced air oven at 60 and 90°C. To reduce the influence of the heat-up time on the gelation rates at 60 and 90°C, the samples with gelation times of less than about 1 d were preheated in a thermostatted water bath and then placed in the oven.

The pH of the Cr^{+3}/polymer solutions was redetermined after gelation. The pH of the nonbuffered solutions were found to have changed by up to 1 pH unit at the time of gelation, the variation in pH being more significant at 60 and 90 than at 25°C. For the buffered solutions, the pH was not found in any case to have varied by more than 0.3 pH units at the time of gelation; in most cases, the pH at gelation was within 0.15 pH units of the starting value.

Gelation Times

The gelation time was judged by visual inspection. Solutions were defined as gelled when they first displayed a significant elastic behavior and resistance to flow in the sample tubes. Comparison of the gel time judged by eye with that determined from rheological measurements in dynamic conditions[17] were in good agreement. Measurements on solutions of polymers 4.2 and 8.5% hydrolyzed showed that the elastic modulus, G', at the time of gelation varied within a narrow range from about 1.0–1.7 Pas.

RESULTS

Representative gelation times of solutions of Cr^{+3} (50 ppm) and polyacrylamide (8,000 ppm, 0.7% hydrolyzed) in buffered solution between pH 2.5 and 5.5 at 25 and 60°C are given in Table I. The selection of buffering agents was based on the criterion that they should be substantially inert toward Cr^{+3} ions.[9-12] A variety of observations indicated that the buffers employed do not themselves influence the gelation chemistry under the conditions reported.

Table I   Effect of pH on Gelation Time of Buffered Solutions Containing 50 ppm Cr^{+3} and 8,000 ppm Polyacrylamide (0.7% Hydrolyzed)
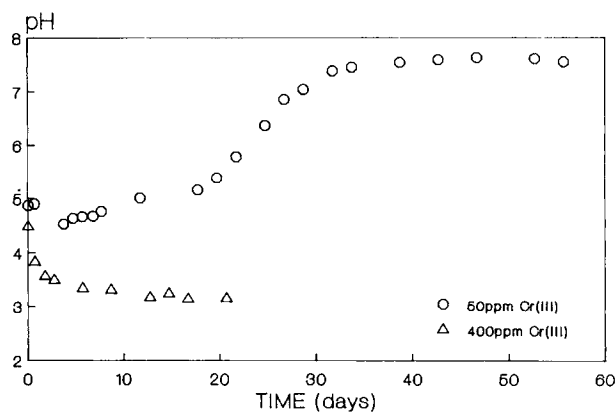
pH	Buffer [conc. (M)]	Gel Time (d)	
		25°C	60°C
2.3	3-Chloropyridine (0.06)	a	32
2.6	2-Nitrobenzoic acid (0.008)	b	22
3.2	3-Chloropyridine (0.03)	315	18
3.8	2-Nitrobenzoic acid (0.008)	56	8
4.1	2-Chlorobenzoic acid (0.008)	19	2
4.7	2-Chlorobenzoic acid (0.008)	11	2
5.3	Pyridine (0.03)	< 1	< 1
6.1	Pyridine (0.06)	< 0.5	< 0.5

a Not gelled after 315 d.
b Not gelled after 176 d.

The maximum pH investigated in these experiments, 6.1, was chosen so as to avoid complications arising from the precipitation of Cr(OH)$_3$(H$_2$O)$_3$.[9,11]

Experiments on unbuffered solutions of polyacrylamide (8,000 ppm, 0.7% hydrolyzed) and 50 or 400 ppm Cr^{+3} showed that the pH is unstable over time at 60°C (Fig. 1). Two distinct phenomena can be identified in the experimental curves. On a time scale comparable with that for gelation, there is a marked decrease in the solution pH (from 0.3-1 pH units), the extent of which depends on the concentration of Cr^{+3} employed. Similar observations have been described by Willhite and coworkers.[14] We presume that this pH drop reflects chemistry involving Cr^{+3}. A second process leads to a slow pH rise in the gel over longer periods of time (upper curve, Fig. 1). The pH of polyacrylamide solutions
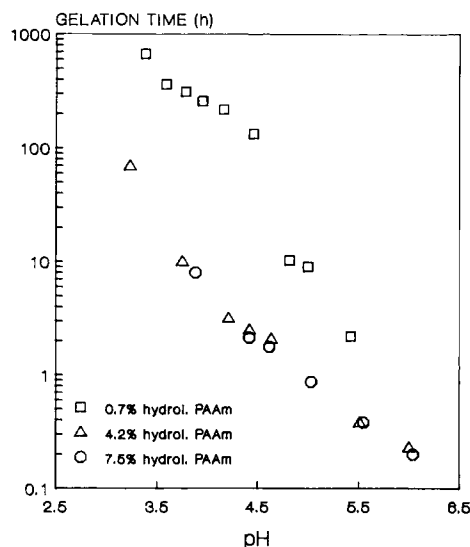
(without Cr^{+3}) was found to undergo a similar slow rise under the same conditions. This pH change is attributed tentatively to low levels of polymer hydrolysis by which ammonium acrylate ion pairs are produced.

Figure 2 shows the influence of the degree of polyacrylamide hydrolysis on the gelation time at 25°C for buffered solutions containing 100 ppm Cr^{+3} at 25°C over a wide range of pH. The polyacrylamides used were 0.7, 4.2, and 7.5% hydrolyzed and were all of approximately the same molecular weight (5–6 × 10^6). The temperature dependence of the gelation time from 25-90°C is illustrated in Figure 3 for 0.7% hydrolyzed polyacrylamide in the presence of 50 ppm Cr^{+3} (buffered solutions). Typical gelation time curves as a function of pH in the presence of 50 and 100 ppm Cr^{+3} are shown in Figure 4 for a solution of polyacrylamide 4.2% hydrolyzed at 25°C.

DISCUSSION

Our studies of gelation as a function of pH show that buffered and nonbuffered aqueous Cr^{+3}/polyacrylamide solutions form gels down to at least pH 2.0. At 25°C, extremely long gelation times have been found at low pH: A solution of polyacrylamide 0.7% hydrolyzed (8,000 ppm) and Cr^{+3} (50 ppm) buffered at pH 3.2 gelled in 315 d. An identical Cr^{+3}/polyacrylamide composition at pH 2.3 remained perfectly fluid after 315 d (Table I). When this latter

Figure 1   pH variation over time in unbuffered aqueous solutions of 0.7% hydrolyzed polyacrylamide (8,000 ppm) and Cr^{+3} (50, 400 ppm) at 60°C.

Figure 2   Gelation time of buffered aqueous solutions of Cr^{+3} (100 ppm) and 0.7, 4.2, and 7.5% hydrolyzed polyacrylamide (8,000 ppm) at 25°C as a function of pH.
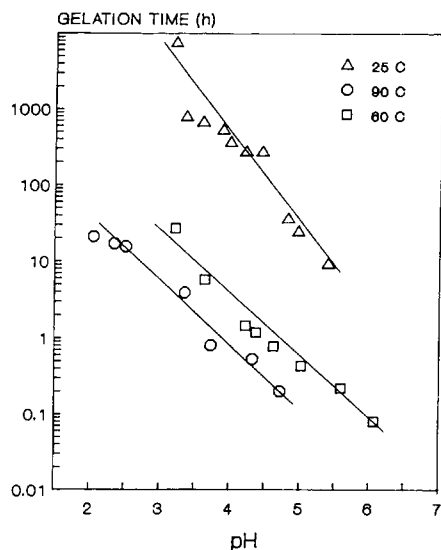
Figure 3 Gelation time of buffered solutions of Cr^{+3} (50 ppm) and 0.7% hydrolyzed polyacrylamide (8,000 ppm) as a function of pH and temperature.

sample was subsequently heated at 60°C, it gelled after an additional 20 d, indicating that the solution was chemically undegraded and implying that it would have gelled eventually at 25°C.

At 60°C, gelation times were markedly shorter than those at 25°C. Nevertheless, below pH 4 gelation times are long enough (up to 32 d) to permit the in-depth placement of Cr^{+3}/polymer solutions within a reservoir at 60°C prior to the onset of gelation. At 90°C, the maximum gelation time, 21 h, was obtained for a solution containing 50 ppm Cr^{+3} and 0.7% hydrolyzed polyacrylamide. Delays of this magnitude are appropriate for near-well gel treatments.

It was anticipated that the unstable pH of the gelation solutions (Fig. 1) might have a significant influence on the rate of gelation. A comparison of the gelation times for unbuffered and fully buffered solutions, however, showed negligible differences up to 60°C. At 90°C, where polymer hydrolysis occurs at a significant rate,[18] significant variations in the gelation times for buffered and unbuffered solutions were found below pH 3. At pH 2.1, for example, a nonbuffered solution gelled in 9.3 h whereas a buffered one gelled in 21 h. Other than for treatments in high-temperature reservoirs, the resistance of buffered solutions to change in pH may offer advantages in the field as a guarantee against pH changes arising from mixing of the gellable solution with connate water (which typically has pH > 4) or from contact with the reservoir rock. The buffered

compositions also facilitate the process of obtaining a final gellable composition having the desired pH.

The gelation time displays an interesting dependence on the degree of hydrolysis of the polyacrylamide (Fig. 2). The longest delays at all temperatures were obtained with the polyacrylamide having the lowest degree of hydrolysis. With an increase in the degree of hydrolysis from 0.7 to 4.2%, the gelation times decreased significantly (by an average factor of about 12) for both 50 and 100 ppm Cr^{+3}. Surprisingly, the gelation times of polyacrylamides 7.5 and 4.2% hydrolyzed were virtually superimposable. This result might reflect either electrostatic retardation of the gelation reaction or a change to zero-order dependence on the degree of polymer hydrolysis above 4.2% hydrolysis. Observations on the influence of counterions on the gelation time, which might provide insight into the possibility of an electrostatic retardation, were ambigous: Salinity (NaCl) was observed to have an insignificant influence on the rates of gelation over the range 0–2 M for polyacrylamides 0.7–7.5% hydrolyzed. In contrast, large accelerating effects were observed for polymers greater than 10% hydrolyzed.

The concentration of Cr^{+3} is another important variable that influences the gelation time (Fig. 4). In practical terms, the slowly forming gels obtained with 50 ppm Cr^{+3} are of moderate strength [elastic moduli 1–16 Pas (1 Hz)] and should be suitable for most in-depth profile modification treatments. The stronger gels obtained with 100 ppm Cr^{+3} may be
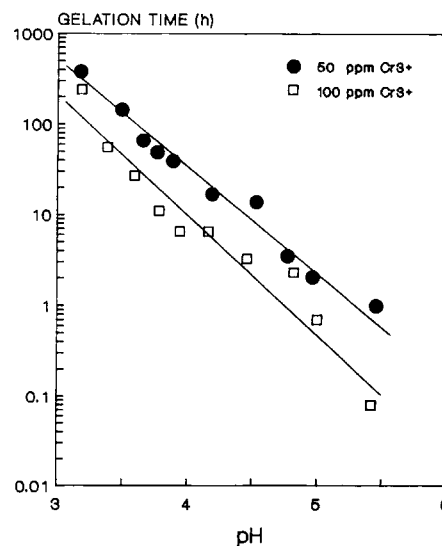

Figure 4 Gelation time as a function of pH and Cr^{+3} concentration for buffered solutions of 4.2% hydrolyzed polyacrylamide (8,000 ppm).

preferred for near-well applications, where the gels are exposed to greater physical stress.

Chemical Basis for the Retardation of Gelation at low pH

It is interesting to consider the chemical basis for the striking pH dependence of the gelation rate of Cr^{+3}/polymer solutions. Prud'homme[19] et al. interpreted the results of rheological studies of the gelation kinetics of Cr^{+6}/reductant/polyacrylamide solutions (under conditions where the reduction of Cr^{+6} to Cr^{+3} was believed to be fast) in terms of a rate determining dimerization reaction of Cr^{+3}. This was postulated to occur either between two Cr^{+3} ions in solution prior to reaction with the polymer, or between a polymer-bound Cr^{+3} with a second Cr^{+3} (either free or bound). Shu[20] showed that the addition of a solution containing preformed Cr^{+3} dimers and other oligomers to a solution of Xanthan gum gave a greatly accelerated gelation rate relative to a fresh Cr^{+3} solution. This result was taken as support for a mechanism involving rate determining dimerization of Cr^{+3} ions in solution (one of the two mechanisms described by Prud'homme), as illustrated in Figure 5.

The formation of Cr^{+3} dimers is known from the chemical literature to take place through the reaction of Cr^{+3} hydroxides [Cr(OH)$_n$(H$_2$O)$_{6-n}$],[21-23] whose concentration is determined by rapid, pH-dependent equilibria. In terms of the proposed mechanism shown in Figure 5, therefore, the rate of the direct reaction of Cr(H$_2$O)$_6^{+3}$ (k_1) or Cr(OH)$_n$(H$_2$O)$_{6-n}$ (k_2) with the polymer must be slower than the dimerization reaction (k_3), which leads subsequently to gelation (k_4). The strong, direct dependence of the rate of Cr^{+3} dimerization on pH is qualitatively in accord with the long gelation times found at low pH.

It is possible to calculate the rate of dimerization as a function of pH by making use of recently published[23] equilibrium and kinetic constants for the Cr^{+3} dimerization reaction. By normalizing the
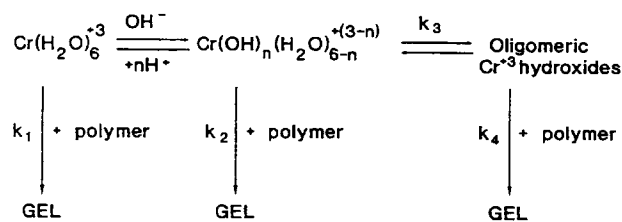

$$\mathrm{Cr(H_2O)_6^{+3}} \underset{+nH^+}{\overset{OH^-}{\rightleftharpoons}} \mathrm{Cr(OH)_n(H_2O)_{6-n}^{+(3-n)}} \overset{k_3}{\rightleftharpoons} \text{Oligomeric Cr}^{+3}\text{ hydroxides}$$

k_1 ↓ + polymer k_2 ↓ + polymer k_4 ↓ + polymer

GEL   GEL   GEL

Figure 5 Proposed mechanism showing the competitive pathways for Cr^{+3} oligomerization and polymer crosslinking in aqueous solution.
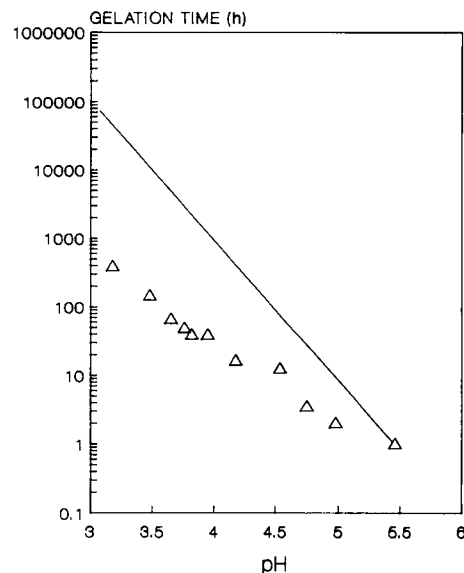

GELATION TIME (h)

Figure 6 Plot comparing the pH dependence of the rate of Cr^{+3} dimerization in aqueous solution (straight line), with gelation data (circles) for buffered solutions of Cr^{+3} (50 ppm) and 4.2% hydrolyzed polyacrylamide (8,000 ppm) at 25°C. The experimental gelation data and calculated dimerization curve have been normalized at pH 5.4.

theoretical curve for Cr^{+3} dimerization (expressed in seconds) with the gelation time data for Cr^{+3}/polyacrylamide solutions at an arbitrary pH value, their relative pH dependences can be compared. Figure 6 shows data obtained for a solution 50 ppm in Cr^{+3} and 8,000 ppm in polyacrylamide 4.2% hydrolyzed normalized with the theoretical curve at pH 5.4. The experimental gelation data clearly display a strongly reduced dependence on pH relative to the Cr^{+3} dimerization reaction. Very similar results were obtained for 100 ppm Cr^{+3} and for the 0.7% hydrolyzed polyacrylamide at 50 and 100 ppm.

This result implies strongly that *the gelation reaction mechanism for the compositions examined in the present study does not involve rate determining dimerization of Cr^{+3} over the pH range studied.* A plausible alternative gelation mechanism is one in which the rate-determining step for crosslinking involves predominantly *monomeric* Cr^{+3}. In this case, the pH dependence could be explained by assuming that the chromium hydroxides, Cr(OH)$_n$(H$_2$O)$_{6-n}$, are of higher reactivity ($k_2 < k_1$ in Fig. 6) toward the polymer than is Cr(H$_2$O)$_6^{+3}$, since the latter is favored by low pH.

Other qualitative insight into the gelation mechanism is provided by the observation that the gelation time depends on the degree of hydrolysis of the

polyacrylamide used for polymers less than 4.2% hydrolyzed. This result indicates that the gelation reaction has a nonzero kinetic order in the number (concentration) of polymer reactive groups in solution, at least for polyacrylamides hydrolyzed less than 4.2%.

CONCLUSIONS

The present studies demonstrate that the gelation time of Cr^{+3}/polyacrylamide solutions is strongly dependent on pH. Other variables directly influencing the gelation time include the Cr^{+3} concentration, the degree of hydrolysis of the polymer, and the temperature. The slow gelation of Cr^{+3}/polyacrylamide solutions at low pH is promising for use in profile modification treatments. For reservoirs at relatively low temperature, adjustment of the solution pH provides virtually unlimited control over gelation time. For moderate temperature reservoirs (up to 60°C or somewhat above), gelation times of several weeks to 1 month can be obtained. The modest gelation delays achieved at 90°C are appropriate for near-well treatments. The most important implication of the present study is that the gelation delays obtainable for Cr^{+3}/polymer solutions at low pH should permit the widescale substitution of Cr^{+3} for the environmentally unattractive Cr^{+6}-reductant system presently in use for deep profile modification treatments.

The influence of pH on the gelation time of Cr^{+3}/polyacrylamide solutions can be attributed principally to its effect on the chemistry of the Cr^{+3} ion. Qualitatively similar results are therefore to be expected for *any* Cr^{+3} crosslinked polymer system, including those formed with acrylamide copolymers and biopolymers. A new gelation mechanism based on a rate determining reaction first order in Cr^{+3} has been proposed to account for the gelation of Cr^{+3}/polyacrylamide solutions. Additional studies of the crosslinking kinetics and mechanism at low pH are presently underway.

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