

Low Molecular Weight Poly(acrylic acid) as a Salt Scaling Inhibitor in Oilfield Operations

S. Moulay^{a,*}, M. Boukherissa^b, F. Abdoune^a and F.Z. Benabdelmoumene^a

^a *Laboratoire de Chimie-Physique Moléculaire et Macromoléculaire, Département de Chimie Industrielle, Faculté des Sciences de L'Ingénieur, Université de Blida, B.P. 270, Route de Soumâa, 09000, Blida, Algeria*

^b *Centre de Recherche et Developpement-Sonatrach, Boumerdes, Algeria*

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Poly(acrylic acid) (PAA) samples with molecular weights between 820 and 2950 were synthesized by a solution polymerization process using an initiating redox system. The obtained PAAs were then screened for their ability to inhibit salt scale formation. In this screening system, salt scale was formed by injecting pit water into the oil. The salt scale inhibition efficiency was higher for PAAs at a higher concentration and for lower molecular weight PAAs. A reduction of pH, extension of stirring time, or an increase in temperature caused the inhibition efficiency of the PAAs to drop. An optimal inhibition efficiency of 98.70% was observed using a PAA with a molecular weight of 820 at a concentration of 20 ppm, at 20 °C, while being stirred for 1 h at a pH of 6.029.

Keywords: Poly(acrylic acid), Scaling, Barium sulfate, Oilfield

INTRODUCTION

Industrial plants such as those that conduct seawater desalination, sugar evaporation, as well as geothermal plants, oil fields, boilers, and process cooling systems are continuously facing salt scale formation or caking. Ordovician water is omnipresent in oilfield wells. To accelerate the oil recovery process, external water (pit water or Lias water) is deliberately injected to alter the existing pressure in the underground environment, thus, forcing the oil up the well. At a certain point in this process, the pressure becomes low enough to cause the water to boil. On boiling, mineral salt deposits are readily formed.

Salt scaling is an obstacle to the oil recovery process because it causes fouling of the pipe-line and obstruction of the tanks, pumps and fittings at the field production facilities,

thus the prevention of salt scaling is of great interest. The salt deposit consists of mainly brine, calcium carbonate, calcium sulfate, strontium sulfate and barium sulfate. Worst of all, oilfield scale also contains naturally occurring radioactive materials (NORM). The amount of NORM in the USA has been reported to be 300,000 to 1,000,000 tons per year [1]. Of these salts, barite (barium sulfate) induces incrustation faster because of its low solubility in water, 2.4 mg l⁻¹, while CaCO₃, CaSO₄, SrSO₄, and NaCl have solubilities of 6.92, 1053, 99.76 and 350,000 mg l⁻¹, respectively. Moreover, barium sulfate scale is very difficult to remove and mechanical means are employed for this purpose.

Although the obvious remedy to the scaling problem is treating the external water prior to injection, such as water softening, this precaution is not practical as the daily quantity of this water usually exceeds 30,000 m³ [2]. Although phosphonic acids, such as [nitrilo(methylenephosphonic) acid]

* Corresponding author. E-mail: saadmoul@yahoo.com

and [hexamethylenediaminetetra(methylenephosphonic acid)], are widely used as effective scale inhibitors, they are poorly biodegradable and, consequently, they burden the environment. Mono carboxylated starch and polyaspartic acid have been evaluated as antiscalants for the mining industry by Henkel [3]. Water-soluble polymers have been used to modify the rheology, gel strength, and filtrate loss of aqueous oilfield drilling fluids. One of the mechanisms by which polymers prevent scaling is the sequestration of metallic ions [4]. Polycarboxylates were used as builders in laundry detergents to inhibit or reduce scale formation during washing at elevated temperatures [4]. Indeed, a copolymer of acrylic acid and maleic acid (70:30) with an average molecular weight of 70,000 prevents the agglomeration of CaCO_3 nanoparticles that form calcite. There is a unanimous point of view on the fact that scale inhibitors either prevent salt precipitation or act as a crystalline morphology modifier. Also it is commonly agreed upon that, because of the multicomponent nature of the cake, the use of a single inhibitor is not effective and an inhibitor system consisting of a threshold inhibitor, a chelating agent, a corrosion inhibitor and a dispersant is most effective.

Algeria, being an OPEC member, relies primarily on oil revenues to support its economy. It is therefore imperative to avoid any burden on its oil production. The present work includes the synthesis of low molecular weight PAAs and their evaluation as scale inhibitors in the oilfield at Tin Fouyé Tabankort (400 km south of Hassi Messaoud, Algeria). The inhibition efficiency was studied as a function of the molecular weight and concentration of PAA, the pH and the stirring time of the tested water solution, as well as the temperature and amount of ferrous salt added.

According to the literature, polyacrylics are quite versatile in many applications, particularly in the removal of heavy and radioactive metallic ions, and new applications are ever increasing [5-11]. Doherty *et al.* recently reported a study of the inhibition of calcium oxalate using poly(acrylic acid)s [12].

EXPERIMENTAL

General

Acrylic acid, potassium persulfate, thioglycolic acid (mercaptoacetic acid), and sodium thiosulfate were purchased

from Prolabo (Paris, France). Acrylic acid and potassium persulfate were purified by vacuum distillation and recrystallization from water, respectively. Thioglycolic acid and sodium thiosulfate were used as delivered. Deionized water was used in the polymerization reaction and in the inhibition tests.

PAAs obtained were analyzed by infrared spectroscopy using FT-IR Perkin Elmer. Molecular weights (M_{GPC}) of the PAA's were determined by gel permeation chromatography using a Waters Associates GPC model 150C.

The turbidity was measured with a Hach 2100N turbidimeter (Loveland, CO, USA).

Synthesis of PAAs

The following procedure is a general protocol for the PAAs synthesis. A solution of 7.2 g of freshly distilled acrylic acid in 100 ml of deionized water was charged into a 250 ml resin kettle fitted with a mechanical agitator, a reflux condenser, a thermometer and a nitrogen gas inlet. A stream of nitrogen was applied to the solution for 1 h to flush out the dissolved oxygen in the mixture. Equal amounts (wt%) of sodium thiosulfate and potassium persulfate were added to the solution while stirring (mechanical, 300 rpm). The mixture was allowed to react under the reaction conditions shown in Table 1. The nitrogen gas flow was maintained throughout the reaction. The polymer was isolated by precipitation by mixing the aqueous solution with ethyl acetate, and drying at 40-50 °C *in vacuo* for three days.

The yields and molecular weights (M_{GPC}) of the obtained PAAs are shown in Table 1.

Estimation of the PAA Inhibition Efficiency

The compositions of the systems of water employed in this study are given in Table 2, and were based on those used at the Tin Fouyé Tabankort oilfield.

The method for estimating the inhibition efficiencies of the PAA samples was as follows: To a set of beakers each filled with 30 ml of injection water, samples of PAA were added to achieve the following final concentrations by syringe: 10, 20, 50, 70, 100, and 150 ppm. Then, 70 ml of oilfield water was poured into each of these solutions. The mixtures were allowed to stir according to the conditions described in Table 1. Afterwards, the optical density, as a measure of turbidity,

Low Molecular Weight Poly (acrylic acid)

Table 1. Yields and Molecular Weights of PAAs

M_{GPC}	820	856	881	801	926	940	955	976	990	1000	1320	1535	1700	2190	2350	2950
Yield (%)	75	61	64	53	34	24	71	77	66	48	72	66	66	66	32	64
T (°C)	60	30	30	30	30	30	30	30	30	30	50	30	40	30	30	70
Time (min)	30	30	45	30	30	30	60	90	30	120	30	30	30	30	30	30
[TA] (wt%)	10	20	10	10	5	0	10	10	10	10	10	10	10	10	10	10
[In] (wt%)	5	5	5	5	5	5	5	5	15	5	5	10	5	7	2	5

Table 2. Compositions ($g\ l^{-1}$) of Simulated Lias Water (Injected Water) and Ordovician Water (Oilfield Water)

Components	Lias water (pH = 7.6)	Ordovician water (pH = 6.6)
NaCl	3.9659	101.564
KCl	0.1468	4.1566
MgCl ₂	-	26.0306
CaCl ₂	-	119.8111
SrCl ₂	-	2.2822
BaCl ₂	-	1.8320
Na ₂ SO ₄	1.8735	-
MgCl ₂ .6H ₂ O	0.6106	-
CaCl ₂ .2H ₂ O	1.1026	-
NaHCO ₃	0.2602	-
Na ₂ CO ₃	0.0042	-

T_u , expressed in NTU (Nephelometric Turbidity Units), of each solution was measured and the inhibitor efficiency was computed using Eq. (1).

$$\text{Eff.(\%)} = \frac{(T_u)_0 - (T_u)}{(T_u)_0} \times 100$$

$(T_u)_0$ is the turbidity of the solution in the absence of the inhibitor

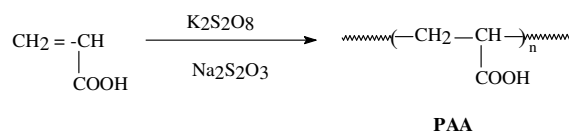
(T_u) is the turbidity of the solution in the presence of the inhibitor

(1)

RESULTS AND DISCUSSION

Synthesis of PAA's

PAA samples were obtained by polymerizing acrylic acid



(2)

in water using an initiating redox system as illustrated in Eq. (2). The PAAs were characterized by FT-IR and their spectra were similar to that reported in the literature [13]. Table 1 gathers the yields and molecular weights of PAAs under the different reaction conditions. In order to obtain the PAAs of low molecular masses, the effects of the temperature, the polymerizing time, the chain transfer agent concentration and the initiator concentration were studied.

As shown in Table 1, increasing the chain transfer agent concentration and lowering the initiator concentration afforded lower molecular weights, and these findings are in accordance with the literature [14]. While no precise trend of the molecular weight was observed by varying the temperature, longer reaction times yielded higher molecular masses. Yet, the highest molecular weight, 2950, was obtained at 70 °C and the lowest one, 820, at 60 °C under identical reaction conditions. However, the yields did not show any systematic dependence on the parameters studied other than time and were in the range of 24 to 75%. The yields were found generally to increase with time.

Study of the PAAs Inhibition Efficiency

First, we determined an optimal mixture ratio of Lias water/ordovician water that resulted in the greatest salt scale, so as to optimize the inhibition efficiency. As seen in Table 3, the appropriate mixture ratio used for the inhibition study was 30:70, which yielded the highest turbidity, 602 TNU.

The effects of the molecular weight and concentration of PAA, the temperature, the stirring time, the amount of ferrous ions added and the pH on the inhibition by the PAA with a molecular weight of 820 (PAA₈₂₀) were assessed. PAA₈₂₀ was the sample that gave the optimal inhibition efficiency, as discussed below.

Effects of the molecular weight and the concentration of PAA. Figures 1 and 2 present the data regarding the effect of the molecular weights of PAA on inhibition efficiency at

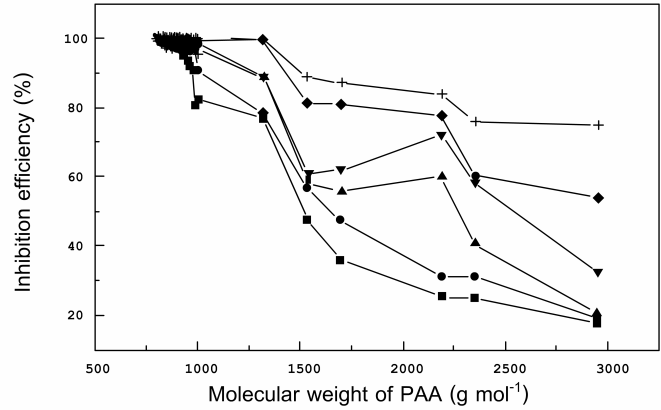


Fig. 1. Inhibitor efficiency vs. molecular weight and concentration of PAAs. Operating conditions: room temperature; stirring time, 1 h; pH, 6.209. (■) 10 ppm, (●) 20 ppm, (▲) 50 ppm, (▼) 75 ppm, (◆) 100 ppm, (+) 150 ppm.

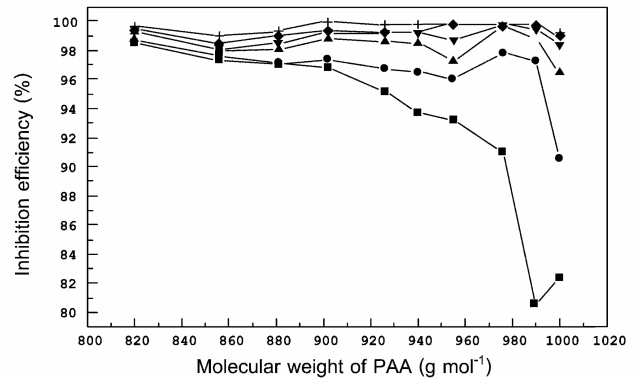


Fig. 2. Fig. 1 restricted to PAAs with molecular weights between 820 and 1000. (■) 10 ppm, (●) 20 ppm, (▲) 50 ppm, 75 ppm (▼), (◆) 100 ppm, (+) 150 ppm.

Table 3. Turbidity, (T_u), as a Function of the Varying Mixture Ratio, Lias Water/Ordovician Water*

V _{Lias} (ml)	0	10	20	30	40	50	60	70	80	90	100
V _{Ordovician} (ml)	100	90	80	70	60	50	40	30	20	10	0
(T _u) (NTU)	162	319	539	602	569	387	321	219	195	96	11

* Room temperature, stirring for 1 h.

different concentrations of PAA. It is clear that the inhibitor effectiveness was lower with higher molecular weight PAAs but was higher with higher PAA concentration.

Indeed, an appreciable inhibition was always observed at a PAA concentration of 150 ppm regardless of the molecular weight. Yet, PAAs with molecular weights higher than 1320, used at lower concentrations, were found to be less effective than those of lower molecular weights. The inhibition by the lower molecular weight PAAs was quantitative and nearly constant at 99% even for the lowest concentration, 10 ppm.

To account for the peculiar effectiveness of the relatively low molecular weight PAAs, one can recall that the chains of most linear and atactic polymers, devoid of secondary and tertiary structures, tend to fold within each other to form a mass of interpenetrating random coils, not unlike a bowl of spaghetti [15], and this tendency increases as the polymer size increases. In solution, the polymeric chains tend to unfold but the extent of this unfolding is a function of the nature of the solvent and the temperature. Under θ conditions, that is the θ solvent and the Flory temperature, an optimal unfolding results and the chains are more opened and disentangled [16]. In addition to the natural folding of linear polymeric chains of PAA, there is the folding due to the hydrogen bonding between the carboxylic groups either intermolecularly or intramolecularly. To recall, the theta solvent and temperature for PAA are dioxane and 30 °C, respectively [17]. However, in our working conditions, the longer PAA chains are folded to a certain degree and the carboxylic functions are not all exposed. Most of them are embedded in the core, and consequently, the sequestration of the metallic ions by the carboxylic groups is not quantitative. In the case of shorter PAA chains, the unfolding is more complete and the carboxylic groups are more accessible and prone to the complexation with metallic ions.

On the other hand, increasing the PAA concentration would obviously provide a greater number of exposed carboxylic groups irrespective of the size, and thus the sequestration is enhanced.

Effect of added ferrous ions. Compared to other metallic species present in water, iron tends to be more troublesome in industrial water. Iron in the form of Fe(II) can be readily oxidized to Fe(III) in an aqueous medium, provided that there is enough dissolved oxygen. Fe(III) then will precipitate as

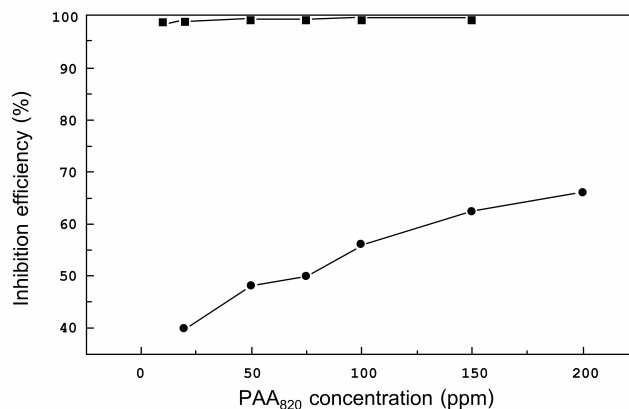
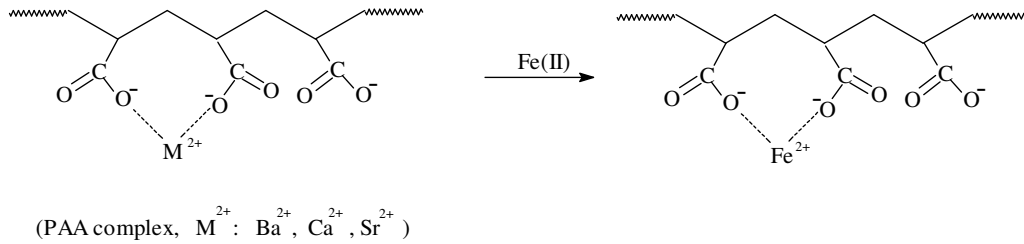


Fig. 3. Inhibitor efficiency vs. PAA₈₂₀ concentration in the absence/presence of FeCl₂. Operating conditions: room temperature; stirring time, 1 h; pH, 6.029. (■) In the absence of Fe(II), (●) In the presence of Fe(II).

Fe(OH)₃. Therefore, it was important to assess the effect of Fe(II) on the inhibitory activity of PAA in the present water mixture system.

Figure 3 shows the impact of the added ferrous ion at a concentration of 0.5321 g l⁻¹ on the inhibition capacity at different PAA₈₂₀ concentrations. The presence of ferrous ions appreciably reduced the inhibition efficiency even at higher inhibitor concentrations; a 34 to 60% decrease in inhibition was observed for the PAA₈₂₀ concentrations studied.

This finding can be explained by the fact that ferrous ions either strongly displace the ions that are complexed by the polymer chain through the carboxylate functions as illustrated in Eq. (3), or, by itself, to form the PAA-Fe(II) complex prior to its oxidation to Fe(III). The latter form of iron will precipitate either as Fe(OH)₃ or as a ferric-PAA salt [6]. The results are quite understandable if one considers the formation constants at the molecular level, K or logK, of the complex Fe(II)-acetate and Fe(II)-ethylenediaminetetraacetate and those of the corresponding complexes of Ba(II), Ca(II), and Sr(II). The greater K or logK, the more stable the complex. Indeed, the complex formation constants of Fe(II) are higher in both cases. LogK for acetate and ethylenediamine-tetraacetate complexes are as follows: Fe²⁺ (3.2, 14.33), Ba²⁺ (0.41, 7.78), Ca²⁺ (0.6, 11), and Sr²⁺ (0.44, 8.80) [18,19]. At



(3)

the macromolecular level, this trend can also be true to some extent.

Effect of the stirring time. The effect of the stirring time of the mixture on the inhibition potency of PAA₈₂₀ is shown in Fig. 4. It is interesting to note that beyond 4 h of agitation, the PAA₈₂₀ inhibition declined to a very low value. The optimal stirring time was 1 h, affording an inhibitory activity of 98.70%. This result would suggest that applying a continuous mechanical force may promote the decomplexation that took place throughout the operation; the complexes PAA₈₂₀-M²⁺ degraded to liberate the complexed ions which would be involved in the crystal growth.

Effect of the temperature. Figure 5 depicts the variation of the inhibition efficiency at different temperatures. It is apparent that an increase in temperature led to a lower inhibition capacity of PAA₈₂₀ and more significantly above 50 °C, where it dropped to 4.65%. The scale inhibition dropped drastically at 70 °C. This study showed that a substantial inhibition, 98.70%, can be favorably obtained at a temperature as low as 20 °C. By elevating the temperature, the stability of the formed complexes may decrease which results in the collapse of the complexes releasing the metallic ions, and hence, the onset of scale formation [5].

Effect of the pH. The above experiments were conducted at a pH of 6.092, which is higher than the pK_a of PAA (4.7) [20]. This would indicate that the carboxylic groups are in their dissociated forms which would accelerate the sequestration process, and increase the inhibition efficiency of PAA. Indeed, a 98.70% inhibition was found at this working pH, at the optimal temperature and time established above. At a basic pH, the inhibition efficiency was not substantially altered from that at pH = 6.03. In fact, at pH = 10.32, the

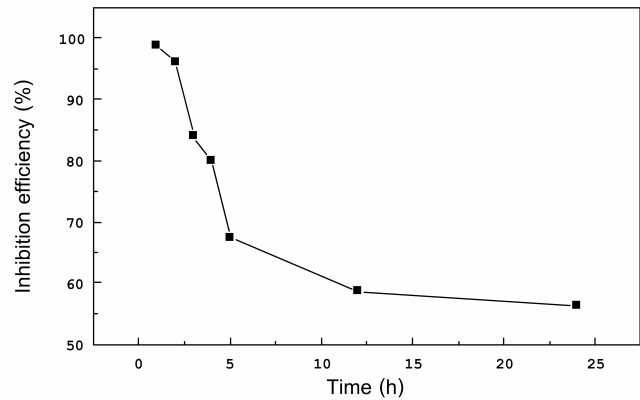


Fig. 4. Inhibitor efficiency *vs.* stirring time. Operating conditions: PAA₈₂₀ concentration, 20 ppm; room temperature; pH, 6.029.

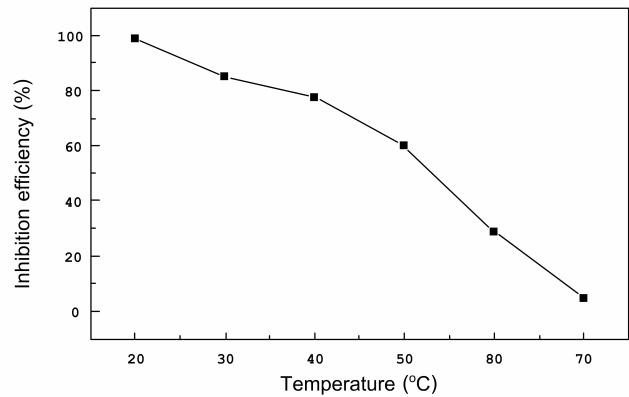


Fig. 5. Inhibitor efficiency *vs.* temperature. Operating conditions: PAA₈₂₀ concentration, 20 ppm; stirring time, 1 h; pH, 6.029.

estimated inhibition ability was 97.14%. However, working at a pH lower than 4.7 would lower this potency. At pH = 1.26, the inhibition efficiency was unfavorably reduced to 37.37%. This is an acidification process and, consequently, the ionized forms would vanish and a complete rebuilding of the PAA (pH < pK_a) would occur, disfavoring the complexing phenomenon in the nonionized state.

CONCLUSIONS

Optimal reaction conditions for synthesizing PAAs with molecular weights as low as 820 were experimentally established. PAAs with molecular weights lower than 1320 were determined to be appropriate materials for the scale inhibition in oilfield operations. The effectiveness of fighting incrustation using PAAs as scale inhibitors is clear, providing the following optimal conditions are used: PAA₈₂₀ concentration: 20 ppm; stirring time: 1 h; temperature: 20 °C.

ABBREVIATIONS

PAA	- Poly(acrylic acid)
PAA ₈₂₀	- Poly(acrylic acid) with a molecular weight of 820 g/mole
M _{GPC}	- Average molecular weight estimated by gel permeation chromatography
GPC	- Gel permeation chromatography
TA	- Chain transfer agent
In	- Initiating redox system
(T _u)	- Turbidity
NTU	- Nephelometric turbidity unit
ppm	- Parts per million

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