

# pH Effects on the Solubility of Polyacrylamides in Hard Brines

PAOLA ALBONICO and THOMAS P. LOCKHART\*

Eniricerche SpA, 20097 San Donato, Milan, Italy

## SYNOPSIS

Solubility tests have been conducted on hydrolyzed polyacrylamide (PAAm) polymers to define the pH range for solubility as a function of the salinity of the solutions. These tests show for the first time that pH is a critical variable determining the solubility of extensively hydrolyzed PAAm in brines containing divalent cations. The pH range for solubility of PAAm and an acrylamide copolymer as a function of aging in synthetic seawater at elevated temperature is also reported. The underlying mechanisms for the pH-dependent solubility behavior observed and the implications for petroleum applications of acrylamide polymers are discussed. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Partially hydrolyzed polyacrylamide (PAAm) polymer has been extensively investigated and employed in the field both in polymer flooding and polymer gel treatments.<sup>1–3</sup> While aqueous solutions and gels of PAAm are stable in a wide range of brines at low-to-moderate temperatures, it is widely recognized that PAAm is unsuitable for use at elevated temperature in the presence of divalent cations ( $Mg^{+2}$ ,  $Ca^{+2}$ ).<sup>3,4</sup> This limitation derives from the thermally induced hydrolysis of the amide groups to form carboxylate groups; the interaction of the latter with divalent cations leads to a sharp reduction in polymer solubility.<sup>5–9</sup> Similarly, gels formed with polyacrylamide suffer extensive *syneresis* in the presence of divalent cations (that is, contraction of the gel volume with concomitant expulsion of the aqueous medium) as a consequence of the hydrolysis of the polymer.<sup>10–13</sup> It has been suggested,<sup>11,14</sup> in fact, that the basic requirements for polymer solution and polymer gel stability—retention of polymer molecular weight and insensitivity to divalent cations at high temperature—are essentially equivalent for the two applications.

Extensive laboratory studies have been carried out to define the effective working limits of PAAm solutions. These studies have shown that the specific degree of hydrolysis at which PAAm separates from aqueous solution depends directly on the divalent cation concentration and inversely on temperature.<sup>8</sup> On the basis of these studies, a maximum “safe” temperature of 70–82°C has been recommended by various authors for the use of PAAm in polymer flooding.<sup>7–9</sup> With the noteworthy exception of PAAm polymer gels prepared with low molecular weight PAAm,<sup>15</sup> the same upper temperature limit would appear to apply to the use of PAAm gels prepared in seawater and other brines as well.

In view of the limited stabilities of PAAm, the industry has made a significant effort to identify and develop new synthetic polymers with improved stability. The effort to develop divalent cation-resistant synthetic polymers has focused for the most part on copolymers of acrylamide<sup>3</sup> with comonomers resistant to hydrolysis and inert toward divalent cations. While the new copolymers commercialized over the past several years effectively offer the possibility of carrying out polymer flooding and gel treatments with seawater solutions on reservoirs at temperatures significantly higher than those that can be treated with PAAm, there exists for each of these acrylamide copolymers a limit to their resistance to harsh conditions.

\* To whom correspondence should be addressed.

In the present study, we report experimental results on both PAAm and a commercial acrylamide-2-acrylamido-2-methylpropanesulfonate (PAAm-AMPS) copolymer showing that, in addition to temperature and brine hardness, the stability of aqueous acrylamide polymer solutions (or gels) is very strongly influenced by pH as well. Conclusions reached with regard to application limits of PAAm polymer solutions in previous studies, which failed to identify the importance of this parameter, must in some cases be modified.

## EXPERIMENTAL

### Materials

Three polyacrylamides were employed in the present studies. These are Aldrich 19,093-4, a  $2 \times 10^5$  mw, 67% hydrolyzed PAAm and two high molecular weight ( $6 \times 10^6$ ) PAAms: Lamflood 0175 (7.5% hydrolyzed) and Aldrich 18,127-7, which was hydrolyzed to 31% with base at elevated temperature (polymer % hydrolysis determined by NMR). The PAAm-AMPS copolymer employed was analyzed by  $^{13}\text{C}$  NMR and found to contain 25 mol % of the AMPS comonomer.<sup>16</sup> Within the limits of detection (< 1%), the polymer contained no acrylate functionality. Fresh water solutions were prepared with distilled water; the synthetic seawater (SSW) employed contained 10,818 ppm  $\text{Na}^+$ , 448 ppm  $\text{Ca}^{+2}$ , and 1,288 ppm  $\text{Mg}^{+2}$ , all added as the corresponding chlorides (21,233 ppm total  $\text{Cl}^-$ ).

### Polymer Solubility Tests

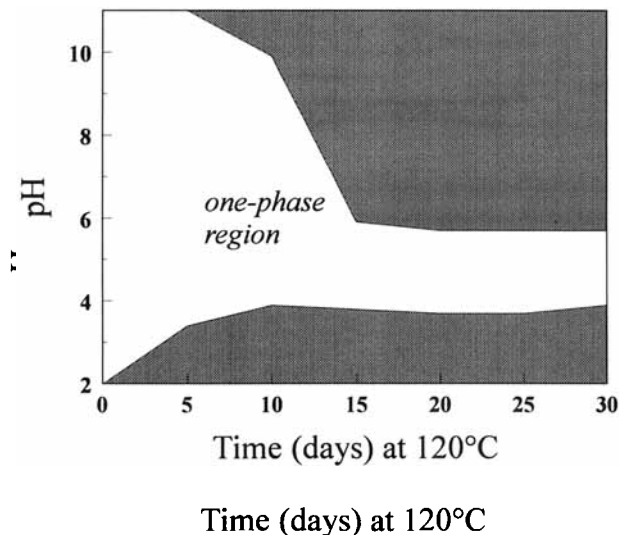
Solubility tests on PAAm and PAAm-AMPS copolymer as a function of salinity, polymer solution

**Table I** pH Range for Solubility of 67% Hydrolyzed PAAm (0.5 wt %) as a Function of Salinity and Temperature

Aqueous Solution	Temperature (°C)	Solubility (pH Range)
Fresh water (de-ionized)	20	2.7-14
NaCl (30,000 ppm)	20	3.7-14
SSW	20	3.7-5.5
	90	2.0-4.6 <sup>a</sup>
	120	2.0-4.4 <sup>a</sup>
Hard brine <sup>b</sup>	20	Insoluble

<sup>a</sup> pH determined at room temperature.

<sup>b</sup> Composition:  $\text{Ca}^{2+}$ , 2,000 ppm;  $\text{Mg}^{2+}$ , 2,000 ppm;  $\text{Na}^+$ , 10,000 ppm;  $\text{Cl}^-$ , 18,000 ppm.

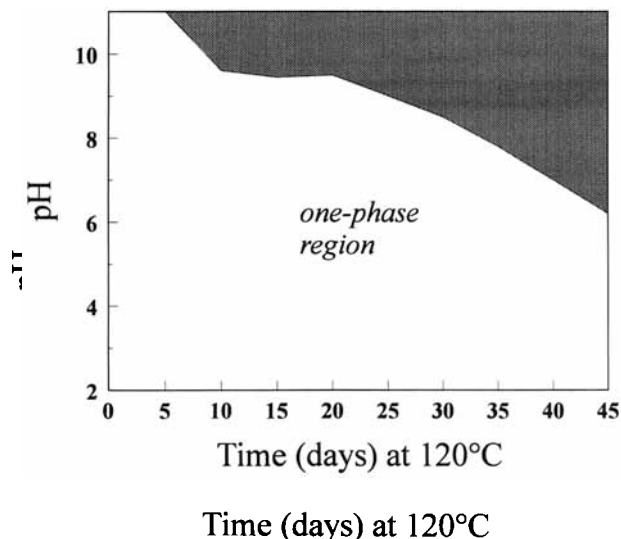


**Figure 1** Phase behavior of 7.5% hydrolyzed PAAm solution (5,000 ppm) in SSW on aging at 120°C.

aging, etc., were carried out. One sample of the polymer solution was titrated with acid (HCl) to determine the lower pH solubility limit, another with base (NaOH) to determine the upper pH solubility limit. Excessive dilution of the polymer solutions was avoided by employing concentrated acid and base solutions until near the pH limit for phase separation. Several titrations back over the pH for phase separation of the polymer gave results in very good agreement with the initial titration (hysteresis less than 0.2 pH units), suggesting that kinetic effects on the polymer phase separation were insignificant.

Solubility tests on 67% hydrolyzed PAAm at 90°C and 120°C (Table I) were carried out by placing a number of polymer solutions, each at a different pH value (determined at room temperature), to heat in an oven. After 1.5 h, the samples were examined for phase separation and the pH was redetermined, again at room temperature. These measurements indicated a pH change of less than 0.1 as a result of heating.

The aging of PAAm and PAAm-AMPS copolymer solutions at 120°C (Figs. 1 and 2) was carried out by placing a number of samples of the polymer solutions, initially at pH 7-8, in a hot air oven. Periodically, a sample of each was removed and the solubility pH range was determined, as described above. After several days' heating, the pH of both polymer solutions had risen to above pH 8. For the PAAm solutions, a precipitate was first detected in the still-hot samples after 6 days; for the PAAm-AMPS copolymer solutions, after 15 days. In both cases, the polymer precipitates initially redissolved spontaneously upon cooling the samples, as would be expected on the basis of the cloud point studies



**Figure 2** Phase behavior of PAAm-AMPS copolymer (2,000 ppm) solution in SSW on aging at 120°C.

reported in ref. 8. After additional aging, and hydrolysis of the polymer, the precipitates no longer dissolved at room temperature until after the pH had been adjusted to a lower range.

## RESULTS AND DISCUSSION

In the course of our studies<sup>13</sup> to develop metal ion-crosslinked polymer gels having improved stability in harsh brines at elevated temperature, it was of interest to compare the stability of the acrylamide polymer gels with those of simple solutions of the polymer in the same brines. Our initial tests on a 67% hydrolyzed PAAm in synthetic seawater (SSW) immediately brought to light a strong and unforeseen dependence of the polymer solubility on pH. Below we describe a series of experiments that serve to define the nature of this pH dependence, suggest possible underlying physical and chemical mechanisms governing the polymer solubility, and serve to clarify the implications of this solubility behavior on technological applications of PAAm and acrylamide copolymers in petroleum production.

Table I presents the results of solubility tests on a 67% hydrolyzed PAAm in aqueous solutions of varying salinity. The choice of this polymer was dictated by the consideration that the extended exposure of PAAm at elevated temperature eventually leads to a similar, high degree of hydrolysis;<sup>8,9</sup> this polymer, hence, constituted a convenient, commercially available model for the PAAm present in aqueous media after significant aging.

Whereas the solubility tests showed that unhydrolyzed PAAm is soluble to below pH 2 in both fresh water and SSW, 67% hydrolyzed PAAm was soluble in fresh water only above pH 2.7. In a 30,000 ppm NaCl solution and in SSW, this lower solubility limit increased to pH 3.7. The hydrolyzed PAAm remained soluble to high pH in both fresh water and the NaCl solution, but was insoluble above pH 5.5 in SSW.

The increase in the lower pH solubility limit with increased PAAm hydrolysis may be attributed to the need to develop a sufficient electrostatic charge on the polymer backbone to overcome intra- and intermolecular hydrogen-bonding interactions of the polymer and to improve polymer solvation by the aqueous medium. The fact that an identical lower pH solubility limit was found for both the NaCl and SSW solutions establishes that divalent cations play no special role in determining this limit. In contrast, the marked decrease in the upper pH limit (5.5) for solubility in SSW and fresh water or NaCl solutions of the PAAm may clearly be attributed to the presence of the divalent cations.

At pH 5.5, the upper solubility limit of the hydrolyzed PAAm in SSW, the polymer acrylate groups are only partially deprotonated.<sup>17</sup> This consideration suggests that the onset of phase separation may be connected to the production of a certain number of deprotonated, and hence divalent cation-reactive, acrylate groups along the polymer backbone. Above this threshold number of acrylate groups, the polymer suffers a collapse of its conformation and separation from the aqueous phase. On the basis of this explanation, and considering the modest equilibrium constant for  $\text{Ca}^{+2}$ -acrylate complexation,<sup>18</sup> we would expect the upper pH limit for polymer solubility to decrease as the concentration of divalent cations is increased. In fact, the solubility window of the 67% hydrolyzed PAAm disappears entirely in a hard brine containing 2,000 ppm each of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  (Table I).

Similar experiments showed that a 31% hydrolyzed PAAm is soluble from below pH 2 to pH 9.9 in SSW at room temperature. This polymer<sup>17</sup> is likely to be fully deprotonated at a pH well below 9.9; hence, there would appear to be still other factors, beyond the number of deprotonated acrylate groups, that contribute to determining the ultimate pH limit for polymer solubility. One such factor could be an increase in the polymer-divalent ion complexation constants with increasing pH.

Experiments were also carried out to determine the solubility range of 67% hydrolyzed PAAm in SSW at elevated temperature. These experiments

were performed by heating PAAm solutions prepared at different values of pH (measured at room temperature) in an oven for 1.5 h, after which they were examined visually for evidence of PAAm phase separation. The results (Table I) clearly establish that the pH window for PAAm solubility persists even at considerably elevated temperature, although the exact pH solubility range cannot be accurately defined from the experiments because of the room temperature pH determinations.

As noted above, the solubility tests conducted on the 67% hydrolyzed PAAm were expected to provide useful indications of the behavior that PAAm polymer solutions might display after prolonged exposure to high temperature. The influence of aging on PAAm solutions was also analyzed directly in experiments in which a 7.5% hydrolyzed PAAm (5,000 ppm) was aged at 120°C in SSW. Samples were removed periodically, and the pH range for solubility of the PAAm was determined at room temperature. The pH range of solubility decreased smoothly over the course of 14 days or so, as reported in Figure 1, at which time it was nearly identical with that determined for 67% hydrolyzed PAAm (Table I).

In an identical experiment carried out with the PAAm-AMPS copolymer, the upper pH solubility limit decreased more gradually (Fig. 2), but eventually approached a value close to that for PAAm. This result shows that the hydrolysis of the acrylamide comonomers in the copolymer ultimately produces the same effect on solubility as for the PAAm homopolymer. Unlike PAAm, however, the lower pH solubility limit of the PAAm-AMPS copolymer (pH 2) was uninfluenced by the aging. The solubility of the PAAm-AMPS copolymer to low pH presumably is a function of the presence of the sulfonate-functional comonomers. Following the logic employed above to rationalize the increased lower pH solubility limit of hydrolyzed PAAm in NaCl or SSW solution, we reason that the substantial deprotonation of the strongly acidic sulfonate groups, which are substantially inert toward divalent cations, provides an electrostatic driving force for dissolution of the polymer even at pH 2.

As noted in the Introduction, earlier publications<sup>5-9</sup> have shown that the solubility of PAAm in brine is a function of the degree of polymer hydrolysis, the concentration of divalent cations, especially  $\text{Ca}^{+2}$ , and the temperature. However, *the influence of pH on the aqueous solubility of hydrolyzed PAAm in the presence of divalent cations has not been previously reported.*

The results of the present investigation are in clear contrast with the prior literature on several

points. First, whereas 31% hydrolyzed PAAm is predicted to be soluble in SSW up to high temperature ( $> 100^\circ\text{C}$ ),<sup>7,8</sup> our experiments show that there is a finite window of pH for solubility even at room temperature. Second, PAAm polymers 64% and 66% hydrolyzed have been reported<sup>18</sup> to be soluble (at 1,000 ppm) up to about 85°C and 70°C, respectively, in a brine of 5% NaCl and 500 ppm each of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ . We find instead that a 67% hydrolyzed PAAm is soluble in SSW at room temperature *only over a narrow pH range*. On the other hand, we find that this solubility persists to at least 120°C, again, within a specific pH range. Additional experiments showed that the pH solubility range for a 1,000 ppm solution of the 67% hydrolyzed PAAm in SSW was the same as that for 5,000 ppm (Table I), thus ruling out the possibility that the discrepancies might arise from a polymer concentration effect.

## CONCLUSIONS

The results reported here establish pH as a fundamental variable determining the solubility of PAAm and acrylamide copolymers in aqueous solutions containing divalent cations. To the extent that previous studies defining the solubility limits of PAAm in terms of brine hardness and temperature did not explicitly report the experimental pH or take it into account as a variable, the earlier conclusions reached should be treated with some caution. In fact, the results of the present study suggest that PAAm and acrylamide copolymer solutions may have a wider range of applicability (in terms of temperature, degree of polymer hydrolysis, and divalent cation concentration) than has generally been recognized. The significance of these results for petroleum applications (specifically, polymer flooding or gel treatments) will clearly depend on the pH environment encountered in the reservoir rock. The use of PAAm and PAAm-AMPS copolymer in SSW or similar brines at high temperature would appear to be reasonable only in acidic conditions (pH  $< 5$ ).

We thank A. Belloni for her assistance with the experimental work reported. Support for this project was provided by the ENI Group and AGIP S.p.A.

## REFERENCES

1. A. Moradi-Araghi, D. H. Beardmore, and G. A. Stahl, in *Water-Soluble Polymers for Petroleum Recovery*, G. A. Stahl and D. N. Schulz, Eds., Plenum Press, New York, 1988, pp. 299-312.

2. J. K. Borchardt, *ACS Symp. Ser.*, **396**, 3-54 (1989).
3. K. S. Sorbie, *Polymer-Improved Oil Recovery*, Blackie, London, England, 1991.
4. H. W. Gao, Topical Report Niper-146, DOE Distr. Cat. UC-92a (Jan., 1987).
5. G. Muller, J. P. Laine, and J. C. Fenyo, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 659-672 (1979).
6. T. Schwartz and J. François, *Makromol. Chem.*, **182**, 2775-2787 (1981).
7. A. Zaitoun and B. Potie, paper SPE 11785 presented at the SPE Int. Symp. on Oilfield and Geothermal Chemistry, Denver, CO, June 1-3, 1983.
8. A. Moradi-Araghi and P. H. Doe, *SPEERE*, 189-198 (paper SPE 13033), 1987.
9. R. G. Ryles, paper SPE 13585, presented at the Int. Symp. on Oilfield and Geothermal Chemistry, Phoenix, AZ, April 9-11, 1985.
10. P. M. DiGiacomo and C. M. Schramm, SPE 11787, presented at the SPE Int. Symp. on Oilfield and Geothermal Chemistry, Denver, CO, June 1-3, 1983.
11. A. Moradi-Araghi, G. Bjornson, and P. H. Doe, paper SPE 18500 presented at the SPE Int. Symp. on Oilfield Chemistry, Houston, TX, Feb. 8-10, 1989.
12. P. W. Chang, I. M. Goldman, and K. J. Stingley, paper SPE 14235, presented at the SPE 60th Ann. Techn. Conf., Las Vegas, NV, Sept. 22-25, 1985.
13. P. Albonico and T. P. Lockhart, paper SPE 25220 presented at the SPE Int. Symp. on Oilfield Chemistry, New Orleans, LA, March 2-5, 1993.
14. H. L. Hsieh and A. Moradi-Araghi, *Polym. Prepr.*, **32**, 269-270 (1991).
15. R. D. Sydansk, paper SPE/DOE 20214 presented at the SPE/DOE 7th Symp. on Enhanced Oil Recovery, Tulsa, OK, April 22-25, 1990.
16. T. P. Lockhart and P. Albonico, paper SPE/DOE 24194 presented at the SPE/DOE 8th Symp. on Enhanced Oil Recovery, Tulsa, OK, April 22-24, 1992.
17. M. Mandel, *Eur. Polym. J.*, **6**, 807 (1970).
18. D. M. Chang, *J. Am. Oil Chem. Soc.*, **60**, 618-622 (1983).

Received March 25, 1994

Accepted June 13, 1994