



Evaluation of different polymeric scale inhibitors for oilfield application

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Abstract

The current challenges in oil production involve increase in productivity for high temperature, pressure and salinity conditions. In flow assurance, scale inhibitors injection plays a key role to control scale formation. In this work, homopolymers were synthesized by free radical solution polymerization using sulfonate monomers as sodium styrene sulfonate (NaSS), 2-acrylamido-2-methyl-propanesulfonic acid (AMPS) and sodium vinyl sulfonate (SVS); phosphonic monomer as sodium vinyl phosphonic acid (VPA) and carboxylic monomer as sodium acrylic acid (AA). The influence of the chemical structure and molecular weight of the homopolymers on scale inhibition process at different scenarios was evaluated by static and dynamic efficiency. NaSS homopolymers demonstrated higher efficiency (near to 75%) over time, comparing with other homopolymers specially in a multiple scale condition which presents high ionic forces. These data suggest that NaSS polymeric inhibitor can act in different stages involved on scale inhibition, like as retarding nucleation, crystal modification and charge neutralization. Among the homopolymers tested (varying molecular weight and chemical structure), the best results were obtained using homopolymers from NaSS with molecular weight near to 13,000 Da.

Keywords

polymeric scale inhibitor; sulfate condition, static and dynamic efficiency

Introduction

Inorganic scale causes severe issues for the system, like reduction in production, equipment wear, corrosion and loss in heat transfer [1]. The polymeric scale inhibitor with different functional groups like phosphonates, aminophosphonates, poly carboxylates and sulfonated polycarboxylates, can interact with ions and crystal growing by threshold mechanism, [2-11]. Comparing different carboxylic polymers, like as polyepoxysuccinic acid or hydrolyzed poly (maleic anhydride), showed higher interactions with calcium ions and calcium carbonate and sulfate crystals in surface modification, comparing with polyacrylic acid [11], nonetheless acrylic polymers present low calcium tolerance comparing with sulfonic groups, losing in solubility [12,13]. Regarding to molecular weight, apparently, the low molecular weight chains are more effectively adsorbed on active sites on the crystal surfaces [12]. It was also reported that complexation affinities between scale forming cations and polyelectrolytes for poly (sodium 4-styrenesulfonate) and polyacrylic polymers have different order of priority complexation depending the cation (Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+}) [14,15]. This work presents the synthesis and characterization of homopolymers with different functional groups and molecular weight and their inhibition performance in three salinity conditions: sulfate scale and multiple scale. The influence of the chemical structure and molecular weight of the polymers on scale inhibition process at different

scenarios with high electrolyte concentration was investigated. The homopolymers were prepared by free radical solution polymerization from acrylic acid (AA) sodium salt, sodium styrene sulfonate (NaSS), 2-acrylamido-2-methyl propanesulfonic acid (AMPS) sodium salt, sodium vinyl sulfonate (SVS) or vinyl phosphonic acid (VPA) sodium salt.

Methodology

Experimental Procedure

Synthesis of homopolymers: different homopolymers, using high purity monomers (Fig. 1), were synthesized using deionized water as solvent and ammonium persulfate used as initiator, in a molar ratio monomer/initiator range from 2 to 300. Polymerization was performed at 70 °C during 24 h. After adequate precipitation, the polymers obtained were dried at 40 °C until constant mass.

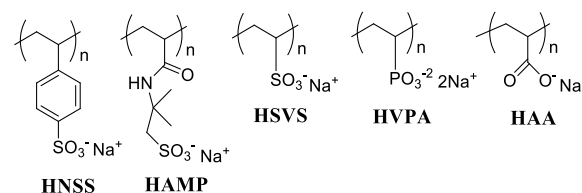


Figure 1: Chemical structure of synthesized homopolymers.

Characterization: all polymers were characterized by ¹H-NMR to quantify the conversion of the monomers using a Bruker 400 MHz equipment.

Size Exclusion Chromatography (SEC) was used to determine molecular weight using Viscotek VE 2001 equipment with RI detector, using NaNO₂ 0,1 M as eluent and calibrated using poly (ethylene oxide) standards.

Static efficiency (bottle test): bottle test (NACE TM0197-2010) was performed as static efficiency for scale inhibitor, preparing different synthetic brines (Table 1). The efficiencies of different homopolymers were calculated according to Eq. (1), where A is the quantity of metallic cation present in the solution with scale inhibitor (ppm) after the test; B is the quantity of cation present in the solution without scale inhibitor (ppm) after the test; O is the quantity of cation present in the solution without scale inhibitor (ppm) before starting the test. The anionic brine presented NaCl, Na₂SO₄ and NaHCO₃ composition. The cationic brine presented all chloride salts. The both brines were filtered using 0.45 µm, and adjusted pH. The polymers were dosed firstly to anionic portion and after completed the volume with cationic brine. 5 ppm of each polymer were dosed in bottles of 100 mL with brine and kept in the oven for until 24 h. After, samples were collected to measure the metal ion concentration using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The scales obtained were washed with water, dried and the change in morphology was analyzed by scanning electron microscopy (SEM).

Equations

$$\% \text{ Efficiency} = [A-B] / [O-B] \times 100 \quad (1)$$

Table 1: Different brine composition used for static and dynamic efficiency.

Ion	Sulfate condition		Multiple scale condition
	60% (v/v)	40% (v/v)	
	ppm	Ppm	ppm
Na ⁺	12,007	5,000	79,630
Ca ²⁺	504	4,220	6,100
Mg ²⁺	1,390	886	607
K ⁺	226	470	3,280
Sr ²⁺	9	423	2,950
Ba ²⁺	1	233	35
Cl ⁻	21,493	80,921	142,400
SO ₄ ⁻²	2,843	1,8	95
HCO ₃ ⁻	150	40	334
pH	8.0	6.5	6.7
Total of solids	38,623	91,269	234,730
Scale prediction - Pitzer theory (16)			
Calcite (CaCO ₃)	-		207 ppm
Anhydrite (CaSO ₄)	1,316 ppm		-
Celestite (SrSO ₄)	288 ppm		83 ppm
Barite (BaSO ₄)	160 ppm		49 ppm

Dynamic efficiency: The polymeric scale inhibitors efficiencies were evaluated in a PMAC dynamic scale looping equipment (DSL), using a coil with 3 m and diameter of 0.5 mm, at 120 °C and 500 psi and 10 mL min⁻¹ as flow rate. Homopolymers concentration fixed dosage used as 2 ppm based on solids content (17).

Results and Discussion

Polymerization: the polymerization conditions and homopolymers characterization results are summarized in Table 2. Homopolymers from different monomers (SVS, VPA, AMPS, NaSS and AA) were synthesized having a molecular weight from 790 to 43,100 Da to evaluate the influence of the different functional groups on the scale inhibition.

Static efficiency: static efficiency for sulfate condition (Table 1), was carried out by measuring the inhibitor performance 24 h, according to Fig. 2- Fig. 3. All homopolymers showed a strong decrease on inhibition static efficiency mainly for calcium sulfate. Only the polymeric scale inhibitors based on NaSS and AA (Fig.2-3) demonstrated some efficiency inhibition for strontium and barium sulfate. Surprisingly, compared with other sulfonic groups, the improvements in efficiency observed using NaSS can be related to the spatial hindrance of the aromatic group.

Long-time efficiency test (Fig. 3) showed no stronger influence of the molecular weight for barium and strontium sulfate scale inhibition. For calcium sulfate only the homopolymers HNSS2 and HNSS3 with molecular weights of 13,000 and 25,600 Da, respectively, showed inhibition efficiency.

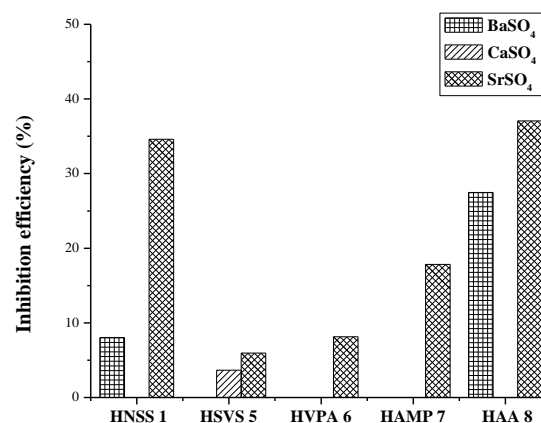


Figure 2: Static efficiency of different homopolymers (790 to 1,100 Da), for sulfate cond., 24h at 50 °C.

The best result in efficiency for barium and strontium sulfate was obtained for the polymer molecular weight of 13,000 Da (HNSS 2). For calcium sulfate, HNSS 4 (43,000 Da) and HNSS 3 (25,600 Da) showed the best results.

Table 2: Homopolymers obtained by radical polymerization.

Code	Monomer	[Monomer]/[Initiator]	Conversion by ¹ HNMR	Mn (Da)	Mw (Da)	Đ
HNSS 1	NaSS	2.8	>99%	800	1000	1.2
HNSS 2	NaSS	7.8	>98%	13,000	33,900	2.6
HNSS 3	NaSS	49	>98%	25,600	82,300	3.2
HNSS 4	NaSS	196	>98%	43,100	244,950	5.7
HSVS 5	SVS	300	>96%	1100	2000	1.8
HVPA 6	VPA	14.4	65%	790	1200	1.5
HAMP 7	AMPS	2.0	>98%	790	940	1.2
HAA 8	AA	22.5	>98%	795	1000	1.3
HAA 9	AA	22.5	>99%	7600	15,200	2.0

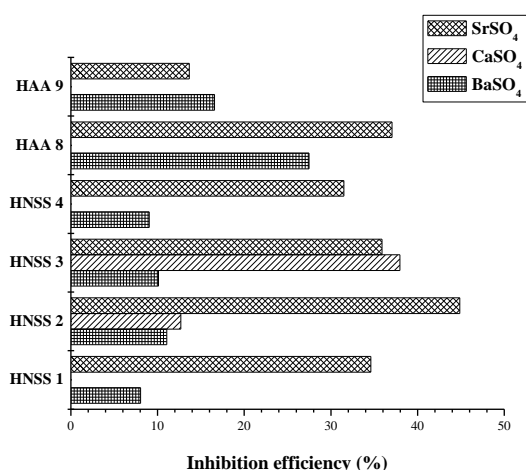


Figure 3: Static efficiency of different of homopolymers of NaSS (800 to 43,100 Da) and AA (795 to 7,600 Da) for sulfate cond., 24h at 50 °C.

These results suggest, in addition to effectively modifying the crystals, that NaSS polymeric scale inhibitors can act as dispersant to the medium, neutralizing charge and minimizing the interactions of divalent ions with active sites of the crystal.

To verify this hypothesis, the morphology of the scales formed under sulfate condition after 24 h was analyzed by scanning electronic microscopy (Fig. 4). For comparison, a mixture of rhombic bipyramidal crystal morphology of scales obtained from a solution without inhibitor is presented in Fig. 4a (blank). Changes on crystal morphology were observed mainly for phosphonic (HVPA 6) and acrylic (HAA 8) homopolymers suggesting that they can act efficiently on crystal modification. For sulfonated homopolymers (HAMP 7 and HSVS 5) no crystal modification was observed, however for poly (sodium 4-styrenesulfonate) changes on the crystal morphology was pronounced as the molecular weight increases. All homopolymers caused morphological changes in the crystal morphology compared with blank.

Dynamic efficiency: dynamic efficiency on DSL equipment was carried out using multiple scale condition, high salinity and high temperature. According to Fig. 5, homopolymers with similar molecular weight were selected to evaluate the efficiency under this condition. All homopolymers presented a scale inhibiting effect since a pressure increase of 10 psi was observed at longer times. The best performance was evidenced for HVPA 6,

where the pressure increased linearly with time reaching a value lower than 7 psi after 30 min.

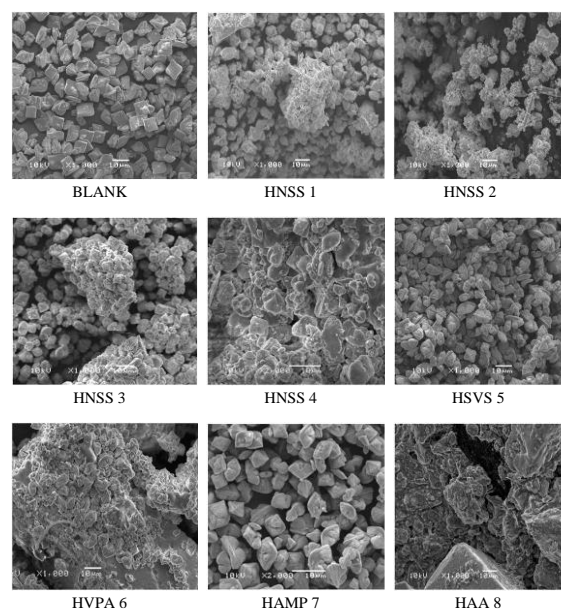


Figure 4: SEM of scales obtained by static efficiency in sulfate (24 h)

As DSL analysis induces highly nucleation tendency, it was expected better efficiency using HVPA 6 homopolymer due to the strong interactions of phosphorus with divalent ions. For homopolymers prepared from NaSS monomer, dynamic efficiency was carried out varying molecular weight. Comparing HNSS 1 (800 Da), HNSS 2 (13,000 Da) and HNSS 4 (43,100 Da), the best results with 2 ppm dosage was found using HNSS 2, according to Fig. 6. Increasing molecular weight, increases the dynamic efficiency probably due to a higher adsorption on the crystal surfaces, inducing an irregular, noncrystalline form. Further increase in molecular weight, decreases the inhibitor solubility causing a loss in efficiency. Increasing dosage of HNSS 2 to 4 ppm, improved the performance showing that the efficiency of HNSS homopolymers can be optimize, since this polymeric scale inhibitor act by different mechanisms on scale inhibition, mainly: delay of nucleation, crystal grow modification and dispersive effect.

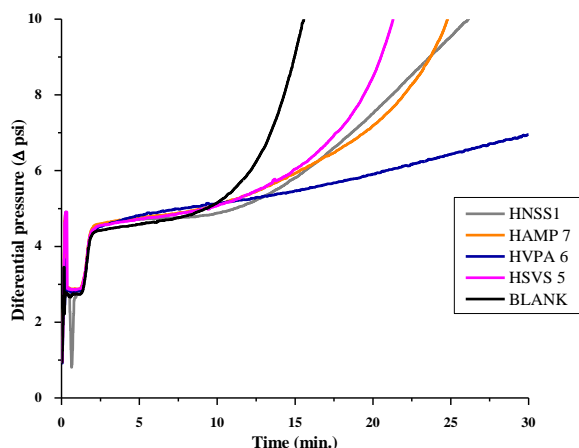


Figure 5: Dynamic efficiency of different homo-polymers (multiple scale cond., at 120 °C, 500 psi).

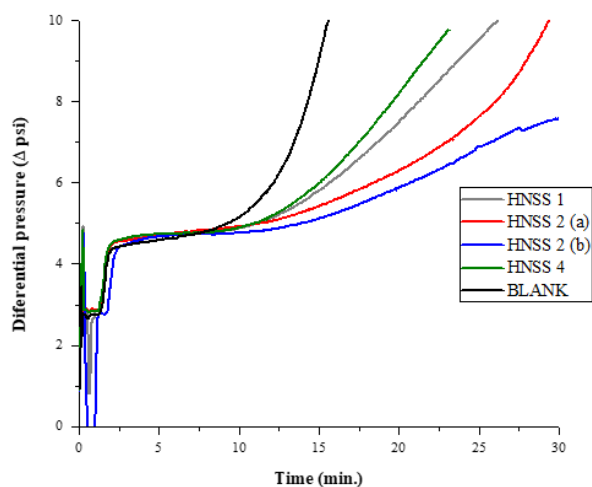


Figure 6: Dynamic efficiency of NaSS homopolymers with different molecular weight under multiple scale condition, at 120 °C, 500 psi.

Conclusions

Homopolymers from monomers with different functional groups (AA, VPA, SVS, AMPS and NaSS) were synthesized by aqueous radical polymerization with number average molecular weight varying from 790 to 43,100 Da. All polymers demonstrated potential to be used as scale inhibitors. For static efficiency under sulfate condition, higher efficiency for barium and strontium sulfate was observed for low molecular weight acrylic acid homopolymer. Specifically, for calcium sulfate the homopolymer containing phosphonic groups presented higher efficiency at short times, suggesting an action on nucleation inhibition mechanism. The homopolymers from sodium 4-styrenesulfonates showed higher efficiency for strontium sulfate and calcium sulfate, comparing with other homopolymers. In general, they showed good efficiency for sulfates over time and carbonates when evaluated in multiple scale condition (DSL measurements). For NaSS homopolymers, the best efficiency result was obtained with an average molecular weight of approximately 13,000 Da. This characteristic indicates that they can act inhibiting scale by

crystal growth mechanism combining with dispersive effect.

Acknowledgments

This work was supported by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brazil (CAPES). The authors acknowledge the PPGQ (Programa de Pós-Graduação em Química) from UFRGS (Universidade Federal do Rio Grande do Sul) and DORF KETAL BRASIL LTDA company for the support on analysis.

Responsibility Notice

The authors are the only responsible for the paper content.

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