APPLICATION OF NOVEL N – ALKYLACRYLAMIDE HOMOPOLYMERS AS $CaCO_3$ SCALE INHIBITORS: PART-II.

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Abstract: Calcium carbonate scales are predominantly deposited in water cooling system, oil & gas industry and desalination plant which causes severe technical problems. To control $CaCO_3$ scale formation in these industrial processes and with environmental guidelines a well-designed low molecular weight n-alkyl acrylamide homopolymers were synthesized and examined for its scale inhibition efficiency against $CaCO_3$ scale under varying concentration and temperature. The scanning electron microscopy (SEM) of $CaCO_3$ scales in the absence and presence of inhibitors was done to study the morphological changes. The relation of scale mass with temperature was determined from experimental data. The results indicate that the inhibition efficiency of n-AAA homopolymers was in range of 50 – 60 % with 5 ppm dosage at 70°C. It was observed that the inhibition efficiency of n-AAA homopolymers increases with increasing concentration. But with increasing temperature the inhibition efficiency decreases.

KEYWORDS: Novel Homopolymers; $CaCO_3$ Scale inhibitor; Static scale inhibition test.

INTRODUCTION

The formation of insoluble mineral salts in artificial cooling system, desalination plants, secondary oil recovery, heat exchangers and other industrial equipment's which employed seawater is a difficulty faced in these processes. Often affecting and increasing the production and maintenance cost [1]. Scaling in oilfield can be specified as the solid mineral scale precipitate from the produced water and settling inside the pipelines while transportation along its pathway. Mechanism of depositions is influenced by different parameters which includes ions concentration, its conductivity, high temperature, pressure, pH, dissolved gases such as H_2S and CO_2 [2]. The formation of these scales is temperature-dependent i.e. with increasing temperature the solubility of carbonate scale decreases and starts precipitating. Among calcareous scales, the most important scales encountered are calcium carbonate ($CaCO_3$) scale whose solubility decreases with increasing pH and temperature. However, with a decrease in CO_2 concentration in the bulk of solution the $CaCO_3$ scale solubility shows an inverse trend. Calcium carbonate scales are readily precipitating with the change in temperature, pH, or pressure and form deposits that are thin and easily removable to a hard crust. $CaCO_3$ is the most found mineral salt and is present in chalk, marble, and limestone [3]. The calcium carbonate scales are of different forms and show polymorphism such as calcite, aragonite, and vaterite. [4]. The most common way to control or prevent the scaling is to add chemical inhibitors.

Different polymers consisting of amide and carboxyl groups are in trend and are the most efficient scale inhibitors [5-6]. Scale inhibiting polymers consisting of carboxyl and amide functional groups disturb the nucleation and crystal formation by attaching with crystals forming in supersaturated solution [7]. N-alkyl acrylamide homopolymers are efficient and have the potential to prevent scaling in water cooling systems [8], oilfield [2], and geothermal wells [9]. So, the main aim of the present research is to synthesize different homopolymers of n – alkyl acrylamide (n - AAA) which are efficient $CaCO_3$ scale inhibitor [10]. Calcium carbonate ($CaCO_3$) scale inhibition efficiency of homopolymers were studied by static scale inhibition test at varying concentration (1, 3, 5 ppm) and temperature (30, 50, 70˚C).

EXPERIMENTAL METHODS

Materials

n – hexyl amine (Fluka, 98%), n – butyl amine (Fluka, 98%), n – propyl amine (Fluka, 98%), calcium chloride dehydrate (Merck, 99%), sodium chloride (Merck, 99.5%), sodium hydrogen carbonate (Merck, 99%), magnesium chloride (Merck, 99.5%), sodium hydroxide (Merck, 99%), titriplex III (Merck, 99%), hydroxy naphthol blue (Merck), acryloyl chloride (Fluka, 96 %), barium hydroxide (Sigma, 98%), benzoyl peroxide (BPO) (Fluka, 97 %), was used as received without further purification. Tetrahydrofuran (Sigma-Aldrich, 99.9%) for spectroscopic analysis was of analytical grade and used as such without further purification. Grade A glassware was used for all experimental works. Saturated calcium carbonate brine was prepared as per NACE standard TM0374-95.

Instruments

The molecular weight of synthesized polymers was determined by using gel permeable chromatography. Tetrahydrofuran (THF) was used as the solvent and standards polystyrene was used to analyse the molecular weight of the polymers.

Field Emission Scanning Electron Microscopy was done by Joel JSM-7001F, after coating the specimens with a thin layer of gold or pt – pd.

Isotemp oven from Fisher Scientific was used for static scale inhibition test. The temperature can be set from 20 – 220 ºC. A timer allows us to set the desired time for the inhibition test.

Polymer Synthesis

Homopolymers of n – alkyl acrylamide monomers were synthesized by solution polymerization using 0.02 mole % monomer concentration and taking BPO (7.5 mole %) as an initiator and o – xylene as a solvent. Homopolymers so produced by solution polymerization are n – hexyl acrylamine (AAH), n – butyl acrylamine (AAB), n – propyl acrylamine (AAP). The polymerization reaction was carried out at 150 ºC for 10 hours and using N_2 to create an inert atmosphere [10].

Static Scale inhibition test

The scale inhibition efficiency of n – AAA homopolymers was determine by using static scale inhibition test. The $CaCO_3$ scale formation was controlled or prevented by using different concentration (1, 3, 5 ppm) of scale inhibiting polymers and at varying temperatures (30, 50, 70 ˚C). Trend with an increase in temperature and concentration was studied to understand the effects of different parameters on $CaCO_3$ crystal growth in a supersaturated solution. Moreover, the tests were conducted as per ASTM (D1126-02) and NACE (TM0374-95) standards [11-12].

RESULTS AND DISCUSSION

The n – AAA homopolymers were tested for their $CaCO_3$ scale inhibition efficiency and inhibition was calculated as % inhibition values as per equation given below, where the calcium ion (Ca^{2+}) concentration of the supersaturated $CaCO_3$ blank solution was used as a reference with calcium ion (Ca^{2+}) concentration of the solution before and after precipitation in a supersaturated $CaCO_3$ solution containing inhibitors.

$$\%\ \boldsymbol{Inhibition} = \frac{\{\mathbf{Ca^{2+}}\}_{\mathbf{after\ ppt}} - \{\mathbf{Ca^{2+}}\}_{\mathbf{blank}}}{\{\mathbf{Ca^{2+}}\}_{\mathbf{before\ ppt}} - \{\mathbf{Ca^{2+}}\}_{\mathbf{blank}}}\ \boldsymbol{X}\ \mathbf{100}$$

Where:

$\{Ca^{2+}\}_{after\ ppt}$ is the dissolved concentration (mg/L) of Ca^{2+} ions after precipitation in the solution containing scale inhibitor.

$\{Ca^{2+}\}_{before\ ppt}$ is the concentration of Ca^{2+} ions before precipitation in the solution containing scale inhibitor.

$\{Ca^{2+}\}_{blank}$ is the concentration of Ca^{2+} ions in the blank solution.

Detailed study of these homopolymers at varying temperatures and concentrations are discussed below:

The relation between inhibition % and temperature

The inhibition efficiency of n – AAA homopolymers for $CaCO_3$ scales was studied at three different temperatures (30, 50, and 70 ˚C). The inhibition efficiency is said to decrease with increasing the reaction temperature [8]. The n – AAA homopolymers show the highest inhibition efficiency at 30 ˚C but as the temperature increases to 70 ˚C the inhibition efficiency decreases almost by 50 %. In Fig. 1, the inhibition % with varying temperature is illustrated. It was observed that the inhibition efficiency of AAH decreases to 73.9 % from 98.6% when the reaction temperature was increased from 30 to 50˚C respectively. Similarly, for AAP and AAB the inhibition efficiency decreases to 72.9% from 90% and 65.6% from 82 % respectively.

However, when the temperature was further increased from 50˚C to 70˚C, the inhibition efficiency was reduced to 50% for AAH, 45% for AAB and 49% for the AAP homopolymer. The inhibition efficiency of n – AAA homopolymers was decreased by four folds when the temperature was increased from 30˚C to 70 ˚C, whereas in the above-mentioned literature it reduces to eightfold at 60˚C temperature. The inhibition efficiency trend among three n – AAA homopolymers is AAB < AAP < AAH.

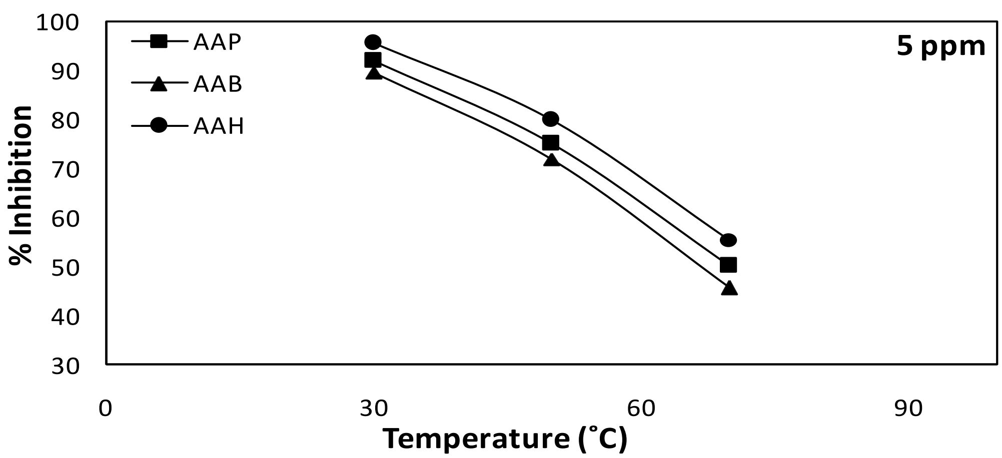

Figure 1: Plot showing inhibition % of different n – AAA homopolymers at varying temperatures for, 5 ppm concentration and 24 Hrs time.

The relation between inhibition % and concentration

The relation between inhibition % and varying concentration of n – AAA homopolymers were studied to check the effect of increasing concentration on inhibition % at a constant temperature (70ºC). Previous studies show that the inhibition efficiency of polymers increases with an increase in concentration [11-12]. The inhibition % tests were conducted using three concentrations (1, 3, and 5) of n – AAA homopolymers.

With increasing the concentration from 1 to 3 ppm the inhibition efficiency of n – hexylamine (AAH) was increased by 8 % and reached 44.4 %. While in n – propylamine (AAP) it reached 36.4 % at 3 ppm when kept at 70 ºC under NACE standards. The inhibition efficiency achieved by n – butylamine (AAB) was 36.3 % at 3 ppm. With a further increase in concentration from 3 to 5 ppm, the inhibition efficiency increased by 6 % in AAH, whereas, in AAB and AAP it was increased by 9 %. The highest inhibition efficiency achieved by AAH was 50 % at 5 ppm concentration at 70 ºC. The results for inhibition % at different concentrations are represented in Fig.2.

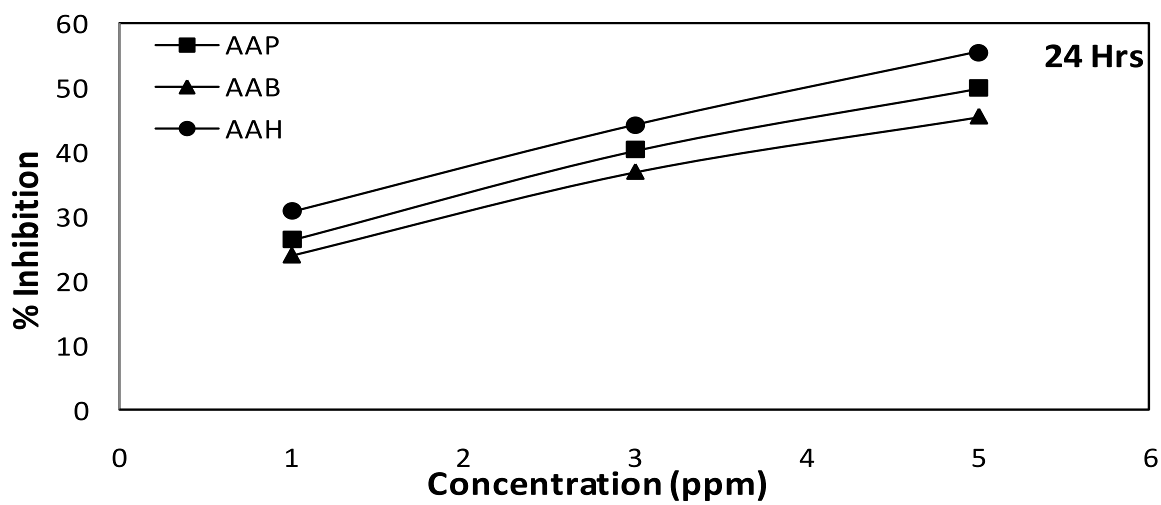

Figure 2: Plot showing inhibition % of different n – AAA homopolymers at varying concentrations for constant temperature and time.

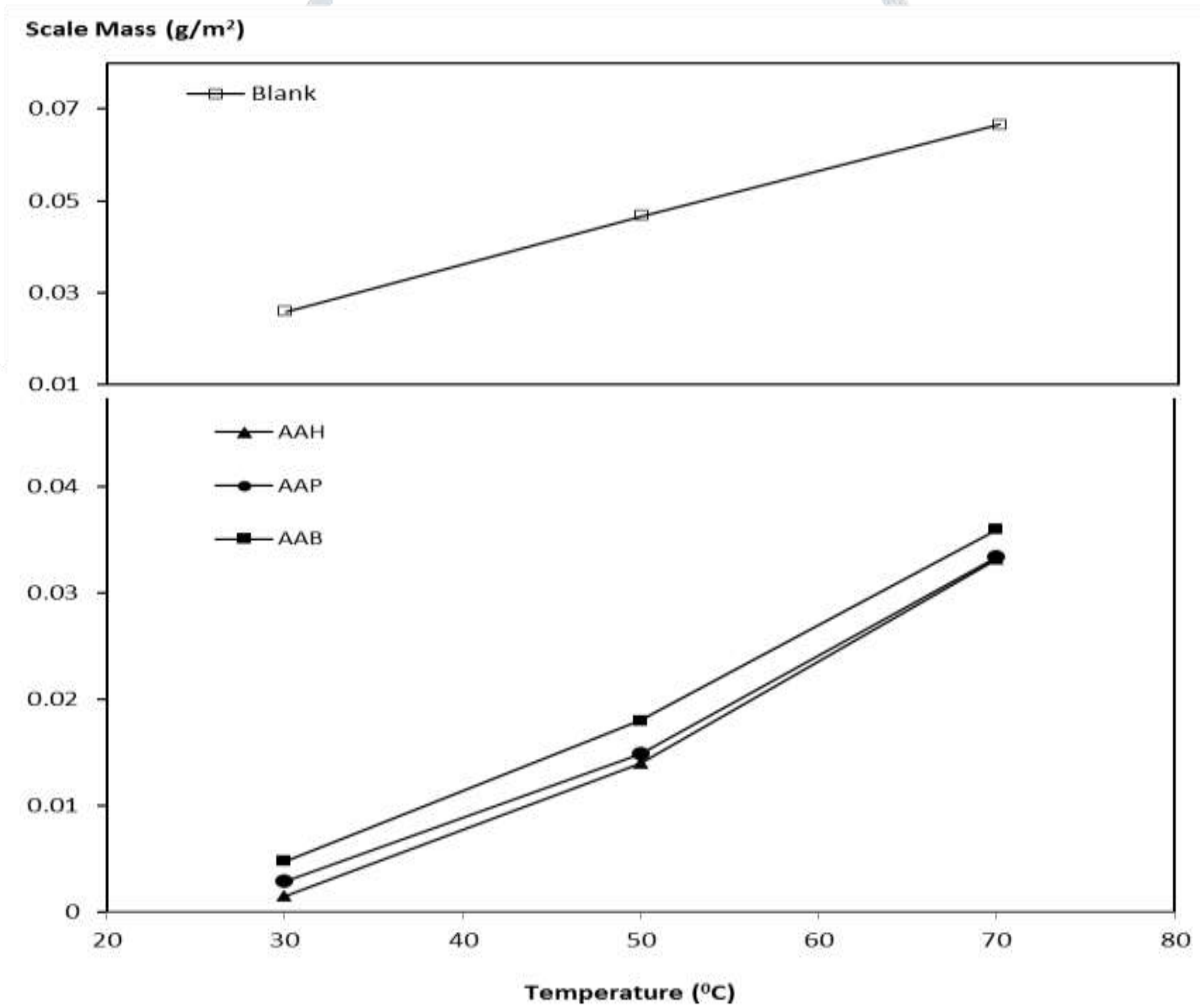

Figure 3: Relation Between Scale Formation and Varying Temperature for n – Alkyl Acrylamide Homopolymers.

Relation Between Scale Formation and Temperature

The reason behind it can be due to an increase in temperature, the solubility of $CaCO_3$ scales decreases and it starts to precipitate [11]. In previous studies, it was found that the reason for precipitation of $CaCO_3$ scales was the activation energy required by soluble $CaCO_3$ to become insoluble and form precipitates can be overcome by increasing the reaction temperature [12].

The effect of different temperatures on scale formation in blank solution and solution containing different n – AAA homopolymers at 5 ppm concentration were studied and graphically presented in Fig. 3. It is observed that the scale formation in blank solution was almost doubled from 0.0246 g/m^2 to 0.0468 g/m^2 when the reaction temperature was increased from 30 ºC to 50 ºC respectively. The scale formation after 24 hrs was 0.0468 g/m^2 at 50 ºC but as the temperature was increased to 70 ºC the scale formation increased drastically to 0.0666 g/m^2.

However, in n – AAA homopolymers when the temperature was increased from 30 ºC to 50 ºC, the scale formation was increased from 0.0015 to 0.014 g/m^2 for AAH homopolymer respectively. For the AAP homopolymer, it was increased from 0.0029 to 0.0149 g/m^2 and for AAB homopolymer it was 0.0048 g/m^2 at 30 ºC which increased to 0.018 g/m^2 at 50 ºC. As the temperature was increased to 70 ºC, the scale formation was also increased and reached to 0.0332 g/m^2 for AAH homopolymer. Similarly, for AAB and AAP homopolymers it was increased to 0.036 g/m^2 and 0.0334 g/m^2 respectively.

Table 1 shows the decrease in scale inhibition % of n – AAA homopolymers when the temperature was increased from 30 to 50 ºC. It was observed that the scale inhibition efficiency of the AAH homopolymer was decreased by 24% at 50 ºC. The scale inhibition efficiency of the AAP and AAB homopolymers was reduced by 20 % when the temperature was increased from 30 ºC to 50 ºC. Further increase in the temperature from 50 ºC to 70 ºC resulted in a decrease in scale inhibition efficiency by 16 to 20 % among the three n – AAA homopolymers.

Table 1: Scale Inhibition percent of n – AAA Homopolymers with Varying Temperatures.

Temperature (ºC)	**AAH %**	**AAP %**	**AAB %**
30	96.5	93.62	90.27
50	80.5	79.1	64.71
70	56.4	54.5	50.95

In fig. 5, the logarithm of scale mass was plotted against the inverse temperature to determine the relationship between scale formation and temperature of blank solution and solution containing n – AAA homopolymers. From the relation, the log (scale mass) for the blank sample is greater than n – AAA homopolymers. From the graphs, it can be observed that the curves for both blank and with n – AAA homopolymers are linear which specifies that the relation between scale formation and the temperature is exponential [14]. Using Microsoft excel we can calculate different equations from the above graph for blank solution and n – AAA homopolymers. Equations are presented in table 3 for blank and n – AAA homopolymers, along with Pearson product-moment correlation coefficient (R^2).

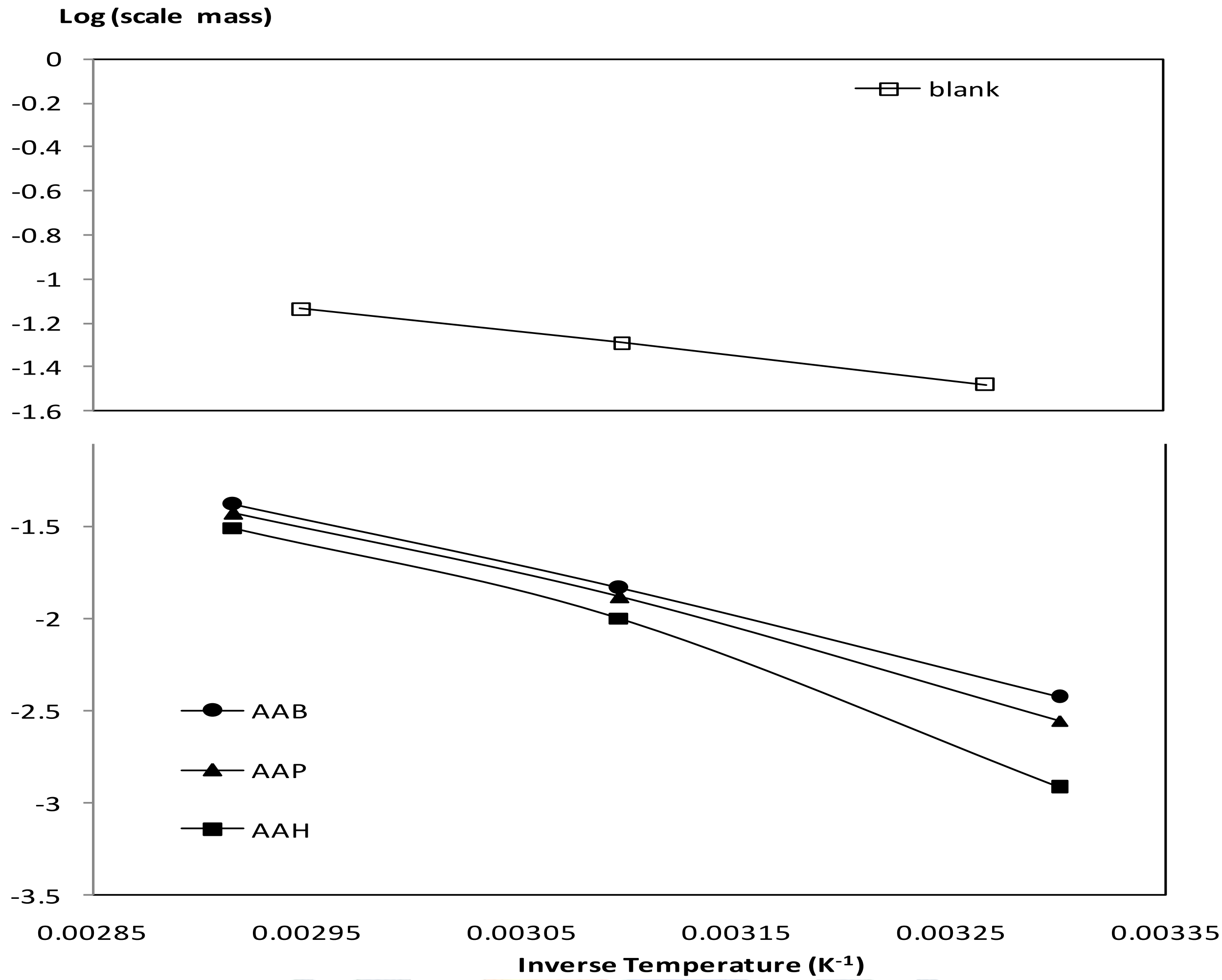

Figure – 5: Relation between inverse temperature (1/T) and Log (scale mass) for blank and n –AAA homopolymers at three different temperatures for 24hrs at 3 ppm concentration

Table 3: Calculated equations from log (scale mass) and inverse temperature graph for blank and n – AAA homopolymers

Antiscalant	Log (scale mass) equation	R2
Blank	[-1129.2(1/T) + 2.133]	0.9829
AAH	[-3522.1(1/T) + 8.8802]	0.9548
AAB	[-2285.3(1/T) + 5.2577]	0.9798
AAP	[-2773.4(1/T) + 6.6615]	0.9753

From table 3, the relation between log (scale mass) and inverse temperature for blank solution and solution containing n – AAA homopolymers gives us different log (scale mass) equations. It shows that when the temperature is high, the log (scale mass) value will be larger and therefore the rise in temperature increases the scale mass exponentially.

Scanning Electron Microscopy (SEM)

The change in morphology (shape and size) of $CaCO_3$ crystals when treated with n-AAA homopolymers were examined by scanning electron microscopy (SEM). The SEM images of $CaCO_3$ crystal with and without the scale inhibiting polymers taken at different magnification are present in Fig.7. It can be observed that the n-AAA homopolymers has changed scales morphology and it is totally deformed to sludge. The morphological changes are attributed to the adhesion of antiscaling polymer on to the nucleation site which alters the crystal shape and size during its outgrowth [15]. n-AAA homopolymers have such influence that it changes the entire crystal shape.

These changes in morphology result in the weakening of crystal strength and distortion of crystals, which ultimately decreases its adhesion to the metallic surfaces.

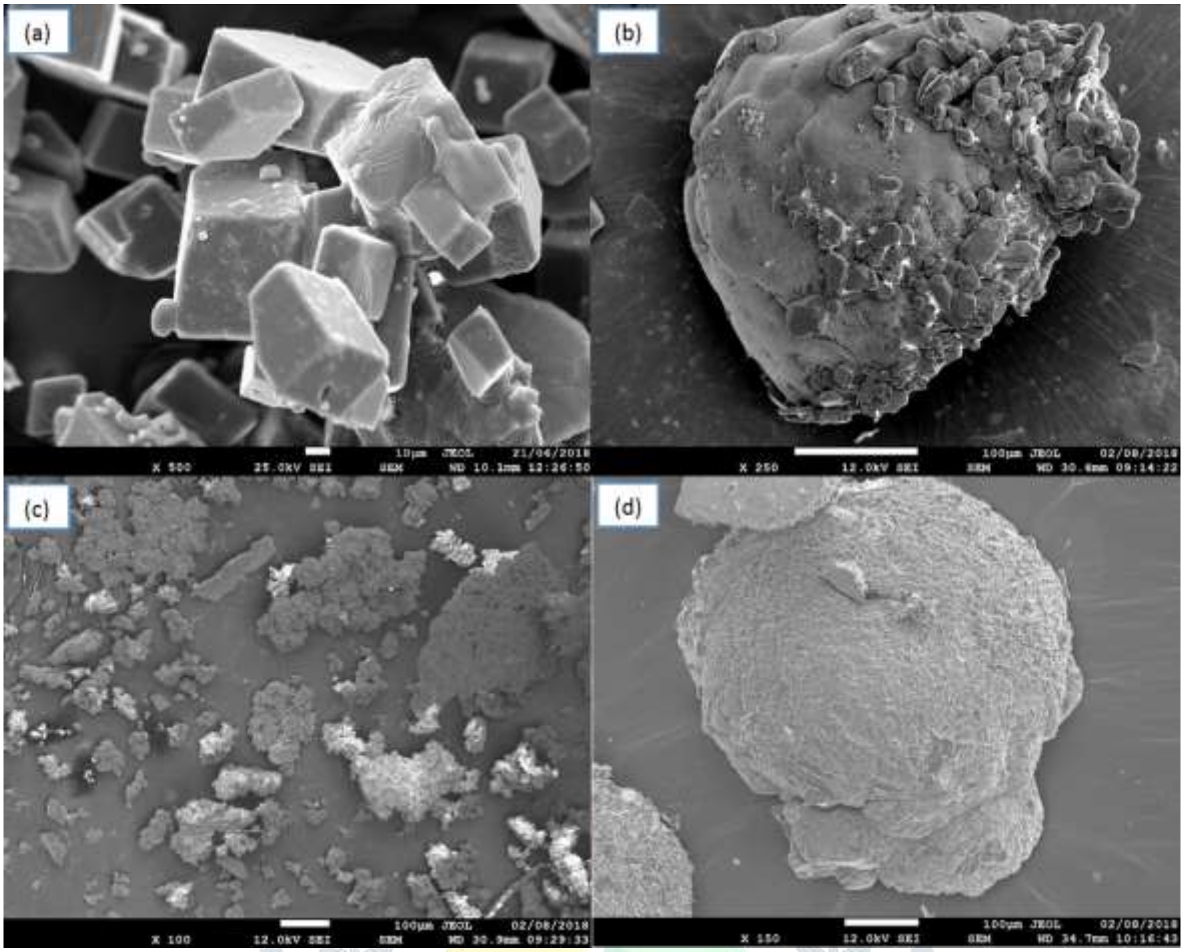

Figure 7: SEM images of $CaCO_3$ scale in (a) absence of inhibitor (blank) (b) presence of homopolymer AAH (c) AAP, (d) AAB.

CONCLUSION

Scale inhibiting polymers are of great value in the oil field and desalination plants for inhibiting $CaCO_3$ scales and are widely used across the globe. Different kinds of scale inhibiting polymers are prepared by using solution polymerization method. The key objective of this study is to develop novel scale inhibitors which have high inhibition efficiency for $CaCO_3$ scales at low concentration (5 ppm) and high temperature (70 ºC). Therefore, n – AAA homopolymers were synthesized and studied for their $CaCO_3$ scales inhibition efficiency at different parameters. Some of the observation are as follow:

- A static scale inhibition test was carried out to study the $CaCO_3$ scales inhibition efficiency of n – AAA homopolymers using different experimental conditions.
- A 5 ppm dosage of n – AAA homopolymers in supersaturated $CaCO_3$ solution showed 82 – 98 % inhibition at 30 ºC and 65 – 74 % at 50 ºC but as the temperature was increased to 70 ºC the inhibition efficiency was decreased by 50 – 60 %.
- It was also observed that with increasing the scale inhibitor concentration, the scale inhibiting efficiency also increased.
- The rate of scale formation is directly proportional to temperature, as the temperature increases the scale formation also speeds up.
- The SEM studies shows that the n – AAA homopolymers has distorted the $CaCO_3$ scale precipitates, and changing them into pallets and loose sludge, thus stopping the formation of cuboidal crystals.

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