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Synthesis and Characterization of Maleic Acid – Itaconic Acid – Acrylamido Tertiary Butyl Sulfonic acid Terpolymer for Barium Sulfate Scale Inhibition

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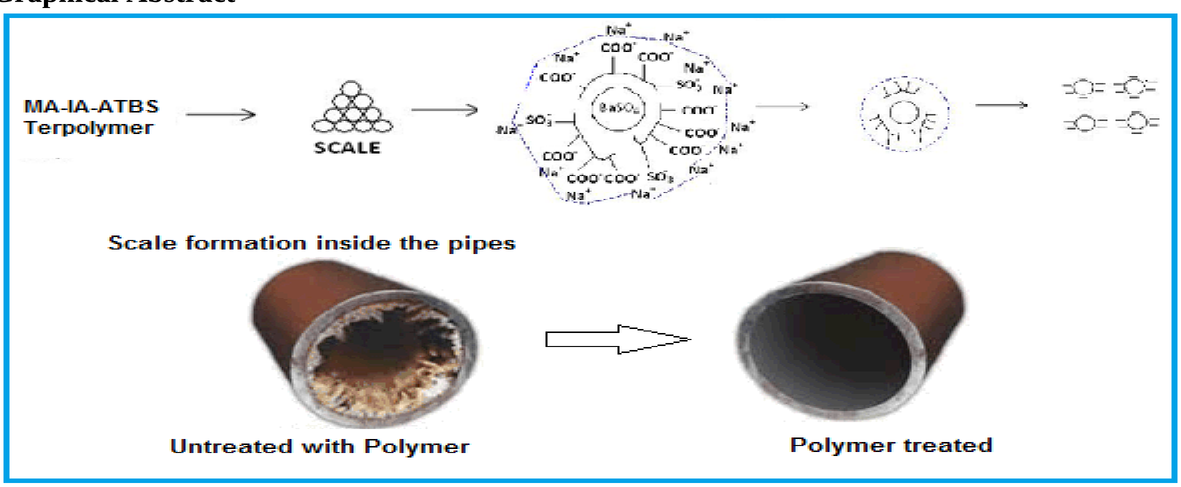
ABSTRACT

In this research, we used redox initiation system consisting of sodium persulfate and sodium hypophosphite to synthesize a low molecular weight of Maleic acid(MA), Itaconic acid(IA) and Acrylamido-tertiary butyl Sulfonic acid(ATBS) terpolymer through aqueous solution radical polymerization. The terpolymer was characterized by FTIR, HNMR and SEM. It's structure,scale inhibition and dispersibility to $BaSO_4$ were investigated. When the terpolymer dosage was 60mg/l, the inhibition and dispersion rate of terpolymer were 90.1% and 82.4% respectively and performance was compared with commercial inhibitors.

Graphical Abstract



Keywords: MA-IA-ATBS terpolymer; Sodium persulfate -Sodium hypophosphite; Barium sulfate inhibition; Dynamic Scale loop test.

INTRODUCTION

Scale is the precipitation of inorganic sediments due to saturation shift resulting from thermodynamic instability. Scale deposition is a very common problem in oil exploration. The scale is prone to occur on oil well casing, oil pipelines and other production equipment. The scale deposition products in oil field are mainly consisted of calcium carbonate, calcium sulfate, barium sulfate and strontium sulfate, iron, silicon sediment and other insoluble solids [1].Scale occurrence can cause production losses, energy wastage, accelerated corrosion, heavy downtime of equipment etc. Hence scale should be prevented to the maximum extent possible. The solution to prevent the scaling lies in usage of polymer which causes chelation effect. The extensive use of carboxylic based polymers attracted an eye for observing the dispersion and inhibition values of scales. Acrylic acid homopolymers/ copolymers of Maleic or sulfonic with Acrylic acid are being used since long time [2]. These products contain high content of carboxylic groups to provide strong chelation and inhibition rates. Previously many literatures were published in synthesis of polycarboxylate with persulfate and sodium hypophosphate. Homopolymer of Itaconic acid and maleic homopolymer was synthesized by sodium hypophosphate, persulfate redox free radical initiation system [3]. Polymers of Itaconic acid are formed by adding neutralized monomer and sodium persulfate initiator solutions at sufficient temperature [4]. Itaconic acid was synthesized by using sodium persulfate and glycerol [5]. Itaconic acid homopolymer and copolymer of Itaconic acid(IA) and sodium allylsulfonate(SAS) synthesized [6]. Sulfonic acid homopolymer and copolymer of maleic acid/acrylic acid, Sulfonic acid / acrylic were synthesized by using sodium hypophosphite and ammonium persulfate [7,8],Sodium methallyl sulfonate and maleic anhydride and acrylic acid terpolymer was synthesized through ammonium persulfate [9].

In the present research, we have used redox initiation system containing of sodium persulfate and sodium hypophosphate to synthesized ATBS, Maleic anhydride, Itaconic acid terpolymer and also evaluated $BaSO_4$ scale inhibition and dispersing performance.

MATERIALS AND METHODS

Maleic anhydride from Taiwan Prosperity Chemical Corporation, Taiwan, Itaconic acid from Radici. Chimica SpA Italy, FLOCRYL ATBS50 LP(50% solution) from SNF INC (US), Sodium Persulfate ($Na_2S_2O_8$) & Sodium Hypophosphite (NaH_2PO_2) from A.M.S.E.R Lyon company, Sodium hydroxide from ARKEMA France and Ethanol, Barium sulfate from Sigma Aldrich analytical grades, Flosperse K40 (Copolymer of Maleic acid and sodium allyl sulfonate copolymer) barium, strontium scale inhibitor & Flosperse 3024 CS (copolymer of Acrylic acid and acrylamido-tertiary Butyl Sulfonic Acid) from SNF SAS, France.

Synthesis of terpolymer: The terpolymer of maleic acid (MA), Itaconic acid (IA) and Acylamido-Tertiary Butyl Sulfonic Acid (ATBS) was synthesized with redox initiation system consisting of sodium persulfate and sodium hypophosphate by adopting aqueous solution polymerization method. Weighed initially, 262.4g of water and 224g of sodium hydroxide solution in beaker and added 68g of maleic anhydride at 50 to 65°C temperature then 90.3g of itaconic acid into the above solution. Later the total solution was transferred to five necked 1lt glass reactor, which was equipped with condenser, temperature sensor, dosing pipes. When the solution temperature reaches to 90°C, start addition of ATBS 50% solution, redox initiator solution of sodium persulfate and sodium hypophosphate 0.75% (wt.) solution slowly drop wise for about 45minutes. Let the solution aged at same temperature for 15minutes before adjusting pH 8 with sodium hydroxide solution at room temperature and the total reaction time was 60 min [4, 5, 6].

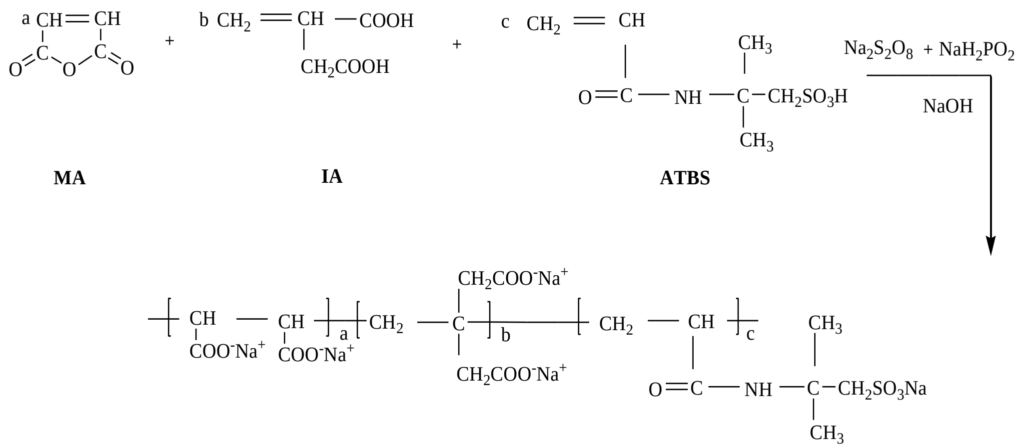


Fig. 1 Synthesis of MA-IA-ATBS terpolymer

Characterization of polymer: The terpolymer was purified by using the mixed solution of ethanol and acetone 3:1 ratios and dried for characterization, FT-IR spectrum-100 model PERKINELMER US range 400-4000cm^{-1}, Bruker AVANCE III HD 400 Proton NMR spectrometer, Gel permeation chromatography from Agilent US model Agilent1260. Scanning electron microscope (ZEISS-GEMINISEM) and Dynamic scale loop equipment (PMAC Dynamic Scale loop).

Evaluation of Scale Inhibition Performance: Investigated the scale inhibition performance of terpolymer through static bottle inhibition test according with NACE standard TM0197-2010 and Chinese petroleum standard SY/T 5673-1993[10]. Scale inhibition performance of terpolymer compare with industrial scale inhibitor through DSL test (PMAC Dynamic Scale loop)[11].

RESULTS AND DISCUSSION

Structural characterization of terpolymer: The structure of MA-IA-ATBS terpolymer was characterized through FTIR, HNMR spectra. The FTIR spectrum showed following Fig.2,the absorption characteristic peak of stretching and vibration of hydroxyl and carboxyl on water molecules appears at wave number 3333.2cm^{-1}, the absorption peak at 1718.46cm^{-1} and 1401.96cm^{-1} are attributed to the stretching vibration of carboxyls, the absorption peak at 1553.80cm^{-1} is attributed to the bending vibration of the N-H bond of acrylamino, the peaks at 1188.35,1046.24 and 622.36cm^{-1} are attributed to the stretching vibration of the sulfonic acid group, we also noticed from Fig.1 that the alkene double C=C stretching and vibration peaks doesn't appears at 1640cm^{-1}, indicating alkene totally polymerized (double bond broken) and no stretching vibrations peak of MA two carbonyls at 1860-1800cm^{-1} and 1800-1740cm^{-1}, it's indicating carboxyls has been generated due to hydrolysis of maleic anhydride and carbonyls have broken. The FTIR spectrum has confirmed the structure of MA-IA-ATBS terpolymer.

^{1}HNMR (Fig.3): 10-11ppm attributed –COOH; 9.81-9.77 attributed –SO_3H; 8.05-7.88ppm –CONH; 3.63-2.89ppm -CH_2; 2.06-1.44ppm –CH; 1.44-1.12ppm –CH_3; no C=C absorption peak at 5.7-4.5ppm it indicates that the double bond of the monomer was broken and polymerized successfully. Both FTIR & HNMR spectrum were confirmed MA-IA-ATBS terpolymer.

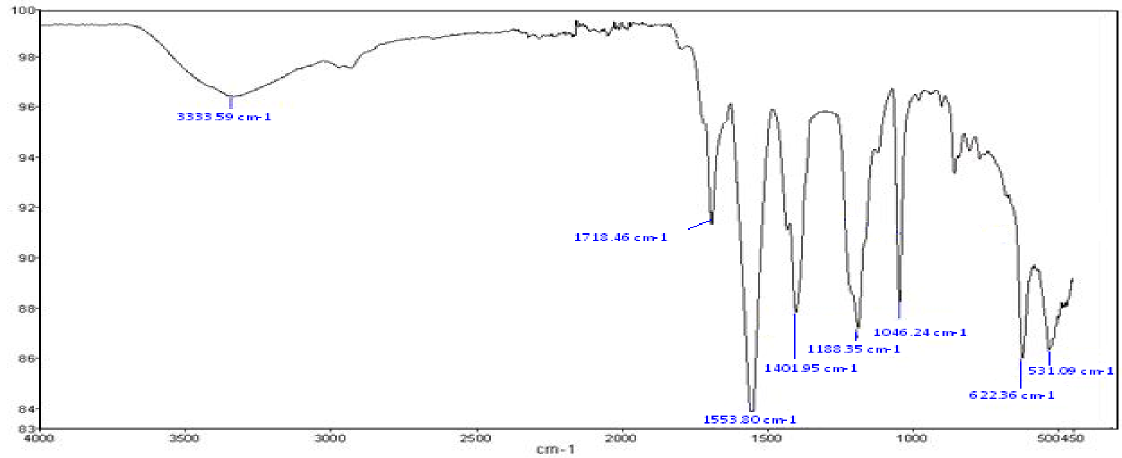


Fig: 2. FTIR Spectrum of synthesized MA-IA-ATBS terpolymer

Molecular weight of the terpolymer: The Gel permeation chromatography was employed to measure the molecular weight of the MA-IA-ATBS.

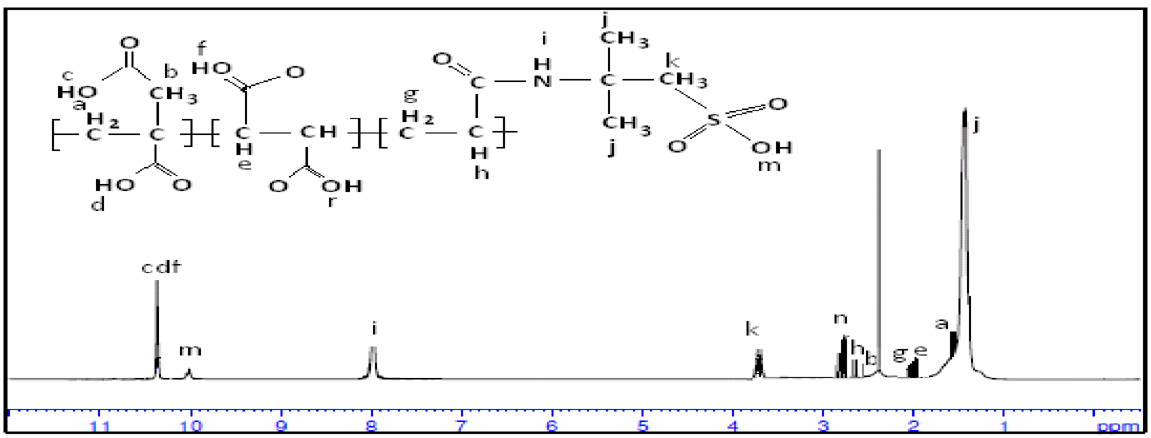


Fig: 3.[1]H-NMR Spectrum of synthesized MA-IA-ATBS terpolymer

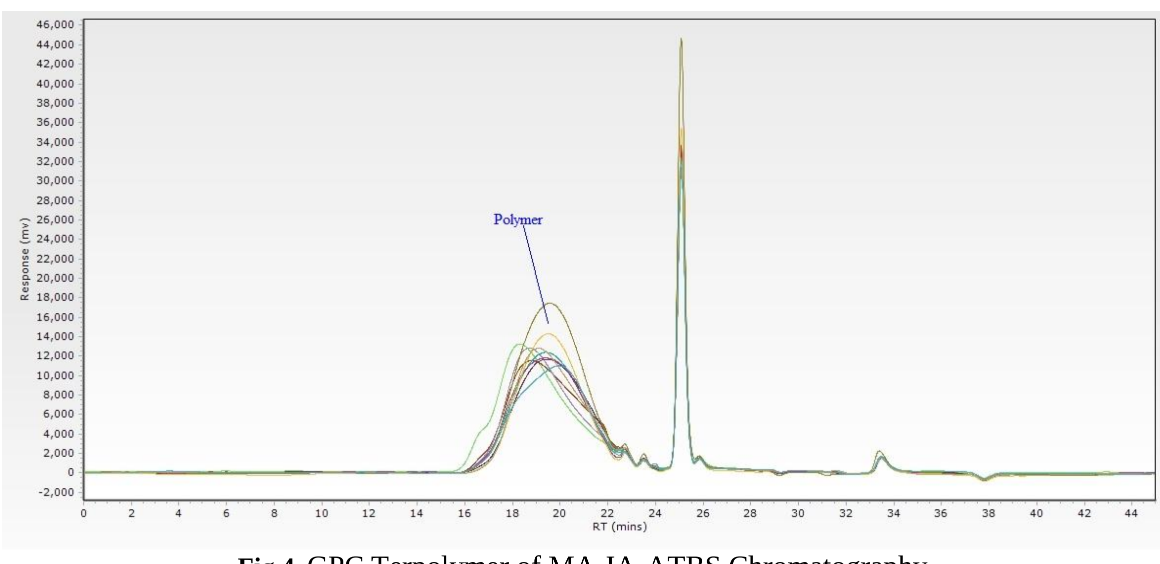
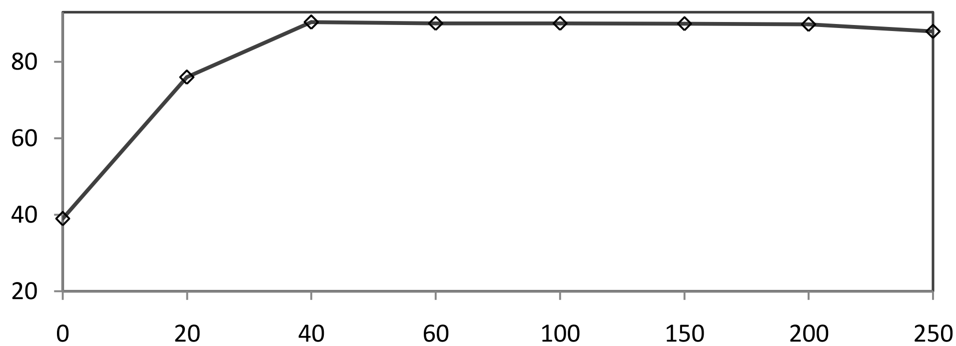


Fig.4. GPC Terpolymer of MA-IA-ATBS Chromatography

Table. 1 GPC Results

Molecular Weight (g/mol)	PDI
4400	1.38

Effect of MA-IA-ATBS terpolymer dosage on $BaSO_4$ Scale Inhibition Performance: Fig.5 shows that the effect of MA-IA-ATBS terpolymer dosage on barium sulfate inhibition performance, as the terpolymer dosage increases, the scale inhibition rate increase, when the dosage reaches inflection point 60mg/l, the inhibition rate is 90.1%. After wards even if increase the terpolymer dosage further, the scale inhibition rate doesn't significantly change, hence 80g L^{-1} is the threshold value of the MA-IA-ATBS terpolymer dosage and the effect is the threshold effect.



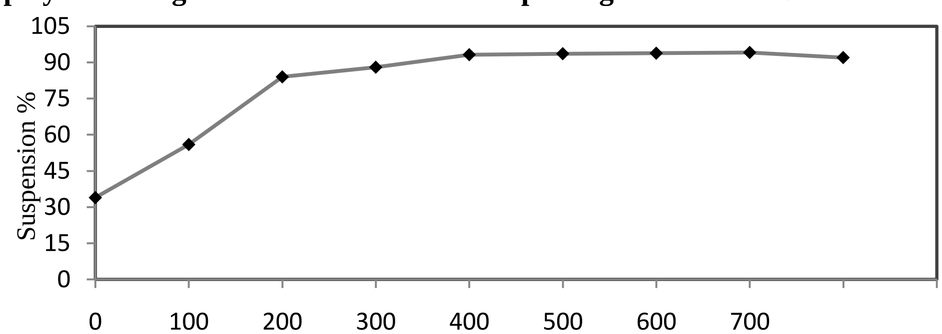
Terpolymer of MA-IA-ATBS dosage(mg L^{-1})

Test conditions: 75°C, 24h, pH=8, c(Ba^{2+})=SO_4^{2-} = 0.1mol L^{-1}, p(NaCl) = 7.5g L^{-1}

Fig 5. Effect of terpolymer of MA-IA-ATBS dosage on the $BaSO_4$ scale inhibition

The MA-IA-ATBS terpolymer has effective barium sulfate inhibition may be due to two factors; First, the terpolymer molecular chain containing chelating groups like carboxyl, sulfonic acid and acylamido functional groups which can easily chelate with Ba^{2+} ions in water to form soluble chelate, thus inhibiting formation of barium sulfate scales($BaSO_4$). Second, MA-IA-ATBS terpolymer may cause lattice deformation and shrinkage of crystals of $Baso_4$ and hence increasing its dissolution rates and dispersion rates due to the adsorption of the dispersant to active growth point. In the actual pipeline application, terpolymer may also adsorb to the inner wall of the pipeline, preventing adhesion, precipitation and scale formation of $BaSO_4$ on the pipe walls so that it can circulate and flow inside the pipelines [10].

Effect of terpolymer dosage on the Barium sulfate dispersing Performance:



Terpolymer of MA-IA-ATBS dosage (mg L^{-1})

Test Conditions: 25°C, 0.5 h, pH=8.0, $BaSO_4$=0.1g L^{-1}

Fig 6. Effect of MA-IA-ATBS terpolymer dosage on the suspension of $BaSO_4$

Fig.6 shows that the MA-IA-ATBS terpolymer effect on barium sulfate dispersing performance, as can be seen from Fig.6, All barium sulfate particles are precipitated before terpolymer addition and suspensibility is very low in water, at only 1.0%. The suspensibility reaches more than 82.4.0% when terpolymer dosages in the range of 40-60mg L^{-1} When the polymer dosages increase to 200mg L^{-1}, the suspensibility increase to 91.4%; when the terpolymer dosage is 200-800mg L^{-1} the suspensibility fluctuates in the range of 91.4% - 94.3% and the suspensibility reaches maximum value 94.3% when the terpolymer dosage 500mg/l and at this point maximum barium sulfate particles have suspended in solution, afterwards suspensibility slightly decreases even if dosage of the terpolymer is further increased. Due to suspension and adsorption of MA-IA-ATBS terpolymer against barium sulfate particles which have reached saturation stage, further the terpolymer of MA-IA-ATBS has been added in the suspension, which reduces the electrostatic force between terpolymer and $BaSO_4$ particles; the terpolymer in excess bridges with terpolymer molecular chains which have adsorbed $BaSO_4$ particles, causing desorption of $BaSO_4$ particle and the adsorption equilibrium in the suspension is broken. Therefore, particles of $BaSO_4$ aggregate and finally sediment, causing decreased suspensibility. Hence the optimum dosage of terpolymer MA-IA-ATBS is 60mg L^{-1} after overall consideration of scale inhibition rate and economical return.

Study on the scale Inhibition Mechanism: The terpolymer scale inhibition mechanism against the $BaSO_4$ is complexing effect, lattice deformation effect and dispersing flocculation effect

Complexing effect: The MA-IA-ATBS terpolymer molecular chains contain functional group of carboxyls, acrylaminos and sulfonic acid and large amount of O and N atoms containing lone pair electrons can work with the scaling ions Ba^{2+} to form stable chelates, thus decreasing the concentration of Ba^{2+} in the solution and significantly reducing the probability of the collision between Ba^{2+} and SO_4^{2-}, Hence $BaSO_4$ crystals or precipitates are not likely to form, thus prevents scaling.

Effect of terpolymer MA-IA-ATBS on the crystal form of $BaSO_4$ scale: Terpolymer of MA-IA-ATBS either adhere on the surface of crystal particles or infiltrate into the crystals, during the period of $BaSO_4$ crystal growth in the nucleus which leads to formation of $BaSO_4$ scales. Thus, complexing with the scaling ions and weakening their crystallizing power, Hence lattice of the $BaSO_4$ crystal deforms and can be easily broken.

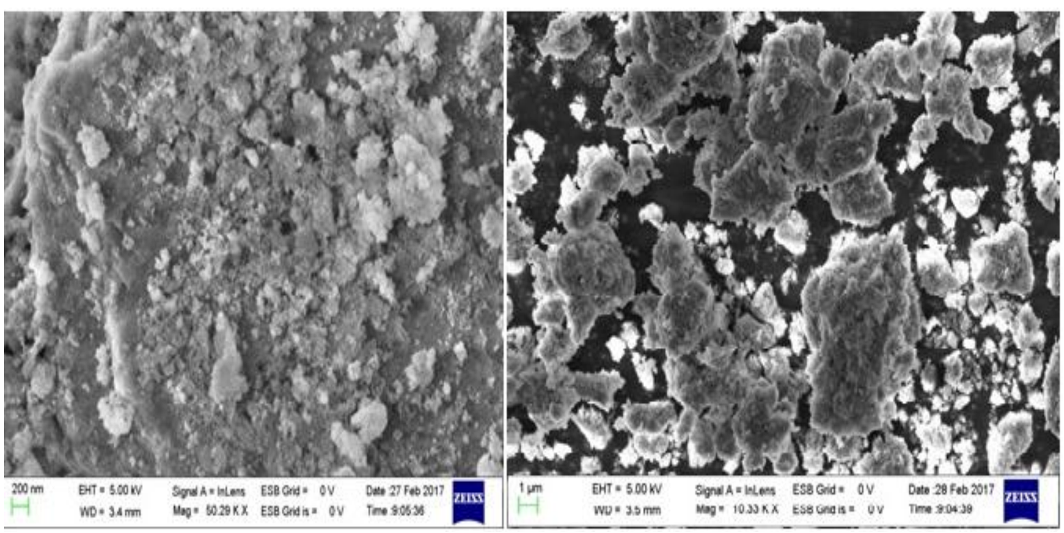


Fig 7.SEM images of Barium sulfate scale images before and after MA-IA-ATBS terpolymer treatment

Fig.7 SEM images represented the $BaSO_4$ scales before and after undergoing MA-IA-ATBS treatment, as can be seen the Fig.7, the barium sulfate crystal scales are like flakes and arranged very large blocked structure like tightly, it indicates that the notable change in the morphology of barium sulfate crystals, after undergoing MA-IA-ATBS treatment: the edges and corners are smoothened and edges are in arc shape, the crystals are randomly and irregularly arranged and disintegrated the crystals form of $BaSO_4$ scales, pushed the solubility equilibrium to shift right, dissolved the $BaSO_4$ scales and disintegrated it into tiny particles. Besides, MA-IA-ATBS terpolymer molecules have also adhered to the surface of the tiny particle of $BaSO_4$ scale and suspends in the solution, prevent further precipitation and scale formation of the crystals [12].

Dispersion effect: Terpolymer of MA-IA-ATBS deionize the ions carrying negative charges with sodium hydroxide solution, which infiltrates and adsorbs to $BaSO_4$ particles; As the result of the repulsion between the $BaSO_4$ particles generated by negative charges, the $BaSO_4$ particles disperse in the water solution forming a charged particle diffusion layer while positively charged particle ions disperse at the outer layer i.e. electric double layer theory, and the process of the formation of electric double layer dispersion is presented in Fig.8.

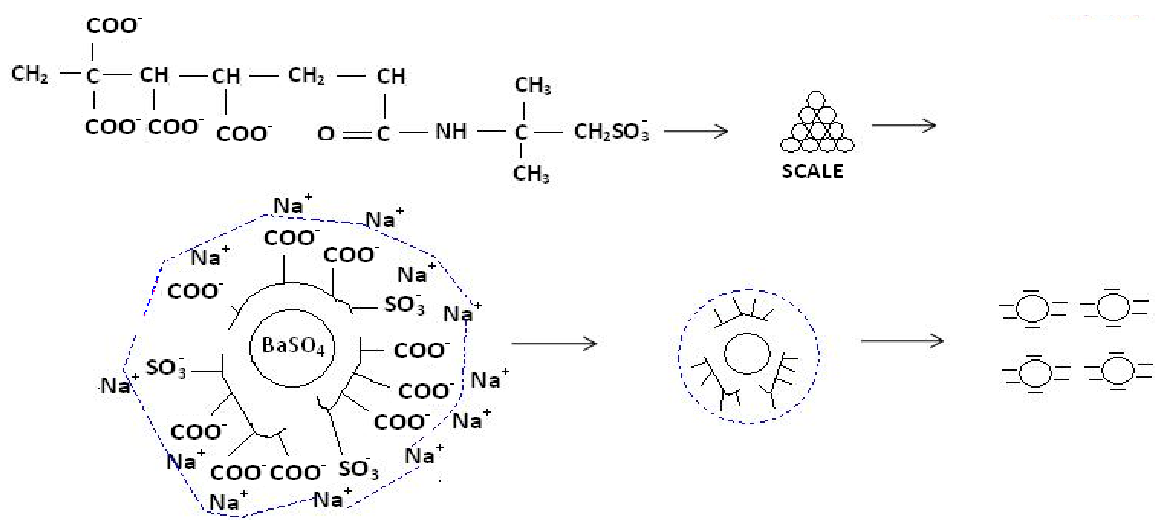


Fig 8. Formation of electric double layer due to the effect of Terpolymer MA-IA-ATBS on $BaSO_4$ Scale

As can be seen from fig.8 the anionic terpolymer of MA-IA-ATBS is adsorbed to the crystal particles of $BaSO_4$ scale, so that the crystal particles carry negative charges on the surface; repulsing each other, the crystal particles carrying negative charges disperse, causing increased contact between the complexing agent in the ant scaling agent and the surface of the scale and enhancement of the dissolution performance. At the same time terpolymer of MA-IA-ATBS envelop the $BaSO_4$ micro particles that have already dispersed, so that $BaSO_4$ crystal particles are stably dispersed, preventing aggregation and precipitation of $BaSO_4$ crystal particles and formation of compact and solid scale layer. This indicates that terpolymer of MA-IA-ATBS can both disperse and loosen the scale, showing good scale control performance.

Performance evaluation with Industrial Scale Inhibitor–DSL: Dynamic scale loop equipment was employed to evaluate the scale inhibition efficiency of three inhibitor in dynamic flowing conditions, the major advantage with dynamic scale loop (tube blocking test) experiment compare with static bottle test, it can be tested in wide range of temperature and pressure condition which is replicate real down hole production conditions. First, Flosperse K40 is an excellent scale inhibition effect on ions of Ba^{2+} and Sr^{2+}; Second, Flosperse 3024CS (copolymer of acrylic acid and 2-acryalamido2-propane sulfonic acid), which is being supplied to oil field industries as water treatment dispersant; Third, MA-IA-ATBS terpolymer. The scale inhibition performance was evaluated by using DSL equipment at 80°C temperature and 1200psi pressure to assess the scale inhibitor performance in preventing scale formation in brine water. The average blank run time was determined to be nearly 5min. So, the scale inhibitor must be preventing scale formation and deposition in tube for period of 15min according to evaluation criteria.

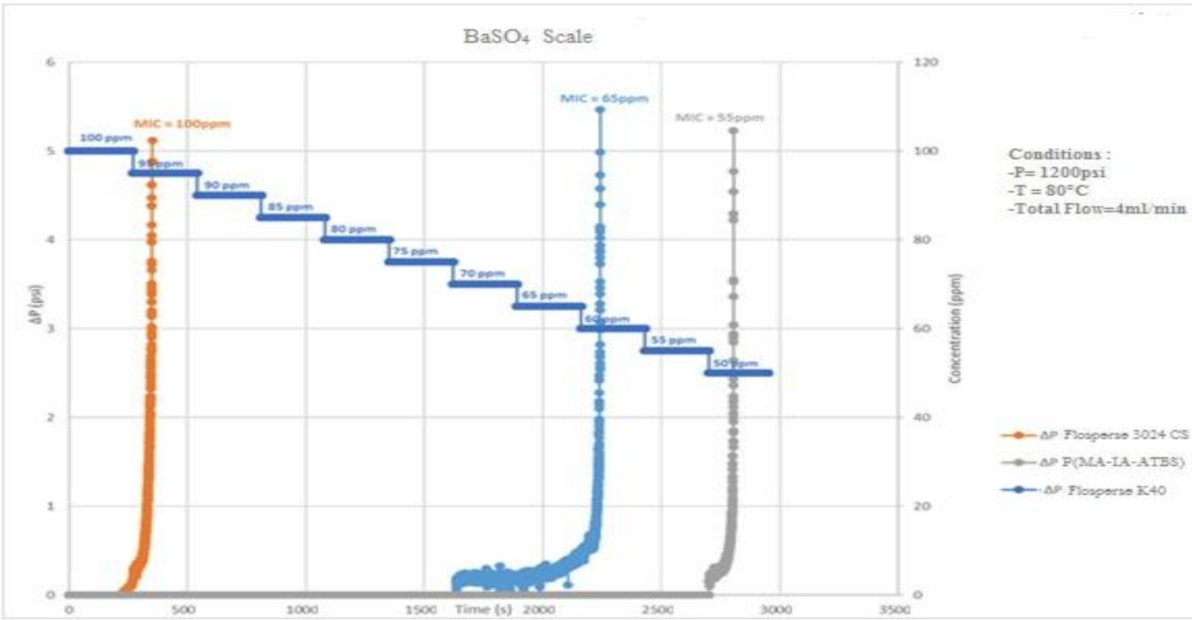


Fig 9. DSL – Differential pressure vs Time plot during barium sulfate scale inhibition test

The scale inhibition efficiency of three inhibitors is shown in Fig.9. As can be seen from Fig.9, the dynamic scale loop test results are indicated that the scale inhibition rate increase with increase the dosage of inhibitor and the differential pressure versus time plot for Flosperse 3024CS polymer the required MIC (minimum inhibitor concentration) is being regarded to 100 ppm or a lower dosage with fail 95 ppm dosage; Second, Flosperse K40 required MIC to prevent or deposition of scale in brine solution is 75 ppm for the period of 15min, which is nearer to the evaluation criteria; Third, Terpolymer of MA-IA-ATBS the required MIC is 50ppm to resist/prevent the scale formation in tube for the period of 40 min; So, terpolymer of MA-IA-ATBS is superior than Flosperse K40 and Flosperse 3024CS.

APPLICATIONS

The results indicate that the terpolymer has showed good scale inhibition performance than the commercial scale inhibitor Flosperse 3024CS and Flosperse K40 under dynamic conditions.

CONCLUSIONS

1) Synthesized terpolymer of Maleic anhydride, itaconic acid and acrylamido-tertiary butyl Sulfonic acid with sodium persulfate and sodium hypophosphite and synthesized conditions monomer ratios MA: IA: ATBS = 1:1:1 and initiator dosage - 0.75% ($Na_2S_2O_8$: NaH_2PO_2), reaction temperature and polymerization time are 90°C, 60 min respectively. Final polymer concentration was 40% solids with average molecular weight 4400g mol^{-1}.
2) 60mg L^{-1} is the threshold value of terpolymer: The terpolymer of MA-IA-ATBS has shown good performance at 60mg L^{-1} in terms inhibiting and dispersing of barium sulfate scale with inhibiting rate of 90.1% and suspensibility of 82.4%.
3) DSL test: The terpolymer has showed good scale inhibition performance than the commercial scale inhibitor Flosperse 3024CS and Flosperse K40 under dynamic conditions.

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