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Kinetics and Mechanism of the Reaction of Hydrated Chromium(III) with Partially Hydrolyzed Polyacrylamide

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ABSTRACT: The kinetics of the cross-linking reaction of partially hydrolyzed polyacrylamide (HPAAm) by Cr^{3+} have been studied over a range of experimental conditions by means of UV spectroscopy. The kinetic rate law, $k = A \exp(-E_a/RT)[Cr^{3+}][H^+]^{-0.8}[P]^{0.8}$, is in reasonable agreement with that reported previously for the uptake of Cr^{3+} by HPAAm for a different range of compositions and agrees closely with that reported for the reaction of Cr^{3+} with carboxylate monomers. The frequency factor A ($(4.9 \pm 0.5) \times 10^8$ s^{-1}) and activation energy E_a (19 ± 1.8 kcal/mol) were derived for the polymer reaction in experiments conducted between 293 and 353 K. Earlier proposals that the rate determining step on the pathway to polymer cross-linking involves the oligomerization of hydrated Cr^{3+} ions are excluded by the present results. EPR studies carried out on the Cr^{3+} solutions and dialyzed gels provide insight into the nature of the cross-linking Cr^{3+} species produced subsequent to the rate determining step.

Introduction

Some of the most important and certainly some of the most remarkable technological applications of aqueous polymer gels are to be found in the field of petroleum production.[1] An important technology currently under active development involves the injection of aqueous solutions of polymer and cross-linking agent through the wellbore and into the porous reservoir rock. The subsequent gelation of these solutions provides a physical barrier within the rock that serves to modify the movement of gas or fluids into the wellbore when the well is put back into operation.[1–3]

Aqueous polymer gels formed by the reaction of partially hydrolyzed polyacrylamide (HPAAm) and Cr^{3+} are of particular interest for this application. One key to their successful application is the ability to predict and control when gelation occurs within the reservoir. With these goals in mind, we have undertaken systematic studies of the cross-linking chemistry of Cr^{3+}/polymer solutions.[4–7] Although previous research has established[8,9] that cross-linking between Cr^{3+} and HPAAm takes place as the result of the complexation of Cr^{3+} with the carboxylate groups present on the polymer, strongly conflicting hypotheses[6,7,10–13] have been proposed with regard to the kinetics and mechanism of the cross-linking reaction. This debate centers, in particular, on the possible involvement of Cr^{3+} oligomers on the pathway to cross-link formation.

The present contribution reports the results of UV and EPR spectroscopic studies of the Cr^{3+}/HPAAm cross-linking reaction that provide a significant insight into the cross-linking kinetics and mechanism. The results obtained allow the kinetic reaction orders in Cr^{3+}, polymer, and hydrogen ion to be defined over a range of compositions and clarify the rate determining step in the cross-linking reaction. The EPR studies lead to interesting conclusions regarding the involvement of Cr^{3+} oligomers on the cross-linking reaction pathway.

Experimental Section

Materials. The HPAAm polymer employed in these studies (Lamberti *Lamflood* 0175) had a MW of 6×10^6 (viscosity determination) and was 7.5% hydrolyzed (^{13}C NMR determination). The cross-linking kinetics of other HPAAm polymers having normal MW $(5–6) \times 10^6$ and being 2.2, 4.2, 12, and 17.5% hydrolyzed were also examined briefly (see text). Solutions of Cr^{3+} were prepared from $Cr(NO_3)_3(H_2O)_6$.

Polymer gels were prepared from a freshly filtered (5-μm Millipore filters) stock HPAAm (10 000 ppm) solution in deionized water. An appropriate amount of the stock polymer solution was combined with a Cr^{3+} (1000 ppm) solution, diluted to the final concentration (8000 ppm of polymer and 100 ppm of Cr^{3+}, except as noted), and then brought to the desired pH with the addition of aqueous NaOH or HCl. The pH of the gelation compositions (measured with a Metrohm EA125 microelectrode) was relatively stable over the life of the experiments (pH variation <0.2 over the course of the gelation) on account of the moderate buffering power of the polymer carboxylate groups.

Polymer gels free of unbound Cr^{3+} ions were prepared for EPR experiments by loading them into a cellulose membrane and dialyzing them against an external aqueous solution at pH 3, as described by Willhite.[8] The equilibrium concentration of Cr^{3+} in the external solution was determined by plasma analysis, and the quantity of polymer-bound Cr^{3+} was determined by difference.

UV–Vis Spectroscopy. UV–Vis studies were carried out on a HP8452A Diode-Array spectrophotometer, working in the range 190–820 nm. Variable temperature UV–vis studies were performed with a HP89090 Peltier temperature control accessory in the range 10–70 °C.

EPR Spectroscopy. EPR spectra were obtained on an X-band Varian E 112 spectrometer equipped with a VT control system in the range 103–423 K (conditions: microwave power 63 mW, modulation amplitude 1 mT, modulation frequency 100 kHz).

Results

UV–Kinetic Studies. Previous studies[14–16] have employed the absorbance bands in the UV and visible spectrum of Cr^{3+} to study the reaction of Cr^{3+} with carboxylate ions. Allain and Salomé,[16] in particular, showed that the absorbance at 250 nm is proportional to the concentration of the 1:1 Cr^{3+}:acetate complex. These results suggested to us that UV spectroscopy might be an effective and convenient means for studying the kinetics of reaction of Cr^{3+} with HPAAm.

Figure 1 shows the evolution of the electronic spectra of an aqueous solution of $Cr(NO_3)_3$ (100 ppm) and HPAAm (8000 ppm, 7.5% hydrolyzed) at ambient conditions. Noteworthy in the spectra is the band centered at 264 nm and the two bands in the visible region, all of which increase in intensity over time as the result of the interaction of Cr^{3+} with HPAAm. The band centered at 264 nm is absent from the electronic spectra of $Cr(NO_3)_3$ alone in aqueous

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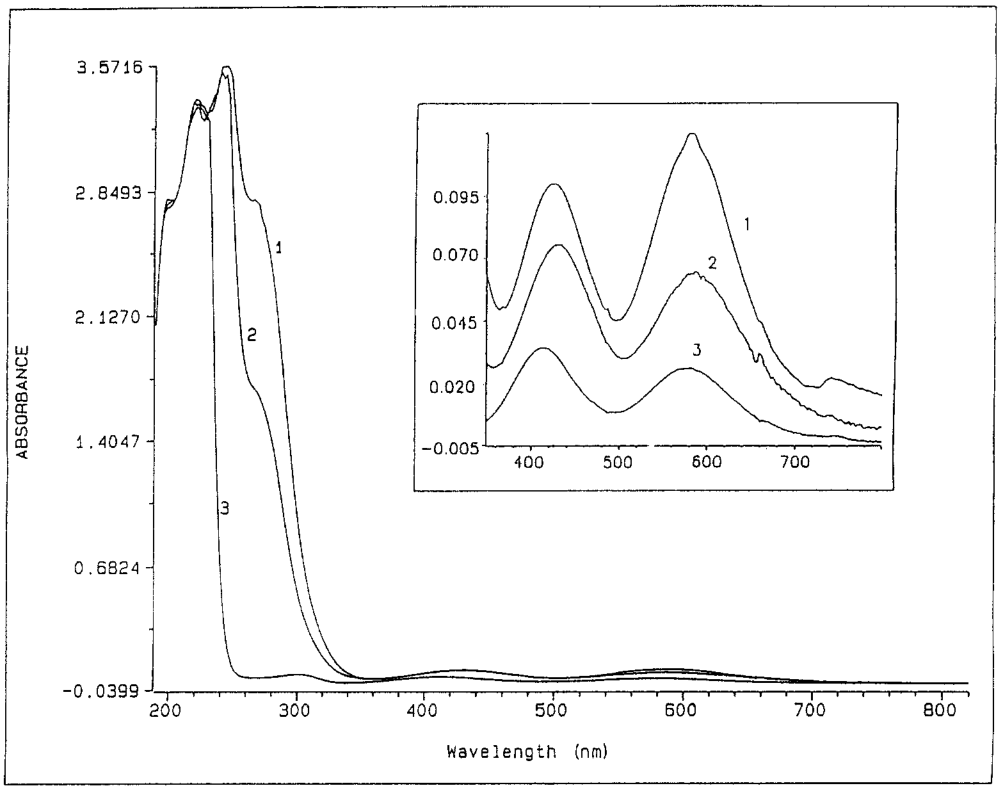
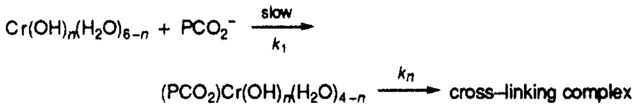


Figure 1. UV–Vis spectra of (3) aqueous Cr^{3+} solution (100 ppm), (2) solution 3 immediately after addition of HPAAm (to 8000 ppm), and (1) solution 2 after gel formation.

Scheme 1



$$Cr(OH)_n(H_2O)_{6-n} + PCO_2^- \xrightarrow[k_1]{\text{slow}}$$

$$(PCO_2)Cr(OH)_n(H_2O)_{4-n} \xrightarrow{k_n} \text{cross-linking complex}$$

solution and may be attributed to a charge-transfer interaction between Cr^{3+} and the polymer. The two visible bands are assigned to Cr^{3+} d–d transitions[14] and move to a longer wavelength (in particular, the band centered at 410 nm shifts to nearly 428 nm) after the addition of HPAAm.

The kinetics of the reaction between Cr^{3+} and HPAAm have been monitored by following the growth of the absorbances at 264, 426, and 580 nm as a function of time (Figure 2). The kinetic form of the reaction was analyzed by evaluating the reaction scheme in Scheme 1. Under the assumption that $k_n \gg k_1$ in the figure (where k_n refers to all of the reaction steps leading up to cross-link formation, subsequent to the first rate determining step) and, in light of the kinetic results reported by Willhite,[8] a first order dependence of the reaction on Cr^{3+} exits, the reaction of Cr^{3+} with polymer is described by eq 1.

$$d[Cr^{3+}]/dt = k_1[Cr^{3+}][H^+]^b[P]^c \qquad (1)$$

Integrating (1) and expressing the concentration of Cr^{3+}, C_t, as the difference between the absorbance at long (infinite) reaction time, A_∞, and the absorbance at time t, A_t, gives

$$\ln C_0/C_t = \ln(A_\infty - A_0)/(A_\infty - A_t) = K't \qquad (2)$$

where

$$K' = k_1[H^+]^b[P]^c \qquad (3)$$

The first order fits of the absorbance maxima at 264, 426, and 580 nm are presented in Figure 2 for a solution of Cr^{3+} (100 ppm) and HPAAm (8000 ppm) at pH 4.7 and 293 K; the sol-gel transition for this solution was about 600 s. Remarkably, although all three bands follow first order kinetics, the actual rate of increase of the d–d transition (426, 580 nm) is significantly slower than that of the 264 nm charge-transfer (CT) band. Considering that the CT band is more directly correlated with the Cr^{3+}–polymer interaction and that other workers have found it to be proportional to the concentration of Cr^{3+} monosubstituted with sodium acetate,[16] we chose to employ this band in our studies of the kinetics of the Cr^{3+}/HPAAm reaction.

Preliminary kinetic experiments with indentical Cr^{3+}/HPAAm solutions at pH 5 showed that the reproducibility of the constant K' was strongly dependent on sample preparation. The most likely source of this problem was identified as large acclerations in the reaction rate a pH >5 caused by local pH gradients or by overdosing with NaOH during sample preparation. To overcome this problem, the dependence of pH on the reaction rate was first evaluated over the range pH 4.2–4.9. Experimentally, reaction solutions were prepared by combining a stock Cr^{3+} (acidic) solution with a polymer solution whose pH was preadjusted to a value slightly higher (<0.3 units) than that desired for the final reaction mixture. The actual pH of the reaction was then determined on the combined Cr^{3+} and polymer solutions and was not further modified. The kinetic order of the hydrogen ion concentration, coefficient b in eq 3, was then determined for the solutions at a fixed Cr^{3+}–polymer concentration by application of eq 4, where B is a constant.

$$\log K' = \log k_1[H^+]^b[P]^c = B + b \log [H^+] \qquad (4)$$

Linear regression (Figure 3) of $\log K'$ vs $\log [H^+]$ for ten solutions (100 ppm in Cr^{3+}, 8000 ppm in HPAAm 7.5% hydrolyzed, and at 293 K) gave -0.8 ± 0.08 as the best estimate of the coefficient b (correlation coefficient R =

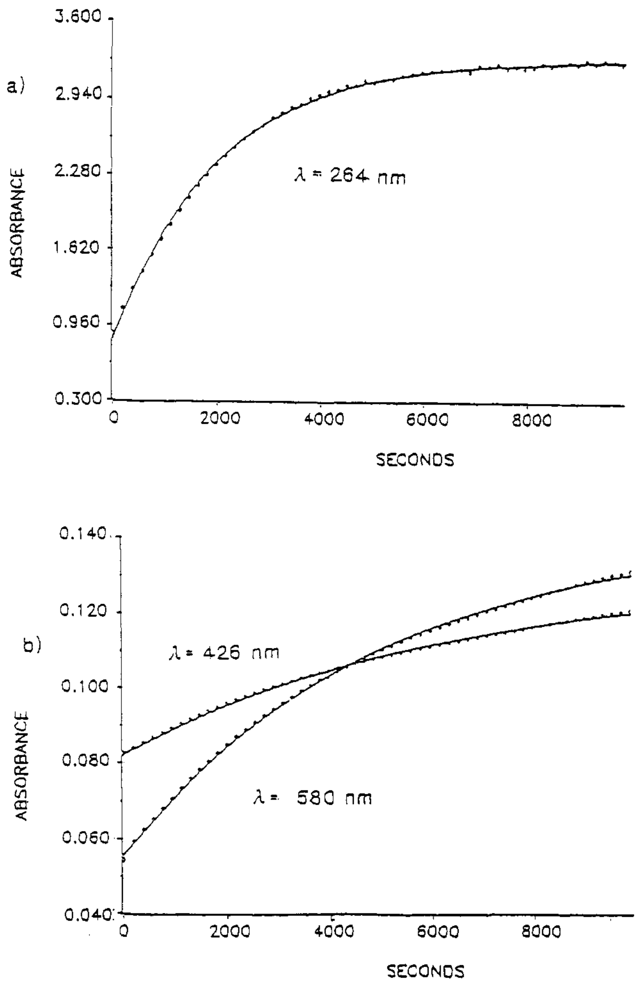


Figure 2. Time evolution and first order regression of the absorbances at (a) 264 nm and (b) 426 and 580 nm for solutions 100 ppm in Cr^{3+} and 8000 ppm in HPAAm (7.5% hydrolyzed).

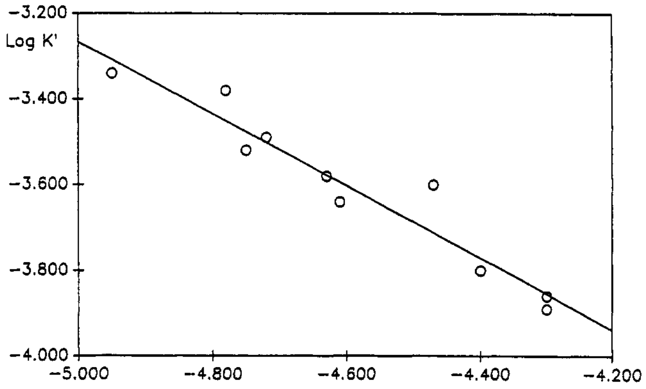


Figure 3. Plot and linear regression of log *K'* *versus* log [H^+] at 293 K.

0.961). In view of the considerable scatter of the experimental data (attributable to the precision of the pH determination and modest variation in the pH over the course of the experiments), however, we do not interpret this result to be significantly different from that (–1.0) reported by Willhite.[8]

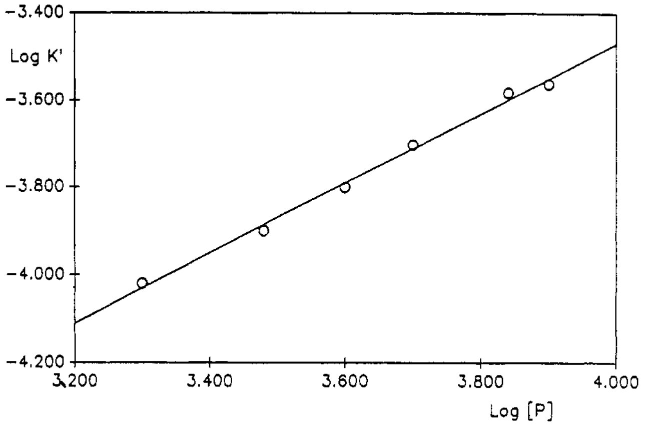


Figure 4. Plot and linear regression of log *K'* *versus* log [P] at pH 4.5 and 293 K.

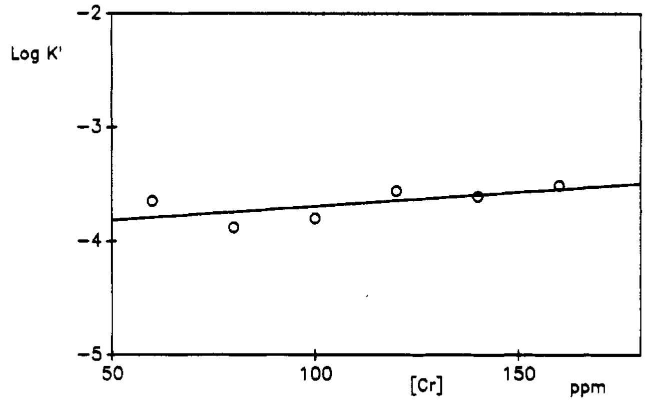


Figure 5. Plot of log *K'* *versus* [Cr^{3+}] at pH 4.5 and 293 K.

In a similar fashion, the coefficient *c* was evaluated for compositions containing 100 ppm Cr^{3+} and polymer concentrations ranging from 2000 to 8000 ppm at pH 4.5 and 293 K. By adjusting the pH of the polymer solution, the reaction solution obtained after addition of Cr^{3+} was made to fall within 0.2 units of the desired pH. The value of *K'* corrected to pH 4.5 (K'_{corr}) for the reaction solutions was then obtained from *K'* at the spontaneous pH (K'_{spont}) (Figure 4) using eq 5,which takes account of the empirical

$$K'_{corr} = K'_{spont}\{[H^+]_{corr}/[H^+]_{spont}\}^{-0.8} \qquad (5)$$

dependence of the reaction rate on pH, as defined above. The coefficient *c* determined from a linear regression (correlation coefficient $R = 0.997$) of the plot of log $K' = C + c$ log [P], where *C* is a constant, was found to be 0.8 ± 0.03 (Figure 4), in agreement with the value reported by Willhite.[8]

A fully satisfactory fit of the experimental data for all the systems studied was achieved by assuming a first order dependence of the Cr^{3+}/polymer reaction on the concentration of Cr^{3+}, as previously illustrated in Figure 2. This Cr^{3+} kinetic order was further evaluated by comparing the values of *K'* obtained for Cr^{3+}/polymer compositions varying in Cr^{3+} concentration from 20 to 180 ppm. The plot of log *K'* *vs* [Cr^{3+}] (Figure 5) does not show a marked variation in the reaction rate with the Cr^{3+} concentration (correlation coefficient 0.421 with $R = 0.592$.

The temperature dependence of the Cr^{3+}/HPAAm reaction was evaluated over the range 293–353 K. From the Arrhenius plot in Figure 6 (correlation coefficient $R = 0.995$) for solutions 100 ppm in Cr^{3+} and 8000 ppm in HPAAm (7.5% hydrolyzed) and at pH 4.5, a frequency factor $A = (4.9 \pm 0.5) \times 10^8$ s^{-1} ($\Delta S_{298} = -87 \pm 9$ J K^{-1} mol^{-1}) and an activation energy, E_a, of 19 ± 1.8 kcal/mol were determined.

The dependence of the Cr^{3+}/HPAAm reaction rate on ionic strength (*I*) of the medium was evaluated in the range 0.1–1.25 M with sodium perchlorate as the electrolyte. A Bronsted–Bjerrum plot of log *K'* *versus* $I^{1/2}$ (Figure 7) gave a linear relationship (correlation coefficient $R = 0.988$), with a slope of 0.8 ± 0.06 $L^{3/2}$ $mol^{-1/2}$. This result is in qualitative agreement with Hamm's findings[17] for

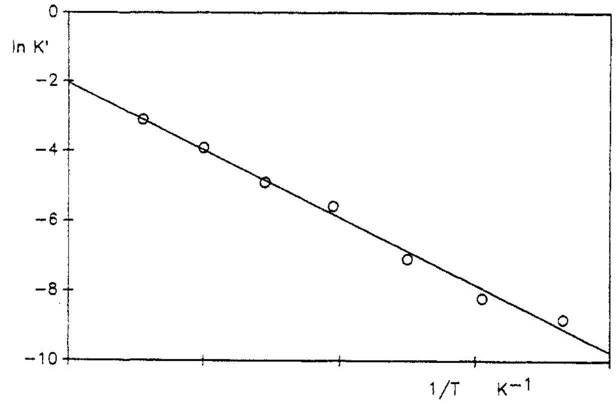


Figure 6. Arrhenius plot of kinetic data obtained on solutions 100 ppm in Cr^{3+} and 8000 ppm in HPAAm (7.5% hydrolyzed) over the temperature range 293–353 K.

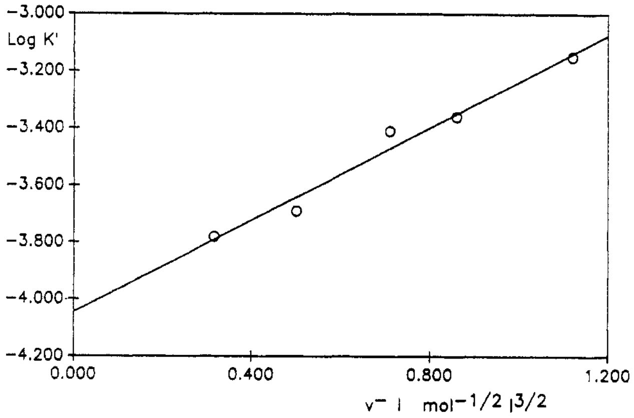


Figure 7. Bronsted–Bjerrum plot of log K' *versus* $I^{1/2}$ for gelling solutions.

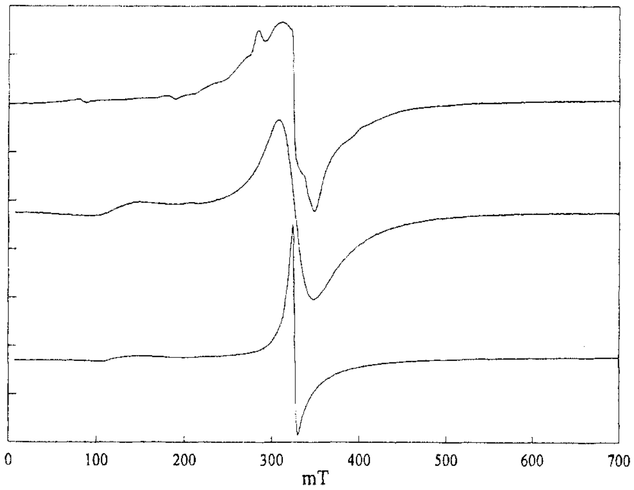


Figure 8. EPR spectra at 103 K of frozen aqueous Cr^{3+} solutions at pH 0.2 (bottom), 3.5 (middle), and 13.5 (top spectrum).

the dependence of the reaction of Cr^{3+} with monomeric organic carboxylates.

EPR Studies. Figure 8 reports the EPR spectra obtained for simple (frozen) aqueous solutions of Cr^{3+} (400 ppm) at pH 0.2, 3.5, and 13.5 (the strongly acidic and basic samples were prepared from the fresh parent solution at pH 3.5 by addition of HNO_3 and NaOH, respectively). There are two principal discriminating features of these spectra: (1) the line width of the principal band (0.32 T), which is sensitive to Cr^{3+}–Cr^{3+} dipolar interactions, and hence is expected to be much greater for Cr^{3+} atoms bound in the same complex than for monomeric Cr^{3+} species; and (2) the presence of a "half-field" transition ($\Delta m_s = 2$) near 0.14 T, which is characteristic of monomeric Cr^{3+} species.[18] The principal spectroscopic characteristics of these and other samples discussed further below are summarized in Table 1.

Table 1. EPR Parameters of Some Cr^{+3} Solutions

sample (see text)	pH	linewidth (mT)	half-field line[a]	fine interaction lines (mT)
A	3.5	40.0	+	
A′	nd[b]	4.4	+	
B	<1.0	40.0	+	
B′	nd	14.4	+	
C	0.2	6.0	+	
D	4.4	28.0	+	
D′	1.0	14.0	+	
E	5.1–4.3	36.0	+	
E′	1.0	9.5	+	
F	10.3	37.0	–	
F	1.0	33.5	–	
G	13.5	51.0	–	
G′	1.0	33.5	–	
G″	nd	51.0	–	
H	13.5	38.0	–	83.5, 184.5, 283.5, 324.5
H′	13.5	49.0	–	
I	4.5	11.7	+	
L	nd	47.0	–	27.0, 86.0, 210.5, 255.5, 315.0, 436.3
M	nd	48.0	–	
N	5.4	50.0	–	24.5, 83.5, 208.0, 250.0, 429.0
O	5.4	50.0	–	24.5, 83.5, 208.0, 250.0, 429.0

[a] + line at 0.14 T present, – not present. [b] nd = not determined.

Although the line width of the pH 3.5 (A in Table 1) solution is greater than that at pH 0.2 (C), the half-field transition is apparent in both spectra. The broader line width of the pH 3.5 Cr^{3+} solution is sensitive to the nature of the solution: Addition of acid (C) and ethylene glycol (50% by volume) (A′) both produce a drop in the line width to 4–6 mT. These observations strongly suggest that the dipolar broadening evident in the EPR spectrum of the pH 3.5 solution arises not from the chemical combination of Cr^{3+} atoms in a single complex but from a through-space interaction between solutes. The addition of HPAAm to weakly acidic Cr^{3+} solutions (I) also brings about an initial sharp decrease in the line width of the EPR spectrum, although subsequent chemical reaction brings about other changes (see below).

Other data provide additional evidence that the line-broadening of the pH 3.5 Cr^{3+} solution can be attributed to a through-space interaction between Cr^{3+} solutes. The EPR spectrum of a saturated $Cr(NO_3)_3$ solution at the spontaneous pH <1 (B) was comparable to that for the pH 3.5 Cr^{3+} solution described above, notwithstanding the lower pH. Once again, addition of ethylene glycol to this solution (B′) brought about a significant reduction in the line width. Finally, the conversion of Cr^{3+} to oligomeric species in a 400 ppm solution Cr^{3+} solution at pH 3.5 is expected to be very slow.[19]

The EPR spectrum of the pH 13.5 solution of Cr^{3+} (H) was characterized by a large, broad resonance at 0.32 T. Notably, the half-field transition characteristic of monomeric Cr^{3+} species was absent and no narrowing of the broad band occurred after addition of ethylene glycol. These observations indicate the formation of species oligomeric in Cr^{3+}; other studies have in fact reported trimeric Cr^{3+} hydroxides to be the predominant form of Cr^{3+} at pH >12.[19] Interestingly, several weaker bands (values in Table 1) arising from fine interaction also were evident in the spectra of the fresh pH 13.5 solution (H). Because the fine-structure terms in the spin Hamiltonian for Cr^{3+} ($S = {}^{3}/_{2}$) vary widely depending on their

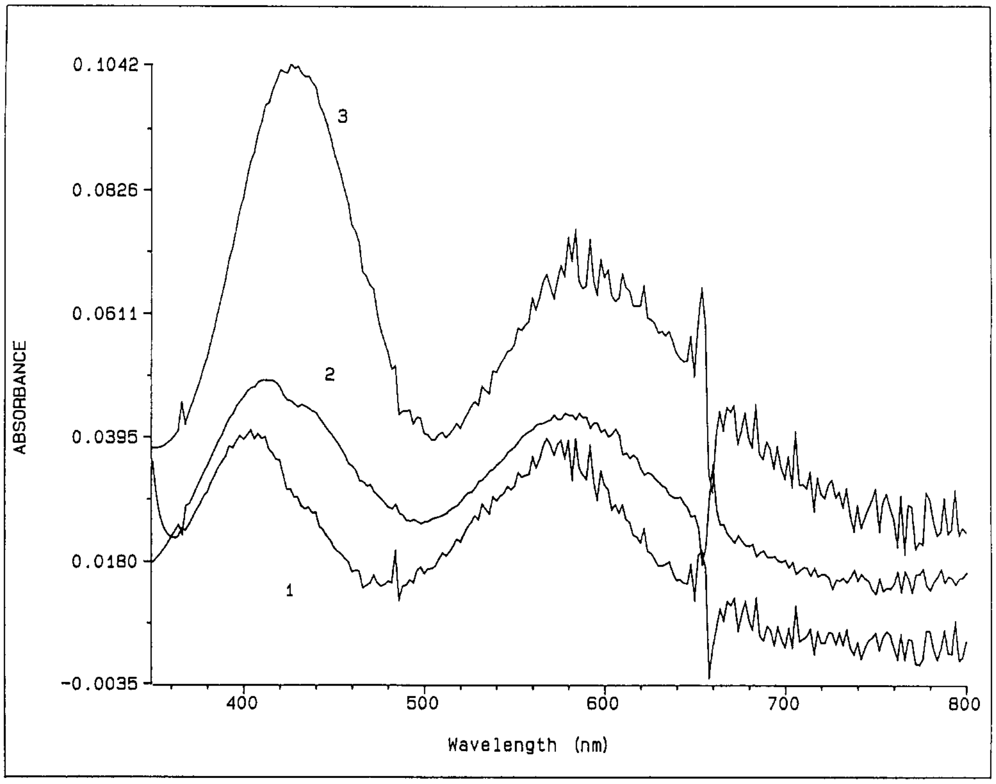


Figure 9. UV-Vis spectra of aqueous Cr^{3+} solutions at (a) pH 0.2, (b) pH 3.5, and (c) pH 13.5.

microscopic origin,[20] the assignment of these lines is nontrivial. Nevertheless, the shape of the spectrum is diagnostic in a qualitative sense of the ligand environment at Cr^{3+}. After several hours (H′) the dipolar coupling prevailed and the fine interaction lines were much reduced in intensity, suggesting the evolution of initially-formed Cr^{3+} oligomers toward other oligomers in which the dipolar interaction is greater.

The absorbances in the visible spectrum of the three C^{3+} solutions are shown in Figure 9. The adsorption band at 410 nm in acid solution shifts to 414 nm at pH 3.5 and to 428 nm at pH 13.5. Comparison with the EPR results suggests that these shifts may be correlated with the increasing dipolar interaction between the Cr^{3+} ions.

To gain further insight into the Cr^{3+} species present in aqueous solution at different pH values, the pH of fresh Cr^{3+} solutions was raised from 3.5 to 4.4 (D), 5.1 (E), 10.3 (F), and 13.5 (G) by dropwise addition of a NaOH solution. The blue color of the fresh pH 3.5 solution turned to a pale green with addition of base, and at about pH 5.5 the solution became turbid owing to the formation of insoluble $Cr(OH)_3$.[19] Above pH 10.3 the solution was once again transparent and dark green in color. The pH of the solution at pH 5.1 (E) was unstable and dropped to pH 4.3 within 30 min. The results of previous studies would suggest that this decrease is due to the formation of Cr^{3+} oligomers.[19] After recording the EPR spectra, the solutions were acidified to pH 1.0 (D′–G′) and their EPR spectra recorded again. The principal observations made on the spectra obtained can be summarized as follows:

(1) Relative to the solution of pH 3.5, there is a progressive decrease of the line intensity at 0.14 T in the solutions at pH 4.4 (D) and 5.1 (E). The EPR spectra of these two solutions after reacidification to pH 1.0 (D′, E′) show unambiguous evidence for the presence of two bands: a broad one arising from the presence of oligomeric Cr^{3+} (and stronger in the solution acidified from pH 5.1) in addition to the sharp one owing to the monomer.

(2) At pH 10.3 (F) and 13.5 (G) only the broad band is present in the EPR spectra; the 0.14-T band of monomeric Cr^{3+} is totally absent. Consistent with this result, addition of ethylene glycol to the pH 10.3 and 13.5 solutions (G″) leaves the line width of the principal EPR resonance unchanged. The slight reduction in line width upon acidification to pH 1.0 (F′, G′) is consistent with the acid–base chemistry of the Cr^{3+} oligomers.[21]

These observations confirm that the EPR method is a valid probe for the presence of Cr^{3+} oligomers in aqueous solution.

The EPR spectra of gelled Cr^{3+}/HPAAm solutions (200 ppm in Cr^{3+}, 8000 ppm in polymer, pH 4.5) (I) were dominated by a sharp signal at 0.32 T and contained the half-field transition characteristic of monomeric Cr^{3+} species. A dialysis procedure was adopted in order to remove any free Cr^{3+} ions present in the gel, and hence permit the EPR spectrum of only polymer-bound Cr^{3+} can be obtained. Analysis showed the residual concentration in Cr^{3+} in the gel after dialysis gel to be 170 ppm. The EPR spectrum of the dialyzed gel (L) is shown in Figure 10. The half-field resonance and sharp line at 0.32 T have disappeared in the dialyzed gel, and a new, broad resonance with weak fine structure (values in Table 1) can be observed. Interestingly, the weak fine structure disappeared upon leaving the dialyzed gel to stand at ambient conditions for a few days (M). Inspection of the fine structure present in the dialyzed gels showed that they are similar to, but not identical with, those in the pH 13 solution of Cr^{3+} (Figure 8). Similarly, the visible absorbance of Cr^{3+} (100 ppm) in an undialyzed gel was shifted to nearly 426 nm, comparable to that observed in the basic Cr^{3+} solution. These spectroscopic features all point to the formation of oligomeric Cr^{3+} species in the polymer gels.

These spectroscopic investigations on aged gel compositions brought to light another interesting observation: The Cr^{3+} absorbance at 264 nm initially increased to a first "plateau" (analyzed in the preceding kinetic part of this study), but at much longer times the absorbance decreased to a value intermediate between the maximum and initial value (Figure 11). In the simple pH 13 solution of Cr^{3+}

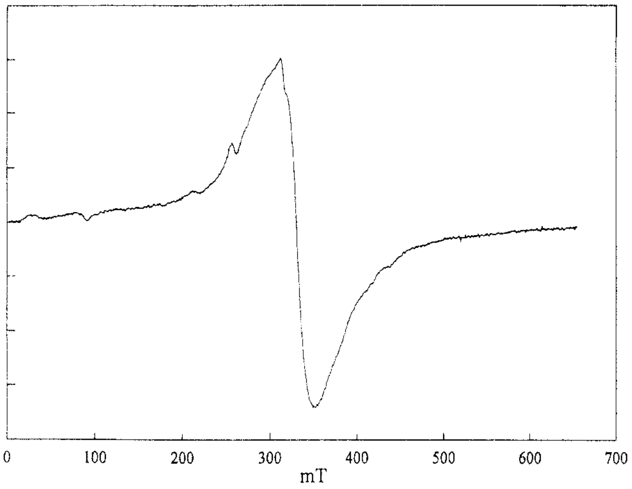


Figure 10. EPR spectrum of frozen, dialyzed gel at 103 K.

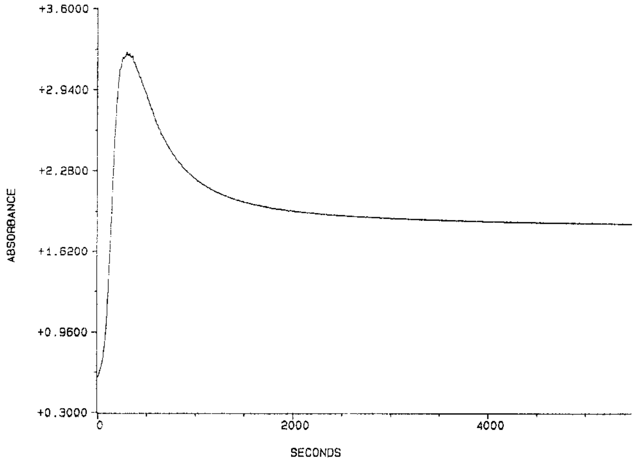


Figure 11. Time evolution of the absorbance at 264 nm of a Cr^{3+}/HPAAm solution at 343 K.

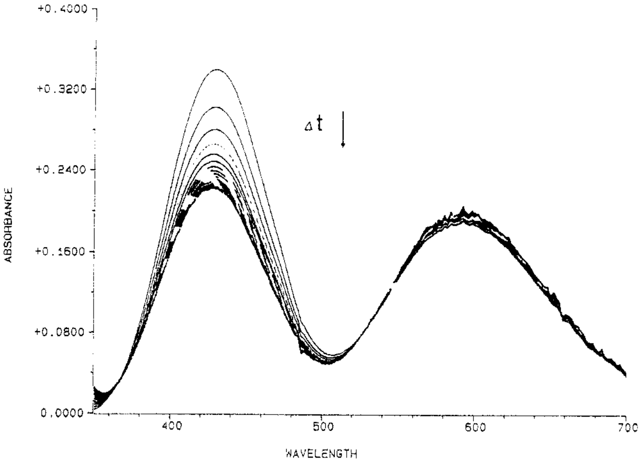


Figure 12. Evolution of the UV–Vis spectra for an aqueous Cr^{3+} solution at pH 13.

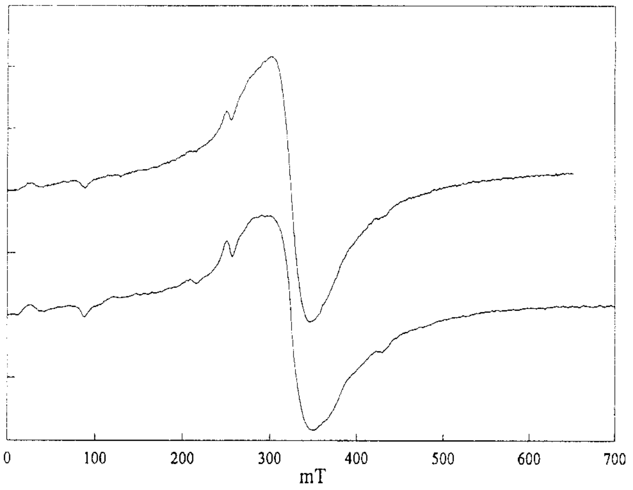
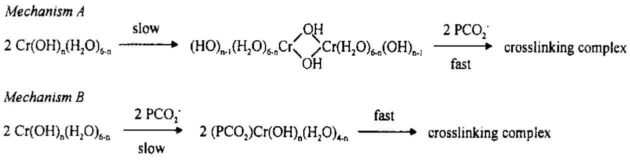


Figure 13. EPR spectra of frozen aqueous Cr^{3+} solutions containing glutaric acid monoamide (bottom) and acetate (top) at 103 K.

Scheme 2



the visible absorbance also moved to a lower value with time (Figure 12), in analogy with the evolution of the absorption spectrum of the gelation reaction at longer times. Possible explanations of this phenomenon include an acid–base reaction which slowly converts the hydroxide-bridged Cr^{3+} oligomers to their oxo-bridged form.[21] Another possibility is that the degree of Cr^{3+} oligomerization in the pH 13.5 solution and polymer gel continues to increase with time.[21]

Additional experiments were carried out with model carboxylate compounds[5,7] in order to obtain further insight into the nature of the reaction of Cr^{3+} with HPAAm. In these experiments, acetate and the monoamide of glutaric acid were combined with Cr^{3+} in a 44:1 molar ratio, similar to the Cr^{3+}:acrylate comonomer ratio in the polymer gel compositions. The EPR spectrum of solutions prepared at very low pH (0.2) remained invariant, indicating no reactivity on the time scale investigated. At pH 5.4, instead, the EPR spectra of the Cr^{3+} species formed within the first hour (N, O in Table 1) are very similar in several respects to those of the Cr^{3+} species formed in the reaction with HPAAm (Figure 13). Again, on the basis of the line width of the resonance at 0.32 T and the absence of the half-field resonance, we interpret the EPR results as indicating the presence of an oligomeric form(s) of Cr^{3+} in the ligand complexes formed. Further, the fine structure evident in spectra taken shortly after mixing suggests that the oligomeric complexes contain a low number of Cr^{3+} ions.

In order to accelerate further reaction, the Cr^{3+}/acetate and Cr^{3+}/glutaric acid monoamide solutions were heated at 60 °C for 3 h. After this treatment the EPR spectra showed a single broad line without fine structure, in perfect analogy with the EPR spectra obtained for a Cr^{3+}/HPAAm gels left to age for 1 week under ambient conditions.

Discussion

The earliest kinetic study of the cross-linking reaction between Cr^{3+} and PAAm was carried out by Prud'homme and co-workers.[10] These authors employed oscillatory rheological measurements in order to study the rate of gel formation in solutions of PAAm and Cr^{3+} where the latter was produced by chemical reduction of the cross-linking-inert Cr^{6+} ion. Their analysis focused on the increase of the storage modulus, G', with time as function of the initial Cr^{3+} and polymer functional group concentrations. When the assumption is made that G' is linearly related to the number of cross-links around the sol-gel transition, the conclusion was reached that the cross-linking reaction is second order both in Cr^{3+} and in polymer.

Two mechanistic alternatives (Scheme 2) consistent with these conclusions were put forth. In both mechanisms, the overall rate determining step for cross-link formation is postulated to be the formation of hydroxyl- or oxygen-bridged Cr^{3+} dimers. The validity of the assumption that G' is a linear function of the number of cross-links over the portion of the gelation reaction monitored, however, is open to question.[22] Even more seriously, the treatment fails to take account of the fact that a significant, but unknown, portion of the initial Cr^{3+} present must already have reacted prior to the point in time when the slope of G' *versus* time was determined. As a consequence, it is impossible, without further information, to associate the measured slope with a specific concentration of unreacted Cr^{3+}, a necessary condition for the analysis attempted.

Subsequently, a qualitative study of the gelation reaction of Cr^{3+} with both HPAAm and the carboxylate-functional biopolymer xanthan gum was reported by Shu.[11] He found that preformed Cr^{3+} oligomers of the type postulated in Scheme 2, mechanism A, are indeed kinetically much more reactive toward polymer cross-linking than is monomeric Cr^{3+}, a result that was taken as confirmation of the proposal that rate determining dimerization of Cr^{3+} lies on the pathway to polymer cross-linking. We note that these experiments demonstrate convincingly that Cr^{3+} oligomers possess greater kinetic reactivity toward the polymer than does monomeric Cr^{3+} and thus satisfy a necessary condition of the proposed mechanism. They do not, however, demonstrate that Cr^{3+} oligomerization is in fact kinetically competitive with the rate of the cross-linking reaction. In any event, these results, coupled with those of Prud'homme, have strongly conditioned subsequent discussions of Cr^{3+}/polymer cross-linking kinetics and mechanism.

More recently, Whillhite and co-workers employed a dialysis method in order to study the kinetics of the uptake of Cr^{3+} by hydrolyzed polyacrylamide.[8] For practical considerations associated with the dialysis method, the experiments were restricted to relatively low polymer and Cr^{3+} concentrations not capable of yielding cross-linked gels. By means of this method, information on the kinetics of the reaction between Cr^{3+} and the polymer functional groups, if not directly on the cross-linking reaction itself, was obtained. These results were employed to derive empirically the kinetic reaction orders in Cr^{3+}, polymer, and H^+. Although it is not clear how the determined kinetic rate law

$$-d[Cr^{3+}]/dt = A\exp(-E_a/RT)[Cr^{3+}]^{1.3}[H^+]^{-1}[P]^{0.8} \quad (6)$$

is compatible with a rate determining Cr^{3+} dimerization step on the reaction pathway, the mechanisms in Scheme 2 were not questioned.

The rate law defined in the present study is given in eq 1. The satisfactory

$$-d[Cr^{3+}]/dt = A\exp(-E_a/RT)[Cr^{3+}][H^+]^{-0.8}[P]^{0.8} \quad (7)$$

agreement of the exponents b and c determined with those obtained by Willhite[8] lends confidence that the spectroscopic method employed is suitable for the study of the kinetics of the reaction between Cr^{3+} and HPAAm. This technique has the advantage of simplicity and rapidity compared with the previous dialysis approach and permits a potentially wider range of compositions and experimental conditions to be investigated, especially those where the gelation kinetics are relatively fast.

The kinetic expression derived in the present study is in remarkable accord with the kinetics reported[17,23] for the reaction between Cr^{3+} and monomeric organic carboxylates under similar conditions. Interestingly, the Arrhenius reaction parameters found for the polymer system are also in good agreement. This comparison suggests that the kinetics of the reaction of Cr^{3+} with HPAAm are not significantly influenced by the fact that the reactive carboxylate groups are located on a polymer molecule which is increasingly bound up in an extended three-dimensional network. In fact, the Cr^{3+}/HPAAm reaction kinetics were monitored to times much beyond the sol-gel transition; thus we conclude that the physical motion of the polymer chains between cross-links remains essentially unrestricted until well after the gelation point. The dependence of the reaction kinetics on the ionic strength of the medium, found to be comparable in magnitude to those reported for monomeric carboxylates[17] suggests further that the polyelectrolyte nature of the systems studied does not have an important influence on the cross-linking reaction.

Straightforward considerations suggest that the experimental evidence for a first order dependence of the reaction kinetics on Cr^{3+} concentration produced in the present study is inconsistent with the existence of a rate determining Cr^{3+} dimerization or oligomerization step on the pathway to polymer cross-linking. This conclusion is strongly reinforced by considering the results of studies[19] on the kinetics of Cr^{3+} dimerization in aqueous solution. Those studies showed that (1) the rate expression for Cr^{3+} oligomerization is second order in Cr^{3+}, rather than the first order dependence reported here or by Hamm[17] for the reaction of Cr^{3+} with monomeric carboxylates, and (2) there is an approximate negative second order dependence on (H^+) for Cr^{3+} dimerization over the pH range of interest (pH 3–6), rather than the approximate negative first order dependence reported here and by Willhite,[8] or reported by Hamm.[17]

Finally, using kinetic data for Cr^{3+} dimerization at 25 °C reported in ref 19, it is possible to estimate the rate of Cr^{3+} dimerization relative to the rate of reaction of Cr^{3+} with monomeric carboxylates reported by Hamm.[17] These calculations show that the initial Cr^{3+} dimerization reaction rate varies from 0.1% of that observed for the Cr^{3+}/carboxylate reaction at pH 3.6 to about 13% of the observed reaction rate at pH 5.5. Similar calculations show an even lower extent of Cr^{3+} dimerization relative to the observed rate of Cr^{3+} uptake by HPAAm found by Willhite.[8]

The generality of these conclusions is suggested by the range of conditions examined: pH 4.2–4.9, Cr^{3+} concentrations from 20 to 180 ppm, HPAAm concentrations from 2000 to 8000 ppm, and temperature range 10–70 °C. Other studies not reported here confirm that the reaction of Cr^{3+} obeys first order kinetics for solutions containing polyacrylamides ranging from 2.2 to 17.5% hydrolyzed. Thus we believe that the mechanistic conclusions reached in the present study accurately describe the cross-linking reaction kinetics for gel-forming HPAAm solutions prepared with fresh Cr^{3+} solutions under all typical conditions of application.

Because the precise attribution of the absorbance band monitored in the present study is uncertain, it is not possible to associate unequivocally the rate determining step monitored by the spectroscopic method with the reaction leading to *cross-linking* of HPAAm polymer by Cr^{3+}. In an earlier study[12] we developed a novel analysis of dynamic rheological data for gel-forming Cr^{3+}/HPAAm compositions in which the time to reach the sol-gel transition was evaluated as a function of the kinetic order of the cross-linking reaction in Cr^{3+}. That study provided evidence that the rate determining step of the cross-linking reaction itself is first order in Cr^{3+}. In view of the agreement with the present study, we may reasonably conclude that the kinetic rate law derived from the UV-spectroscopic measurements effectively provides information on the rate determining step leading to cross-linking.

Curiously, the EPR studies described above offer compelling evidence that *polymer-bound Cr^{3+} oligomers are present in Cr^{3+}/HPAAm gels at the conclusion of the gelation reaction.* Similarly, the EPR spectra of solutions of Cr^{3+} and carboxylate model compounds indicate that Cr^{3+} oligomers appear essentially contemporaneously with the formation of the Cr^{3+}–ligand complex. In light of the kinetic results, we exclude Cr^{3+} oligomerization prior to the rate determining reaction of Cr^{3+} with the polymer. The simplest model consistent with the results is that the rate limiting step involves the pH-dependent reaction between a Cr^{3+} monomer and a carboxylate species (HPAAm or monomeric compound), as shown in Scheme 2. Such a mechanism has been proposed by Hamm[17] and Abdullah[23] in order to account for the reaction of Cr^{3+} with monomeric carboxylates. The interesting contribution from the EPR studies is the indication that Cr^{3+} oligomerization takes place rapidly following the formation of a bond between monomeric Cr^{3+} and the polymer.

Further studies will be required in order to distinguish between these alternate pathways. Nevertheless, from the technological point of view, knowledge of the rate determining step is the key to developing a useful kinetic model for predicting when the sol-gel transition of Cr^{3+}/HPAAm solutions will take place.

Conclusions

UV spectroscopy has proven to be an effective and flexible tool for kinetic studies of the reaction between Cr^{3+} and HPAAm. The good agreement between the UV spectroscopic and previous dialysis kinetic results[8] lends confidence that they provide information on the same chemical reaction, even though the latter studies were carried out with lower concentrations of reagents. The cross-linking reaction kinetics found also are essentially indistinguishable from those reported for the reaction of Cr^{3+} with monomeric organic carboxylates.

In light of the kinetic rate law derived, and on the basis of an analysis of published kinetic data, it may be concluded that *preformed Cr^{3+} oligomers do not participate in the cross-linking of HPAAm*, at least when the reaction solution is prepared with fresh aqueous Cr^{3+} solutions prepared from inorganic salts (*e.g.* $Cr(NO_3)_3$). Clearly, in light of Shu's results,[11] when Cr^{3+} used to prepare the HPAAm solution is present to a significant degree in the preoligomerized form, Cr^{3+} oligomers will be the first species to react with the polymer.

Curiously, the results of the EPR studies suggest that subsequent to the rate determining step of the reaction of Cr^{3+} with polymer, and possibly subsequent to Cr^{3+} cross-link formation, chemically associated (presumably OH- or O-bridged species) Cr^{3+}–Cr^{3+} species are formed. Additional studies will be required in order to obtain further insight into the structure and mechanism of formation of these species.

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