A Study of Cr(III)-Polyacrylamide Reaction Kinetics by Equilibrium Dialysis

A kinetic model was developed to describe the rate of reaction between chromium(III) and polyacrylamide (PAAm) that leads to the crosslinking or gelation of the polymer. Cr(III) was added directly to solutions of polyacrylamide which had a degree of hydrolysis of approximately 4%. The unreacted Cr(III) was separated from that which had reacted with the polymer by equilibrium dialysis and measured by atomic absorption.

The rate of the reaction was described by an empirical model based on the assumption of invariant polymer group concentration during the reaction. The order of reaction was determined to be 1.32 for Cr(III), 0.8 for the polymer group, and −1.0 for hydrogen ion. Modifications were made to the model to allow for variation during reaction of the concentration of the polyacrylamide reactive group. The modified model accurately described the reaction rate for Cr(III) concentration ranging from 0.19 to 1.2 mM, polyacrylamide concentrations from 6.9 to 69 mM, and pH values from 4.0 to 5.5.

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Introduction

The crosslinking of a water-soluble polymer by a metal ion for permeability modification of oil reservoirs is an effective technique to improve reservoir sweep efficiency in a displacement process and thereby recover additional crude oil (Hessert and Fleming, 1979). In a crosslinked polymer treatment, a polymer solution and crosslinking agent are injected together into the high permeability zones or fractures of the reservoir that were previously swept by a displacing fluid. The polymer solution reacts with the crosslinker to form a three-dimensional gel network which reduces the effective permeability of the swept zones. Displacement fluids injected after the polymer treatment are diverted into the lower permeability zones, thereby improving the overall sweep efficiency of the oil displacement process.

One method for the application of a gelled or crosslinked polymer treatment involves the crosslinking of polyacrylamide polymer by chromium(III) ion *in situ*. For this process, chromium is introduced in the (+6) valence state, usually as dichromate and is subsequently converted to the (+3) valence state by a reducing agent such as thiourea or sodium bisulfite. The Cr(III) then reacts with the polyacrylamide, followed by crosslinking of the polymer molecules to form a gel. The process is envisioned to occur by three reactions in sequence (Clampitt and Hessert, 1974):

1. A redox reaction controlling the generation of Cr(III) from Cr(VI).
2. Reaction of Cr(III) with the polyacrylamide.
3. Crosslinking of the polyacrylamide molecules to form a gel.

By controlling the rate of reduction of Cr(VI) to Cr(III), the gelation process can be delayed to allow placement of the gelling solution into specific portions of the reservoir. Critical to the success of the *in situ* gelation process is an understanding of the reaction kinetics governing both the redox and the Cr(III)-polymer reactions.

Although the redox and Cr(III)-polymer reactions occur *simultaneously*, it is believed that only the Cr(III) ion is responsible for the reaction with the polyacrylamide which causes gelation. Kinetic models and reaction studies that describe the reaction of Cr(III) with polyacrylamide are lacking. Knowledge of the rate of this reaction coupled with separate rate models for the redox and the crosslinking reactions could provide a means of predicting the performance of an *in situ* gelation process. For example, a reaction rate model for the rate of change of the crosslinking density of Cr(III)-polyacrylamide gels has been proposed (Prud'homme et al., 1983) which was developed from the kinetic theory of rubber elasticity. This model showed the rate of crosslink formation to be second order in Cr(III) and 2.7

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order in polyacrylamide. A model describing the rate of Cr(III) consumption by the polyacrylamide or chromium density of the gel, combined with a rheological model of the crosslinking density, could be used to predict the rate of gelation for designing crosslinked polymer treatments.

The work described in this paper involved an experimental study of the rate of reaction between Cr(III) and a polyacrylamide polymer having a low carboxyl content. The effects on the reaction rate of Cr(III) concentration, polyacrylamide concentration, and solution pH were examined. The rate data were used for the development of a kinetic model.

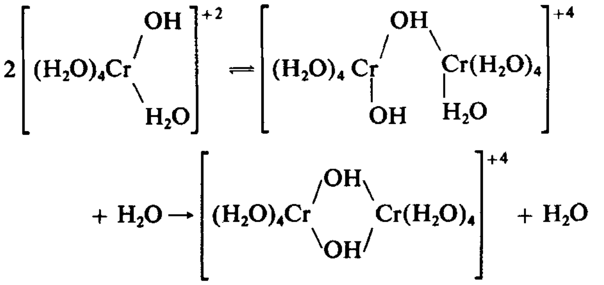
Chromium(III) chemistry

The chromium atom with a secondary valency of six can bond directly with up to six molecules or ligands. The Cr(III) species which causes gelation is known to exist in aqueous solution as a completely hydrated complex with six coordinated water molecules. This hexaaquochromium(III) complex was used in this work to study the gelation kinetics of the Cr(III)-polyacrylamide reaction. Although classified in the chemistry literature as kinetically inert, this chromium species is known to undergo slow ligand displacement reactions with other inorganic and organic ligands such as carboxyl. The hexaaquochromium(III) complex can also undergo a reaction in aqueous solution similar to base hydrolysis in which protons are lost from the coordinated water molecules according to Eq. 1 (Cotton and Wilkinson, 1980).

$$[Cr(H_2O)_6]^{+3} \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} [Cr(H_2O)_5OH]^{+2} \qquad (1)$$

The equilibrium of this reaction is shifted to the right by heating and the addition of base. The stepwise loss of a proton from additional water molecules can occur until a neutral species forms which can precipitate from solution (Thorstensen, 1969). The formation of insoluble chromium hydroxide precipitates has been observed in this laboratory to be detrimental to gel formation. The formation of hydroxyl products of this Cr(III) species can lead, however, to the formation of higher molecular weight chromium species by a process called olation.

Olation is a polymerization reaction resulting in the formation of polynucleate complexes which are composed of chains of Cr(III) ions connected by bridging hydroxyl groups. The olation reaction has been represented by Eq. 2 (Rollinson, 1966).



$$2\left[(H_2O)_4Cr(OH)(H_2O)\right]^{+2} \rightleftharpoons \left[(H_2O)_4Cr(OH)(OH)\,Cr(H_2O)_4(H_2O)\right]^{+4} + H_2O \rightarrow \left[(H_2O)_4Cr(OH)_2Cr(H_2O)_4\right]^{+4} + H_2O \qquad (2)$$

The loss of protons from the bridged hydroxyl groups, a process favored by heating or aging basic chromium solutions, is called oxolation. The oxolation reaction can account for the slow drop in pH of gelling solutions. The possibility of proton loss from water molecules in the olated complex can lead to the formation of higher molecular weight aggregates. It is not understood at this time if the formation of aggregates by olation is required for the crosslinking process. It is known that increasing the pH of the Cr(III)-polyacrylamide mixture favors olation and results in an increase in the gelation rate. It is believed that the Cr(III) species coordinates with functional groups on the polyacrylamide molecule before crosslinking can occur. A standard polyacrylamide is composed of amide functional groups with a small percentage of these groups hydrolyzed to carboxyl groups. The reaction of Cr(III) species with carboxylate is documented well in the literature and is believed to be the crosslinking mechanism for chrome tanning (Thorstensen, 1969). The early work of Hamm et al. (1958) showed Cr(III) complexes would coordinate strongly with carboxylate. No reference in the literature could be found for reactions between Cr(III) and amide functional groups. Although present in very low concentration, the reaction of Cr(III) species with the carboxyl groups on separate polyacrylamide molecules may be responsible for the crosslinking process. Other anions such as sulfate and chloride can compete with carboxylate for coordination with Cr(III) and may interfere with the gelation process.

Equipment and Procedures

Solution preparation

The polymer used for this work was a commercial sample of polyacrylamide obtained from Aldrich Chemical Company as a dry solid. The degree of hydrolysis, or percent of amide groups hydrolyzed to carboxylic acid groups, was found by Carbon 13 NMR to be less than 4%, but the precise value is not known. The active assay was determined by both size exclusion chromatography/UV absorption (Hunt et al., 1986) and by reprecipitation of a 1 wt.% solution into acetone followed by drying of the separated precipitate under vacuum to constant weight. An average assay determined from both procedures was used to calculate polyacrylamide solution concentrations.

A stock polymer solution was prepared for the kinetic experiments by mixing the solid polymer and 0.1 M KNO_3 solvent in a polyethylene bottle and shaking the mixture for three days using an orbital shaker until uniform solutions were obtained. The addition of an innocuous salt was required for the dialysis experiments to prevent an uneven distribution of Cr(III) across the semipermeable membrane and to reduce osmotic pressure effects caused by an immobile charged polyelectrolyte. Nitrate was found to be an anion having one of the least coordinating tendencies with Cr(III) and was expected to interfere least in the kinetic study. Solutions of $Cr(NO_3)_3 \cdot 9H_2O$ prepared in 0.1 M KNO_3 were the source of Cr(III). The solvent was filtered under vacuum through a 0.22 μm Millipore membrane filter.

Kinetic experiments

The equipment used for the kinetic studies consisted of a continuously stirred constant temperature batch reactor with pH control as shown in Figure 1. The reactor was a nominal 100 mL pyrex glass thermo-jacketed beaker with a magnetic stirrer. Water was circulated through the jacket of the beaker to maintain the reaction of 25°C ± 0.2°C using a temperature control bath.

The pH of the reaction was controlled to within ± 0.01 units

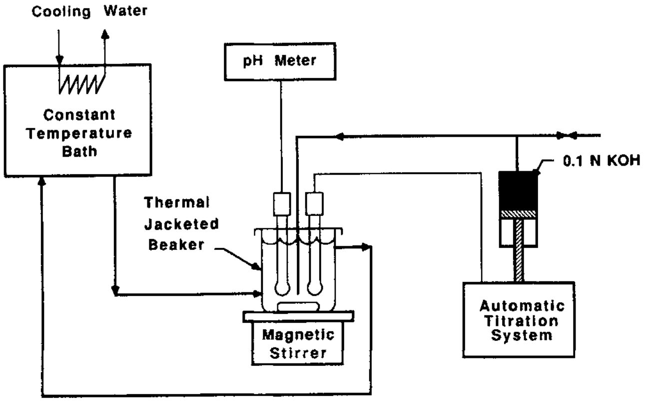


Figure 1. Constant temperature batch reactor for the kinetic studies.

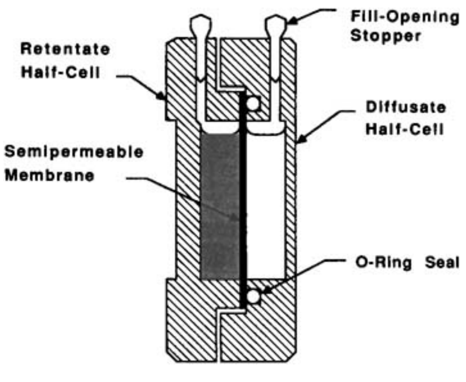


Figure 2. Equilibrium dialysis cell.

of the desired pH using a Fisher automatic titration system in pH-stat mode. Small amounts of a certified N/10 potassium hydroxide solution were added to the reaction mixture using the titration system to counterbalance a normally decreasing pH for the Cr(III)-polyacrylamide reacting system. The KOH solution was maintained under a dry, CO_2-free environment. A separate digital pH meter was used to simultaneously monitor the pH and provide a more accurate reading. A capillary teflon tube connected to the burette dispenser of the automatic titrator was immersed with the pH control electrode and positioned approximately 0.5 cm upstream of the tip of the electrode. Both vigorous stirring and the addition of KOH close to the sensing electrode were required to eliminate shifts in the pH of the reacting mixture.

For a typical kinetic experiment, 100 g total of a Cr(III)-polyacrylamide mixture was prepared. Enough of a nominal 1% polyacrylamide stock solution was added directly to the reactor and diluted by weight with 0.1 M KNO_3 to the desired final concentration, accounting for the later addition of the Cr(III) solution. After the diluted polymer had equilibrated to 25⊥C, the pH of the polymer was adjusted to the desired value with KOH or HNO_3 as needed. With the pH control system activated, a 500 ppm stock Cr(III) solution was slowly added by volume to the stirred polymer solution. During the Cr(III) addition, the pH stat system maintained the pH at the desired value by the addition of base.

Samples of the reacting mixture were removed throughout the reaction and diluted by weight with 0.1 M KNO_3 solvent to quench the reaction. The solvent had the same pH as that of the reacting mixture. An independent study (Hunt, 1987) showed a solvent-to-sample dilution ratio of 30 was adequate to quench reacting systems with Cr(III) concentrations of 1 and 1.2 mM (50 and 60 ppm). A proportionately smaller dilution factor was used for Cr(III) concentrations below 1 mM. The unreacted Cr(III) was then separated from that which had reacted with the polymer by equilibrium dialysis.

Equilibrium dialysis and chromium analysis

A schematic of a dialysis cell used for the separation is shown in Figure 2. The dialysis cell consisted of two teflon half-cells with a nominal volume in each half-cell of 5 cm^3. A Nucleopore polycarbonate semipermeable membrane positioned between the half-cells prohibited the movement of polymer from the retentate side, yet allowed the unreacted Cr(III) and solvent to migrate freely between the half-cells. The dialysis cells were assembled eight to a unit by clamping the cells together, each separated by a spacer.

For the dialysis process, 5 cm^3 of the quenched reacting mixture and 5 cm^3 of solvent were simultaneously placed into separate sides of the dialysis cell. The assembled dialysis units were placed in a constant temperature bath maintained at 25°C ± 0.1°C and rotated at 12.5 rpm. The rotation of the cells provided contact of the retentate and the diffusate with the complete surface of the membrane to speed up the separation process. After equilibrium in the diffusable solute was attained, a process which required three hours, the diffusates were removed from the dialysis cells, acidified with 0.2 mL concentrated HNO_3, and analyzed for Cr(III) concentration by AA. The acidification of the samples was required to prevent Cr(III) losses to containers found to occur at higher pH values. There was a small loss of Cr(III) to the membranes which increased with increasing pH. At a pH of 5.5, the largest value used, the loss was less than 5% (Hunt, 1987).

The Cr(III) concentration was measured using a Perkin-Elmer Model 460 Atomic Absorption (AA) Spectrophotometer at a wavelength of 358 nm in an air-acetylene flame. For each diffusate sample, ten AA readings were taken and averaged. The AA instrument was calibrated using solutions prepared from a 997 ppm chromium chloride standard obtained from EM Science. The calibration standards were prepared in 0.1 M KNO_3 at a pH of 2 and ranged in concentration from 0 to 10 ppm.

Kinetic model development

Measurement of the Cr(III) concentration in the diffusates at equilibrium enabled the monitoring of the unreacted Cr(III) concentration in the reacting mixture versus time. The kinetic data, in the form of either unreacted Cr(III) concentration or fractional conversion of Cr(III) vs. time, were analyzed by the differential method in which the fit of an assumed rate expression to the experimental data was tested. This rate expression was constructed in terms of each reactant and the order of reaction for each reacting species in the system was determined by a partial analysis of the rate equation.

The rate of reaction between Cr(III) and polyacrylamide was observed to be strongly influenced by the system pH, Cr(III) concentration, and polymer concentration. The dialysis of aged gels showed no unreacted Cr(III) remaining in the system. This behavior suggested that the kinetics could be represented as an irreversible reaction with a rate expression of the form

$$-\text{rate} = -\frac{d[\text{Cr(III)}]}{dt} = k[\text{Cr(III)}]^a[\text{H}^+]^b[\text{PAAm}]^c \quad (3)$$

where a, b, c are the orders of reaction for each respective species and k is the reaction rate constant.

The experimental program to determine the parameters in the kinetic equation was divided into three parts. In each part, the effect of one reactant concentration on the rate of reaction was measured and the order of reaction for that species was determined. In all experiments, the pH of the reacting mixture was maintained at a constant value throughout a given run. In the first part, the starting Cr(III) concentration was varied between different runs for the same initial polymer concentration. In the second part, the hydrogen ion concentration was varied between runs for a given initial polymer and Cr(III) concentrations. In the third part, the initial polyacrylamide concentration was varied between different runs for a given initial Cr(III) concentration.

Precision and errors

The precision of the volumetric addition of Cr(III) solution to the reactor at the start of a kinetic experiment was determined from five measurements to be better than 0.6% at a 95% confidence level.

The precision of the dialysis of chromium solutions to equilibrium was determined from seven measurements to be 0.5% at a 95% confidence level.

The precision of the measurement of Cr(III) concentration in the range of 0.2 to 1 ppm by AA was found from ten measurements to be better than 1.3% at a 95% confidence level. The sensitivity of the AA measurement for chromium using an air-acetylene flame at a wavelength of 357.9 nm is reported by Perkin-Elmer (1982) to be 0.08 mg/L. The sensitivity is defined as the concentration required to produce a signal of 1% absorption equal to 0.0044 absorbance units. The detection limit, defined as the concentration which will produce a signal to noise ratio of 2, is also reported by Perkin-Elmer to be 0.003 mg/L for chromium at this wavelength. The optimum concentration range for the direct determination of chromium in an air-acetylene flame is given as 0.2 to 10 ppm (American Public Health Association, 1985).

The precision for the measurement of the Cr(III) concentration as a function of reaction time for the overall kinetic experiment was found from six to eight measurements at each reaction time to be better than 7% at a 95% confidence level.

Results and Discussion

Effect of Cr(III) concentration

The effect of Cr(III) concentration on the rate of reaction between Cr(III) and 5,000 ppm polyacrylamide was determined at a constant pH of 5.0 for initial Cr(III) concentrations ranging from 0.2 to 1.16 mM (10 to 60 ppm). The Cr(III) concentration measured in the diffusate after dialysis equilibrium was used to determine the unreacted Cr(III) concentration in the reacting system versus reaction time for the above set of conditions.

Shown in Figure 3 is the unreacted Cr(III) concentration plotted versus reaction time for each initial Cr(III) concentration. An analytical equation fit to each data set was differentiated to give the rate of reaction for fixed Cr(III) concentrations. It was assumed for the analysis that the concentration of the reactive group on the polyacrylamide, [PAAm], did not significantly vary during the reaction. With this assumption, the model development required no prior knowledge of the specific reaction mechanism nor of the stoichiometry. For a fixed hydrogen ion concentration, Eq. 3 becomes

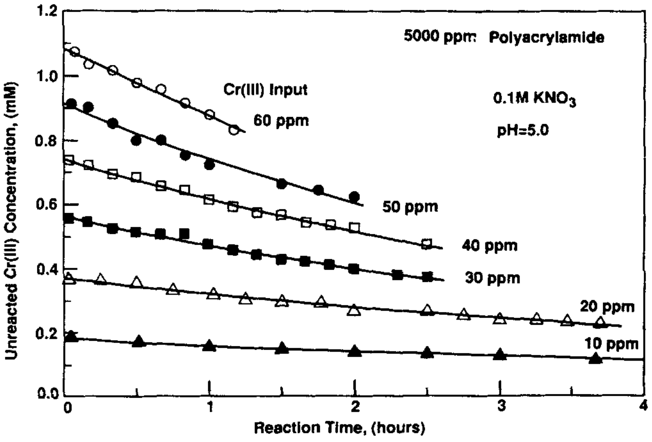


Figure 3. Curve fit of the C_A vs. time data for varying Cr(III) concentration.

$$-\text{rate} = k''' \, [\text{Cr(III)}]^a \quad (4)$$

where $k''' = k\,[\text{H}^+]^b\,[\text{PAAm}]^c$.

Graphed in Figure 4 is the logarithm of minus the initial rate of reaction versus the logarithm of the Cr(III) concentration input to the reacting system. The order of reaction on Cr(III), a, was determined from the least squares slope of the plot to be 1.32 and the pseudorate constant, k''', to be $1.88\ \text{h}^{-1} \cdot \text{M}^{-0.32}$.

The data of Figure 3 were replotted on one master curve for

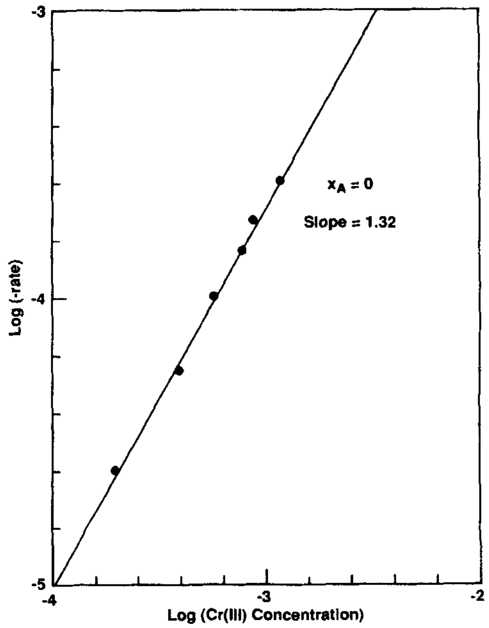


Figure 4. Log (−rate) vs. log (Cr(III) concentration).

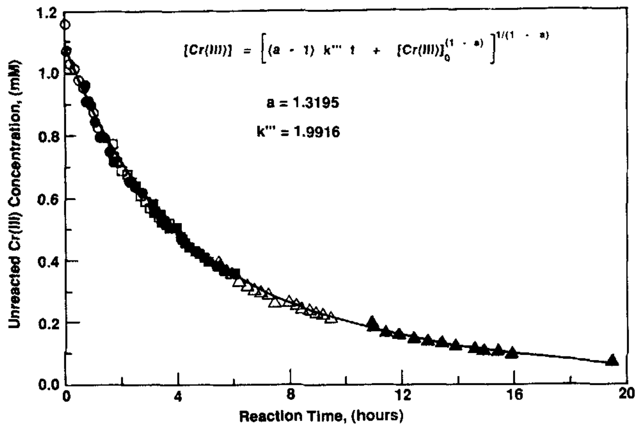


Figure 5. Master curve showing unreacted Cr(III) concentration vs. time.

the complete range of Cr(III) concentrations tested. A fit of all the data to one curve would indicate that the kinetics were consistent over the full range of Cr(III) concentration. The procedure for plotting the curve is given elsewhere (Hunt, 1987). This master curve is shown in Figure 5.

If the polyacrylamide reactive group concentration is assumed not to change significantly during the course of reaction, the general rate expression given by Eq. 3 can be integrated to give

$$[\mathrm{Cr(III)}] = \{(a-1)k\,[\mathrm{H^+}]^b\,[\mathrm{PAAm}]^c t + [\mathrm{Cr(III)}]_0^{(1-a)}\}^{1/1-a} \quad (5)$$

By relaxing two of the parameters, a and k''', Eq. 5 was fit to the [Cr(III)] vs. time data of Figure 5 using the Levenberg-Marquardt optimization algorithm. An order of reaction on Cr(III) of 1.32 and pseudorate constant, k''', of 1.99 $\mathrm{h^{-1} \cdot M^{-0.32}}$ were obtained from the fit. The curve fit to all the Cr(III) data of the master curve using these parameters and Eq. 5 is shown in Figure 5.

It was observed that the value for the Cr(III) concentration determined by extrapolation of the individual data sets back to zero time was on the order of 5% lower than the initial Cr(III) concentration charged to the system. The possibility of a fast initial reaction of Cr(III) with the polyacrylamide or a continued reaction after dilution of the reacting sample and during dialysis may explain the difference. For the kinetic model, the Cr(III) concentration input to the reacting system was adjusted by multiplying by a factor of 0.95. The input Cr(III) concentration was known to be accurate to within 0.6%.

Effect of hydrogen ion concentration

The effect of hydrogen ion concentration on the rate of reaction between Cr(III) and polyacrylamide was determined by varying the pH from 4.0 to 5.5 for a reacting system having a 5,000 ppm polymer concentration and an initial Cr(III) concentration of 50 ppm. The pH of each run was maintained at a constant value throughout the run by the procedure described in the Experimental Section. Although dilution of the reacting mixture to adjust the pH was minimal during a run, the Cr(III) concentration in the system at any time was corrected for this small dilution.

The collected fraction Cr(III) reached, x_A, vs. time data for each pH run were curve fit with a hyperbolic function to enable calculation of the rate of reaction by evaluating the slopes of the curve at specified points. Graphed in Figure 6 are the x_A vs. time data and the curve fits.

For the determination of the order of reaction with respect to hydrogen ion, the derivative, dx_A/dt, is given by

$$\frac{dx_A}{dt} = \frac{k}{[\mathrm{Cr(III)}]_0}[\mathrm{Cr(III)}]^a[\mathrm{PAAm}]^c[\mathrm{H^+}]^b$$

$$= \frac{k'}{[\mathrm{Cr(III)}]_0}[\mathrm{H^+}]^b$$

$$\text{where } k' = k[\mathrm{Cr(III)}]^a(\mathrm{PAAm})^c \quad (6)$$

For a fixed Cr(III) conversion, a plot of the log (dx_A/dt) vs. log ($[\mathrm{H^+}]$) should yield a straight line of slope, b, the order of reaction on hydrogen ion, and intercept, $k'/[\mathrm{Cr(III)}]_0$.

Again, for this analysis the assumption was made that the polyacrylamide reactive group concentration was not significantly changing throughout the run. The slope of the x_A vs. time curve, dx_A/dt, was evaluated for each pH run for $x_A = 0$ and 0.1. Graphed in Figure 7 is the log (dx_A/dt) vs. log ($[\mathrm{H^+}]$) for each Cr(III) conversion. The slopes of the plot, b, were found to be -1 and the intercept averaged $0.22 \times 10^{-5}\ \mathrm{h^{-1} \cdot M^{-1}}$.

Effect of polyacrylamide concentration

The effect of the overall polyacrylamide concentration on the reaction rate was determined by varying the initial polymer concentration from 500 to 5,000 ppm for the reacting system having an initial Cr(III) concentration of 50 ppm. The pH throughout each run was maintained at a constant value of 5.0. The kinetic data were collected as unreacted Cr(III) concentration versus reaction time. The Cr(III) concentration data as a function of time were curve fit with an integrated rate equation of the form

$$\frac{d[\mathrm{Cr(III)}]}{dt} = c_1\ [\mathrm{Cr(III)}]^{1.32} \quad (7)$$

where c_1 is a constant. The results are graphed in Figure 8. For the reaction rate given by Eq. 3 and for a fixed Cr(III) and $\mathrm{H^+}$ concentration, a log-log plot of minus the rate of reaction versus

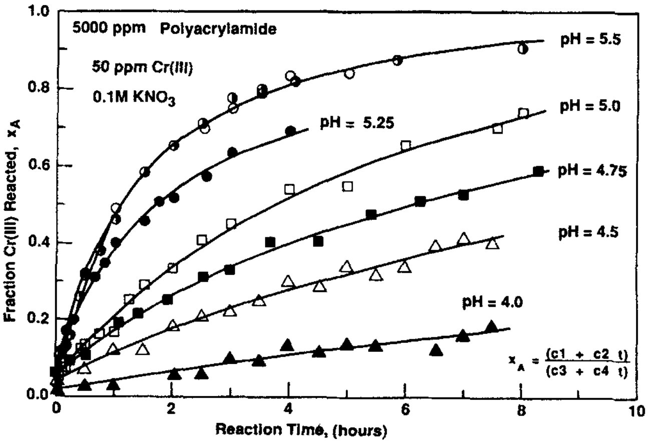


Figure 6. Hyperbolic curve fit of the x_A vs. time data.

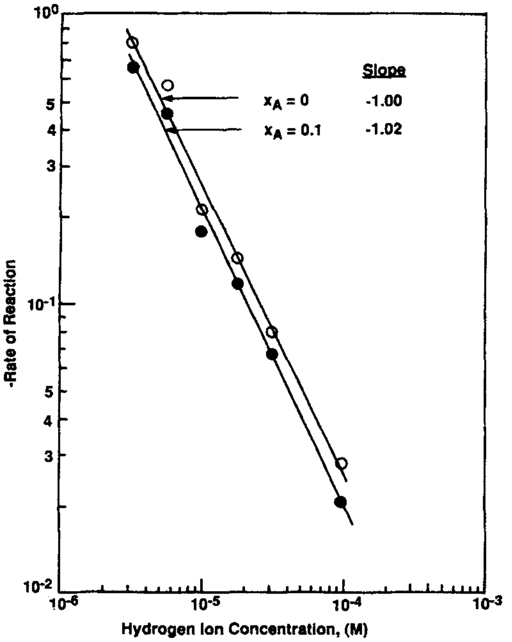


Figure 7. Log (−rate) vs. log (H^+ concentration).

the polyacrylamide reactive group concentration should result in a straight line of slope, c, the order of reaction on polyacrylamide, and intercept, $k'' = k[\mathrm{Cr(III)}]^a\,[H^+]^b$, the pseudorate constant.

The rate of reaction was determined by evaluating the slopes of the curve fits to the data at fixed Cr(III) concentrations. Since there was considerable scatter in the data for Cr(III) concentrations less than 38 ppm (0.73 mM), Cr(III) concentrations ranging from 38 to 44 ppm were used for the determination of the reaction rates. Graphed in Figure 9 is the log (−rate) vs. log ($[\mathrm{PAAm}]_0$), where $[\mathrm{PAAm}]_0$ is the total polyacrylamide concentration in the system for a [Cr(III)] of 44 ppm. The polymer concentration was calculated on a molar basis assuming that the molecular weight of the repeating group of the polymer molecule was 72 g/mol. For a partially hydrolyzed polyacrylamide consisting of amide and carboxyl groups, a formula weight of 72 g/mol for carboxyl was not significantly different from that of 71.1 for amide groups. A slope of 0.81 was determined for the order of reaction with respect to polyacrylamide for all Cr(III) concentrations.

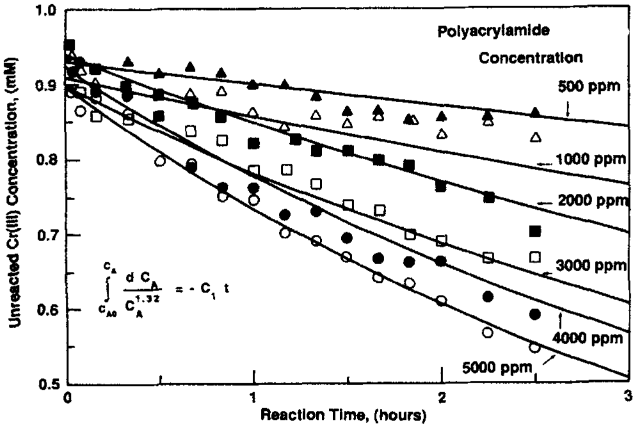


Figure 8. Curve fit of the C_A vs. time data for varying polyacrylamide concentration.

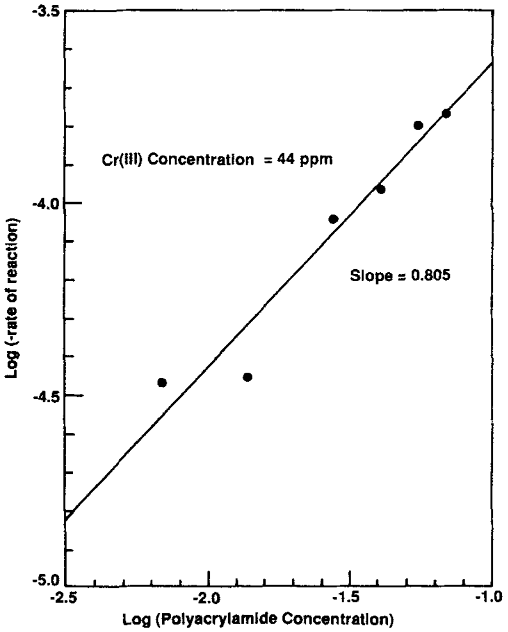


Figure 9. Log (−rate) vs. log (polyacrylamide concentration).

Reaction rate constant

A reaction rate constant, k, could be determined from the individual pseudorate constants developed in each part of the experimental program. In Part I, in which the effect of Cr(III) concentration on the reaction rate was determined, a pseudorate constant of the form $k''' = k[H^+]^b[\mathrm{PAAm}]^c$ and reaction order on Cr(III) were determined. In Part II, a reaction order on hydrogen ion and pseudorate constant, $k' = k[\mathrm{Cr(III)}]^a[\mathrm{PAAm}]^c$, were developed by measuring the effect of pH on the rate of reaction. Finally, in Part III, the order of reaction on polyacrylamide and pseudorate constant, $k'' = k[\mathrm{Cr(III)}]^a[H^+]^b$ were determined by varying the starting polymer concentration. With the orders of reaction for each species determined to be $a = 1.32$, $b = -1$, and $c = 0.8$, the rate constants were calculated for each part and are listed in Table 1.

A k value of $1.6 \times 10^{-4}\,h^{-1} \cdot M^{-0.12}$ was found for the Cr(III) data using initial rates of reaction. An average k value of $1.8 \times 10^{-4}\,h^{-1} \cdot M^{-0.12}$ was calculated from the pH data using rates of reaction at 0 and 10% Cr(III) conversion. A low Cr(III) conversion was desired for the kinetic analysis since the pseudorate constant determined from the pH data, $k' = k[\mathrm{Cr(III)}]^a[\mathrm{PAAm}]^c$, is expected to be closest to the true value near $t = 0$ where the polyacrylamide reactive group concentration is equal to the starting concentration. A k value of $1.7 \times 10^{-4}\,h^{-1} \cdot M^{-0.12}$ was determined from the polyacrylamide data. These rate constants compared closely with the k value of $1.7 \times 10^{-4}\,h^{-1} \cdot M^{-0.12}$ determined by regressing the *Cr(III)* data of the master curve using Eq. 5.

General kinetic model

The integrated form of the general rate expression was given by Eq. 5. The data from each part of the experimental program

Table 1. Reaction Rate Constants Determined from the Kinetic Study

Part I: Cr(III) Effect, $[\mathrm{Cr(III)}]_0 = 0.18$ mM

x_A	$k''' = k\,[\mathrm{H}^+]^b\,[\mathrm{PAAm}]^c$ $\mathrm{h}^{-1} \cdot \mathrm{M}^{-0.32}$	$k \times 10^4$ $\mathrm{h}^{-1} \cdot \mathrm{M}^{-0.12}$
0.0	1.88	1.56
0.1	1.94	1.62
0.2	2.01	1.68
0.3	2.10	1.75
		1.65

Part II: pH Effect

x_A	$k\,[\mathrm{PAAm}]^c \times 10^5$ $\mathrm{h}^{-1} \cdot \mathrm{M}^{0.68}$	$k \times 10^4$ $\mathrm{h}^{-1} \cdot \mathrm{M}^{-0.12}$
0.0	2.48	2.07
0.1	1.78	1.49
0.2	1.17	0.97
0.3	0.66	0.55

Part III: Polyacrylamide Effect

[Cr(III)] (ppm)	$k'' = k\,[\mathrm{Cr(III)}]^a$ $[\mathrm{H}^+]^b \times 10^3$ $\mathrm{h}^{-1} \cdot \mathrm{M}^{0.2}$	$k \times 10^4$ $\mathrm{h}^{-1} \cdot \mathrm{M}^{-0.12}$
Run I: $c = 0.74$		
38	1.24	1.71
40	1.33	1.71
42	1.42	1.71
44	1.51	1.71
Run II: $c = 0.78$		
38	1.23	1.70
40	1.32	1.70
42	1.40	1.70
44	1.49	1.70

were fit with this equation using the following kinetic parameters.

$$a = 1.3$$

$$b = -1.0$$

$$c = 0.8$$

$$k = 1.7 \times 10^{-4}\ \mathrm{h}^{-1} \cdot \mathrm{M}^{-0.12}$$

$$[\mathrm{Cr(III)}]_0 = 0.95\ [\mathrm{Cr(III)}]\ \text{input}$$

Figures 10, 11 and 12 show the experimental Cr(III) concentration or conversion data plotted vs. reaction time and the corresponding curve fits using Eq. 5 and the above parameters. The curve fit of the model to the data appeared to closely match the experimental rate data for low Cr(III) conversions. The general rate model deviated from the experimental data at higher conversions by as much as 10%. The lack of fit at higher conversions was attributed to a deviation from the assumption of invariant reactive group concentration on PAAm during the reaction.

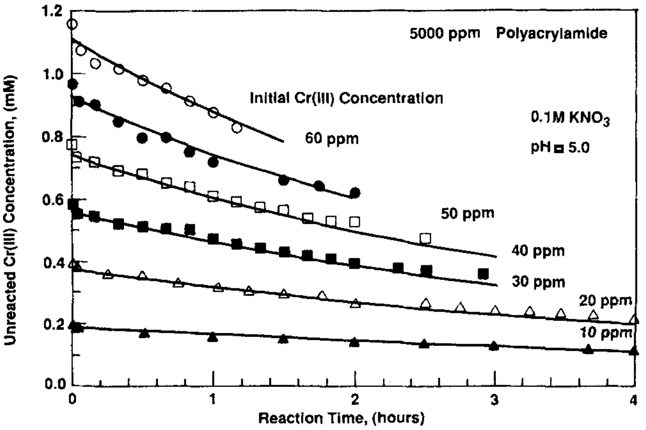


Figure 10. General rate model showing C_A vs. time data for varying Cr(III) concentration.

For the development of this empirical rate expression, it was assumed that all of the functional groups on the polymer molecule, both the amide and carboxyl groups, were equally reactive with the Cr(III) in solution. Also assumed was that the polyacrylamide concentration or functional group concentration was not varying significantly throughout a kinetic experiment. For a 5,000 ppm PAAm and 50 ppm Cr(III) reacting system, the acrylamide monomer to Cr(III) mole ratio was 70. If all functional groups on the polyacrylamide molecule were reactive, this group would remain in large excess over Cr(III) during all reactions and would not explain the lack of fit at higher Cr(III) conversions.

According to the literature (Thorstensen, 1969; Hamm et al., 1958), the carboxyl group on PAAm should be the primary reactive group in Cr(III)-PAAm reactions. An independent study (Hunt, 1987) showed that increasing the carboxyl content of the polyacrylamide increased the amount of Cr(III) reacted with the polymer. If the carboxyl group which is present in low concentration is indeed responsible for reaction with Cr(III), then the reactive group on PAAm would no longer be in large excess to Cr(III). The concentration of this group could change significantly with reaction, particularly at high Cr(III) conversions. It was therefore decided to modify the existing model for the effect of a decreasing reactive group concentration with reaction time in an attempt to better fit the rate data at the higher Cr(III) conversions.

Modified rate model

To develop the modified model to account for the consumption of PAAm reactive group by Cr(III), some assumptions

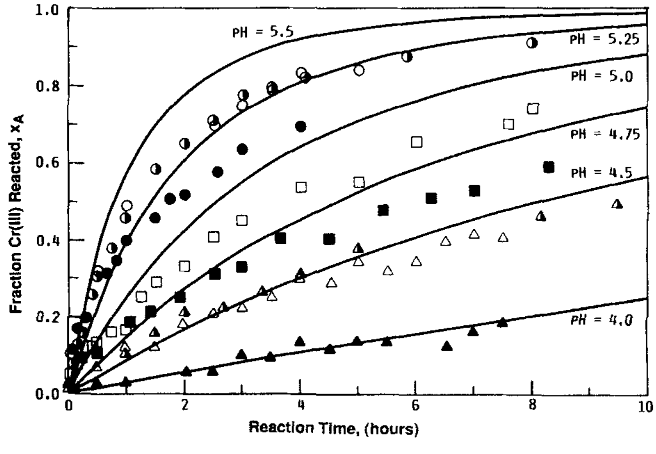


Figure 11. General rate model showing x_A vs. time for varying pH.

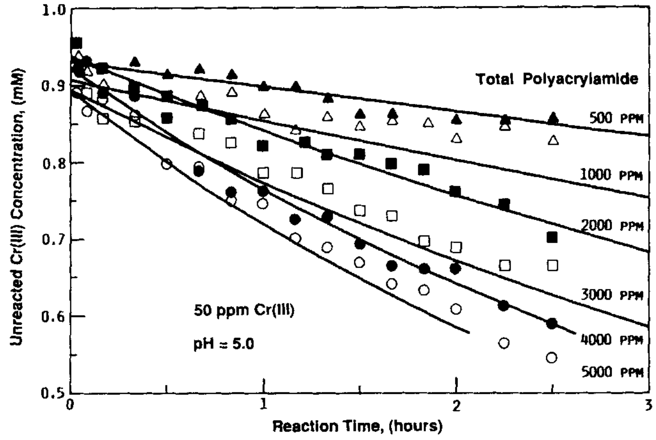


Figure 12. General rate model showing C_A vs. time for varying polyacrylamide concentration.

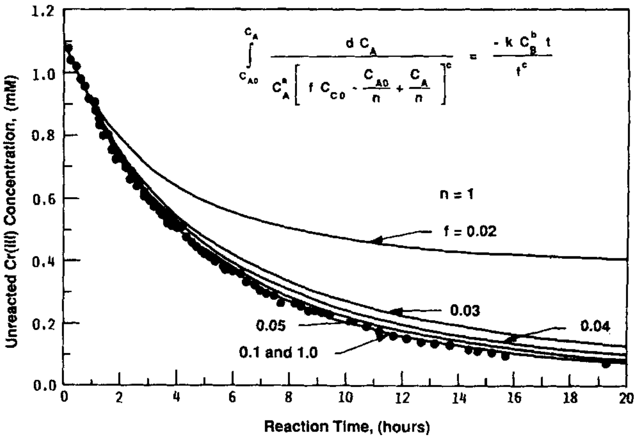


Figure 13. Effect of varying f on curve fit of the C_A vs. time data.

about the reaction mechanism were made. For an assumed reaction mechanism

$$n\,\mathrm{Cr(III)} + \mathrm{PAAm} \rightleftharpoons \mathrm{product} \tag{8}$$

the unreacted polymer concentration at any time during the reaction is given by the initial concentration minus the amount reacted, or

$$[\mathrm{PAAm}] = [\mathrm{PAAm}]_0 - \frac{x_A}{n}[\mathrm{Cr(III)}]_0 \tag{9}$$

where

$$x_A = \frac{[\mathrm{Cr(III)}]_0 - [\mathrm{Cr(III)}]}{[\mathrm{Cr(III)}]}$$

If the concentration of reactive groups on the polyacrylamide molecules is only a fraction, f, of the total monomer concentration, the $[\mathrm{PAAm}]_0$ must be replaced by $f[\mathrm{PAAm}]_0$. Also, the rate constant, k, in Eq. 3 was originally defined assuming all polyacrylamide functional groups were reactive. The original k value was adjusted for each value of f by dividing by f^c. The new rate constant used in this model is then $1.7 \times 10^{-4}/f^c\ \mathrm{h}^{-1} \cdot \mathrm{M}^{-0.12}$. For an f of 0.05, the rate constant would have a value of $1.87 \times 10^{-3}\ \mathrm{h}^{-1} \cdot \mathrm{M}^{-0.12}$. The adjusted rate model is of the form

$$\int_{[\mathrm{Cr(III)}]_0}^{[\mathrm{Cr(III)}]} \frac{d[\mathrm{Cr(III)}]}{[\mathrm{Cr(III)}]^a\left[f[\mathrm{PAAm}]_0 - \frac{[\mathrm{Cr(III)}]_0}{n} + \frac{[\mathrm{Cr(III)}]}{n}\right]^c} = \frac{-k[\mathrm{H}^+]^b t}{f^c} \tag{10}$$

Equation 10 was integrated numerically to determine [Cr(III)] as a function of time. The same kinetic parameters were used as in the earlier fit in which the polyacrylamide reactive group concentration was assumed invariant. The procedure was then to test the fit of Eq. 10 to all the data sets for different values of n and f.

The fit of Eq. 10 to the data of unreacted Cr(III) concentration versus time shown in Figure 5 was first tested for a fixed f of 1 and different values of n ranging from 1 to 100. No difference in the fit could be detected for any of these n values. This is understandable as the amide and carboxyl groups together are in large excess to the Cr(III) present. Next, n was fixed at a value of 1 and f was varied. Shown in Figure 13 are the fits to the data using Eq. 10 with f factors ranging from 0.02 to 1.0 and an n value of 1. The fit to the data was good for f values between 0.1 and 1.0, but became poorer as f was reduced below about 0.05.

The fit of Eq. 10 to the Cr(III) conversion data taken at a pH of 5.5 was tested. Shown in Figure 14 is the effect of varying f from 0.01 to 1.0 for an n value of 1. The fit to the experimental data was significantly improved for f values between 0.03 and 0.05. The fit of the modified rate model to all the pH data is shown in Figure 15 for $n = 1$ and $f = 0.05$. The fit to the data was significantly improved for higher Cr(III) conversions as compared to the original model which assumed constant PAAm concentration. Assuming that the Cr(III) reacts on a 1:1 mole ratio with the carboxyl group on the polyacrylamide molecule, 10 to 20% of the carboxyl groups would be reacted with the Cr(III) at the higher Cr(III) conversions. For reactions at pH 4.5 and lower where the Cr(III) conversion was small, the modified model fit the data as well as the original model.

The fit of Eq. 10 to the Cr(III) conversion data taken at different PAAm concentrations is shown in Figure 16 for $n = 1$ and $f = 0.05$. The fit was satisfactory but was not significantly dif-

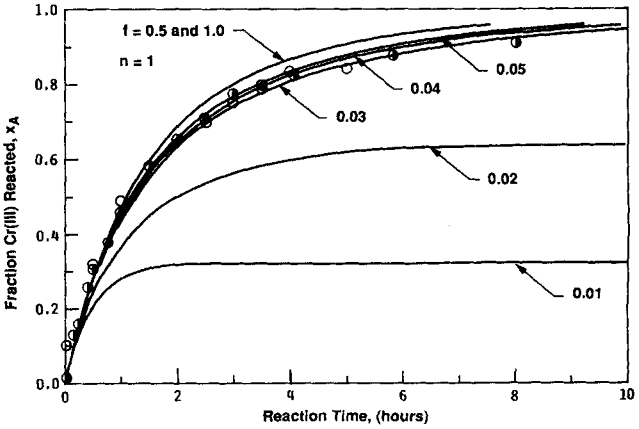


Figure 14. Effect of varying f on curve fit of the x_A vs. time data.

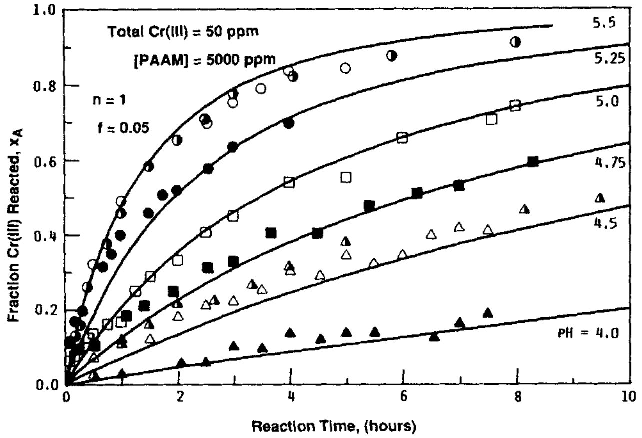


Figure 15. Overall fit of the kinetic model to the x_A vs. time data for varying pH.

ferent than that given by the rate expression developed under the assumption of constant polymer concentration.

Modifications made to the general rate model for a variable polyacrylamide reactive group present at low concentrations significantly improved the fit to the experimental rate data. The polymer reactive group concentration corresponds closely to the experimentally determined number of amide groups on the polymer backbone that were hydrolyzed to carboxyl groups. An f value of 0.05 was close to the fractional degree of hydrolysis, which for this polyacrylamide was about 0.04. This behavior suggests that carboxyl groups on the polyacrylamide polymer may be responsible for the reaction with Cr(III).

Conclusions

1. The rate of reaction between Cr(III) and a slightly hydrolyzed polyacrylamide could be determined using a technique based on equilibrium dialysis and atomic absorption. Dilution of the reacting sample by a factor of 30 sufficiently slowed the rate of reaction to enable separation of the unreacted Cr(III) by dialysis.

2. A general rate model developed with the assumption of a constant polyacrylamide group concentration during reaction provided a good fit to the rate data for low Cr(III) conversions.

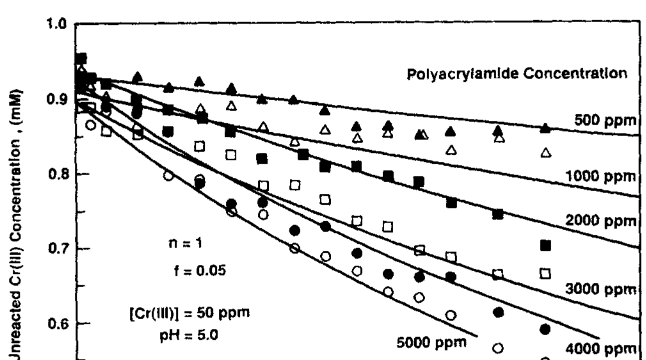


Figure 16. Overall fit of the kinetic model to the C_A vs. time data for varying polyacrylamide concentration.

A modification in this rate model to account for a variable polyacrylamide reactive group concentration improved the fit to the data for higher Cr(III) conversions.

3. The rate of reaction between Cr(III) and polyacrylamide was described by:

$$-\text{rate} = \frac{k}{f^{0.8}} \frac{[\text{Cr(III)}]^{1.32}}{[\text{H}^+]}$$

$$\cdot f[\text{PAAm}] - \frac{[\text{Cr(III)}]_0}{n} + \frac{[\text{Cr(III)}]^{0.8}}{n}$$

where f represents the fraction of polyacrylamide reactive groups. A rate constant, k, was determined to be 1.7×10^{-4} $h^{-1} \cdot (\text{mol/L})^{-0.12}$. The above rate expression provided a good fit to the experimental data for Cr(III) concentrations ranging from 0.19 mM (10 ppm) to 1.2 mM (60 ppm), polyacrylamide concentrations from 6.9 mM (500 ppm) to 69 mM (5000 ppm), and pH values from 4.0 to 5.5.

Acknowledgment

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Notation

a = order of reaction on Cr(III)
b = order of reaction on hydrogen ion
c = order of reaction on polyacrylamide
c_1 = constant
f = fraction of reactive groups on polyacrylamide, dimensionless
k = reaction rate constant, $h^{-1} \cdot M^{-0.12}$
k', k'', k''' = pseudorate constants
n = number of Cr(III) ions reacted with each PAAm reactive group, dimensionless
t = time, hours
x_A = fraction Cr(III) reacted

Literature Cited

Am. Public Health Assoc., *Standard Methods for Examination of Water and Wastewater,* 16 ed., 156 (1985).

Clampitt, R. L., and J. E. Hessert, "Method for Controlling Formation Permeability," U.S. Patent No. 3,785,437 (1974).

Cotton, F. A., and G. Wilkinson, *Advanced Inorganic Chemistry,* 4th ed., Ch. 28, John Wiley, New York, 1188 (1980).

Hamm, R. E., R. L. Johnson, R. H. Perkins, and R. E. Davis, "Complex Ions of Chromium: VIII. Mechanism of Reaction of Organic Acid Anions with Chromium (III)," *J. of Am. Chem. Soc.,* **80,** 4469 (1958).

Hessert, J. E., and P. D. Fleming, "Gelled Polymer Technology for Control of Water in Injection and Production Wells," *Proc. 3rd Tertiary Oil Recovery Conf.,* Wichita, KS (Apr. 25–26, 1979).

Hunt, J. A., T. S. Young, D. W. Green, and G. P. Willhite, "Application of Size Exclusion Chromatography in the Measurements of Concentration and Molecular Weight of Some EOR Polymers," SPE/DOE 14949 (1986).

Hunt, J. A., "An Experimental Study of the Kinetics of the Crosslinking Reacting Between Chromium (III) and Polyacrylamide," Ph.D. Diss. Univ. of Kansas (1987).

Perkin-Elmer, "Analytical Methods for Atomic Absorption Spectrophotometry," *Operation Manual* (1982).

Prud'homme, R. K., J. T. Uhl, J. P. Poinsatte, and F. Halverson, "Rheological Monitoring of the Formation of Polyacrylamide/Cr^{+3} Gels," *Soc. Pet. Eng. J.,* 804 (Oct., 1983).

Rollinson, C. L., "Problems of Chromium Reactions," *Radioactive Pharmaceuticals,* Ch. 24, 429 (1966).

Thorstensen, T. C., "Chrome Tanning," Ch. 8, *Practical Leather Technology,* Reinhold Book Corp., 111 (1969).

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