Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.808589

52 (2014) 5965–5973
September

Control of barium sulfate crystallization in the presence of additives

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Received 20 February 2013; Accepted 21 May 2013

ABSTRACT

The aim of the present work was to investigate the influence of various experimental parameters on inhibiting the crystallization process, size, and morphology of barium sulfate crystals in the presence of polyelectrolytes. The results indicated that the experimental parameters, such as the concentration of the polymer, the pH of solution, the ratio $[Ba^{2+}]/[SO_4^{2-}]$, and temperature, are important for the inhibiting of the crystallization process, size, and morphology of barium sulfate crystals. The effects of all these parameters on the morphologies and crystallization of barium sulfate can be attributed to their influence on the interaction between the carboxylic acid groups of polyelectrolytes and the crystal surface.

Keywords: Barium sulfate; Crystal morphology; Control of crystallization process; Polyelectrolytes

1. Introduction

The formation of mineral scale deposits is a major problem in water containing systems such as cooling systems, heating systems, desalination processes, oil, and gas production systems [1,2]. Although barium sulfate scale is not as common as calcium sulfate and calcium carbonate scales, it is one of the most obstinate scales found in off shore oil and gas production systems [3]. $BaSO_4$ scale, however, is the most difficult to remove because it is extremely insoluble substance (solubility of only in water 2 mg/L in water). Due to its relatively low solubility in water, barium sulfate scale deposits easily from brine once its solubility limit has been exceeded and cannot removed by acid treatment [4]. Barium sulfate precipitates suspended in the water cause problems such as plugging pore spaces in the oil-producing formation and adherent scale on surfaces such as pipe walls, valves, and pumps [5]. Both effects are highly undesirable and result in a decrease in the volume capacity of equipment, a decrease in heat transfer rate, blocking of pipes, restricted fluid flow, and equipment damage [6,7]. In most cases, the only way to remove precipitated barium sulfate is by mechanical scraping or reaming, which is troublesome and costly. Therefore, managing barium sulfate scales economically requires preventing precipitation. Systematic methods to reliably control barium sulfate scale formation results in reduced production and clean-up cost [8]. The most effective way of avoiding the problem of oilfield scale formation is by using chemical scale inhibitors which prevent or delay scale formation [9]. The scale inhibition by trace amounts of inhibitors has long been known. In recent years, several investigations have

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been carried out to inhibit the crystallization of barium sulfate and control of barite crystal morphology by using additives. The effects of phosphonate molecules [10] EDTA [6], poly(methacrylic acid) (PMAA) [11], phosphates, acrylate [12], poly(styrene-alt-maleic acid) (PSMA) [13], poly(styrenesulfonic acid) (PSS) [14] poly(ethylene glycol)-b-poly(sodium 4-styrenesulfonate) (PEG-b-PSSS) poly-phosphinocarboxylic acid (PPCA) [15], and on the growth of $BaSO_4$ crystals were studied. These additives were found to be particularly effective as $BaSO_4$ growth inhibitors. Generally, inhibitors are designed by taking into account parameters such as the interacting ability of the inhibitors with surface-active sites of the potential scale former, the geometry and orientation of the inhibitor when approaching the surface, and the molecular size of inhibitor. Crystallization process, size, and morphology of barium sulfate crystals are profoundly affected by numerous factors. Supersaturation (SS), ionic ratios, temperature, and pH affect nucleation and growth of barite crystals. Liu and Nancollas [16] found, and also others confirmed, the decisive role of initial conditions in barite crystal formation [17,18]. According to Yuan [19], temperature was found to have a significant effect on the solubility of barium sulfate. Jones et al. [10] found that changes in pH show that the greater the degree of dissociation of the inhibitor molecule, the better is the inhibition (up to pH 8). In spite of all these investigations, many questions are still open for this important process and there is a need more effective methods for solving scale formation problem.

Much of our knowledge of molecular influences on crystallization has come from the study of biomineralization [20]. Biological mineralization leads to formation of hard tissues in many species by precipitation of minerals within polymeric tissue matrices and calcium-containing salts are major mineral components [21]. Acidic proteins can be incorporated into mineralizing tissues, and are believed to be responsible for both nucleation and inhibition of crystallization. The discovery and successful applications of chemical additives that have mild environmental impact has been the focus of several researchers [22,23]. The goal of the current study was determination and comparison of the effects of carboxymethyl inulin (CMI) which has three different number of carboxylate group and polyacrylic acid (PAA) on the barium sulfate crystallization and crystal morphology. As many biological molecules contain oxyanion functional groups (carboxylate, phosphate, and sulfate esters), we have been involved in crystallization experiments using carboxylate-substituted polysaccharide, CMI and PAA. CMI is inherently biodegradable and nontoxic [24]. Previous works showed that CMI influences the spontaneous precipitation of calcium carbonate [22,25], calcium oxalate [26], and hydroxyapatite [27]. CMI is also reported as a silica scale remover [28]. PAA is found high effective inhibitor for various mineral scale deposits such as calcium oxalate and barium sulfate in previous studies [14,29].

We also studied the effect of $[Ba^{2+}]_t/[SO_4^{2-}]_t$ ratio, temperature, and pH of solution on barium sulfate crystallization.

2. Experimental

2.1. Materials

Barium chloride (CAS: 103-61-37-2) was purchased from J.T. Baker and sodium sulfate (CAS: 7757-82-6) was from Sigma-Aldrich. CMI (CAS: 430439-54-6) (all three grades) was purchased from ThermPhos, Switzerland as Dequest DPB-116AB (where AB = 15 for CMI-15, AB = 20 for CMI-20, and AB = 25 for CMI-25). The number AB also indicates the degree of substitution (DS). DS is defined as the average number of carboxylate moieties per fructose unit. For example, for CMI-15, DS = 1.5; for CMI-20, DS = 2.0; for CMI-25, DS = 2.5. Molecular weights of CMI-15, CMI-20, and CMI-25 are 3,000, 2,500, and 6,500, respectively. PAA (MW 5,000) (CAS: 9003-01-4) was purchased from Acros.

2.2. Crystal growth experiments

The effects of PAA and carboxymethylinulin (CMI-15, CMI-20, and CMI-25) on the barium sulfate crystallization have been investigated by using spontaneous crystallization method. Crystal growth experiments were made in a water-jacketed Pyrex glass vessel of 1 L capacity. The supersaturated solutions for growth experiments were prepared by the slow mixing of solutions of barium chloride and sodium sulfate. In the experiments where additives were used, a similar procedure was followed and the freshly prepared additive solutions were added to the reaction medium together with the sulfate solution. After temperature equilibration, the second component was added, and pH and temperature of the reaction solutions were monitored during crystallization via personal computer equipped with an appropriate software. All experiments were performed at a temperature of 30 ± 0.1 °C except for a few experiments made to investigate the effect of temperature on the crystallization.

During the experiments, pH was about 5.5. In the experiments, the concentration of additives was varied from 1×10^{-7} to 1×10^{-6} mg/L. In order to determine the effect of barium/sulfate molar ratio on the barium sulfate crystallization, a series of experiments were carried out in different reactant ratios (RR), $[Ba^{2+}]_t/[SO_4^{2-}]_t$. The RR can be defined as the ratio of initial molar ratio of barium to sulfate, $[Ba^{2+}]_t/[SO_4^{2-}]_t$. The effect of additives on the precipitation rate of barium sulfate was evaluated by recording the decrease in $[Ba^{2+}]$ as a function of time in a solution containing 3.5×10^{-4} M $BaCl_2$ and 3.5×10^{-4} M Na_2SO_4. The course of the experiments was followed by removing homogeneous aliquots at various times and quickly filtered through Millipore filters of 0.22 μm pore size. The aqueous phase was analyzed for barium by atomic absorption spectroscopy (Perkin-Elmer AAnalyst 200). The crystals removed by filtration were examined by scanning electron microscopy (SEM) (JEOL JSM-SEM). The effect of additives can be quantified as the ratio of the rate of crystallization of the pure solution (R_0, mol/L min) to the rate of crystallization in the presence of additive (R, mol/L min) at the same concentration and temperature. The rates reported were the initial rapid growth rate calculated from slope of the barium ion concentration vs. time plots for each experiment. The rates were determined from at least three separate experiments and only the average values were reported. The reproducibility of this approach is 4–5%.

3. Result and discussion

3.1. Effects of CMI and PAA polymers on barium sulfate crystallization

Evaluating the effects of additives on crystal growth rate was done by comparing the growth inhibition of barium sulfate crystallization attained in the presence of these polymers by comparison of the slopes of the curves during the growth phase. The effect of additives on crystal growth rate was investigated by comparing growth rate of barium sulfate crystallization in the absence and presence of additive. The ability of additive to act as inhibitor was evaluated by R_0/R ratios. The higher R_0/R values correspond to a better inhibition. The results of crystallization experiments in the presence of additives are summarized in Table 1.

As shown in Table 1, the polymeric additives have a varied effect on crystallization of barium sulfate. The polymers are reasonably good growth inhibitors. The crystal growth proceeded at a rate smaller than those in the absence of additives. For all additives, the crystallization reaction begins immediately; there is no induction effect. The experimental results in the present study show that R_0/R ratio increases with increasing additive concentration. PAA has the most pronounced effect on growth inhibition followed by CMI-25. The growth was almost completely inhibited for several hours at a concentration of $1.0 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$. The effectiveness of biopolymers increases with increasing carboxyl content on the polymer backbone. R_0/R ratio increases from 1.20 to 13.77 as the carboxyl content of CMI increases from 1.5 to 2.5 at $4.0 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$ additive concentration. Several investigations have indicated that polymers that exhibit an inhibitory effect on crystallization kinetics of soluble salts are highly substituted with carboxyl groups [29–33].

The percentage of inhibition was calculated as $[1 - (R/R_0) \times 100]$. The inhibitory effect of the CMI-25 and PAA with regard to the crystallization of $BaSO_4$ indicated 92.7 and 93.63% inhibition respectively, while CMI-15 and CMI-20 inhibition strength was only marginal at $4.0 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$ (see Table 1). PAA and CMI-25 was the best additive for inhibiting growth rate of barium sulfate crystallization. This was evident from highest percent growth inhibiton.

Generally, additives can retard precipitation in two ways. First, the additive may form stable complexes with one or more lattice ions of the crystals' thus reducing the effective concentration of free ions necessary for crystallization. This mechanism requires

Table 1
The effect of additives on barium sulfate crystallization at 30°C

C (mol/L)	PAA		CMI-25		CMI-20		CMI-15	
	R_0/R	I%	R_0/R	I%	R_0/R	I%	R_0/R	I%
1×10^{-7}	1.57	36.31	1.42	29.58	1.11	9.90	1.08	7.40
2×10^{-7}	3.40	70.58	2.82	64.53	1.16	13.79	1.13	11.50
3×10^{-7}	9.31	89.26	6.11	83.63	1.20	16.66	1.16	13.79
4×10^{-7}	15.7	93.63	13.77	92.74	1.36	26.47	1.20	16.66
1×10^{-6}	nc	–	nc	—	13.4	92.53	10.8	90.74

nc: no crystallization, I: inhibition.

relatively large amounts of the sequestering agent. The second way is that the additive may be adsorbed on the initially formed crystallites, either generally or on particular crystal faces or crystal growth sites. This surface poisoning effectively prevents or slows further growth of the crystallites so they never reach critical size and consequently will eventually redissolve. In this study, since the amounts of polymer in solution are small, the growth inhibition is most likely caused by polymer adsorption of the active growth sites on crystal surfaces, leading to a surface controlled growth rate reduction. As the solution concentration of the inhibitor is increased, more active growth sites on the crystal surface are blocked, and the rate of crystal growth decreases. The adsorption of inhibitor molecules on crystal surfaces may be interpreted in terms of equilibrium adsorption isotherms, which was developed for the adsorption of ideal gases onto solid surfaces. This model was used to describe, empirically, the reductions in crystal growth rates of sparingly soluble salts due to the adsorption of a wide variety of inhibitors [1,2,22,34]. The use of a Langmuir model in interpreting the reduction in the growth rates of numerous sparingly soluble salts in the presence of inhibitors has largely been successful.

When a polyelectrolyte poisons active growth sites on the crystal faces, the coverage by polymers, θ, for this adsorption model is described by Eq. (1). [33].

$$\theta = KC_i/(1 + KC_i) \tag{1}$$

where K is the adsorption or affinity constant, which is the ratio of the rate constants for adsorption and desorption, $k_{\text{ads}}/k_{\text{des}}$, and can be considered as a measure for the adsorption affinity of the polymer onto the crystal surface, and C_i is the total equilibrium concentration of the polymer. The rate in the absence of polymer, R_0, is reduced to a slower rate, R, according to the relationship:

$$R = R_0(1 - \theta) \tag{2}$$

Combination of Eqs. (1) and (2) gives

$$\frac{R_0}{R_0 - R} = 1 + \frac{k_{\text{des}}}{k_{\text{ads}}}\frac{1}{C_i} \tag{3}$$

In practice, this relationship is usually tested by plotting $R_0/(R_0 - R)$ as a function of $1/C_i$. Typical plots of data from crystal growth are shown in Fig. 1. The linearity of the plots of Eq. (3) for barium sulfate crystal growth in the presence of polymers suggests that the inhibitory effect of CMI polymers and PAA is due to adsorption at active growth sites. $k_{\text{ads}}/k_{\text{des}}$ can be evaluated from the slope of the resulting straight line. The values of the affinity constant as calculated for PAA, CMI-25, CMI- 20, and CMI-15 are 2×10^6, 3.33×10^6, 1.11×10^6, and 1.01×10^6 L/mol, respectively. The high value of the affinity constant for CMI-25 and PAA may reflect stronger equilibrium adsorption of PAA and CMI-25 on the crystal surface, compared to that of CMI-20 and CMI-15.

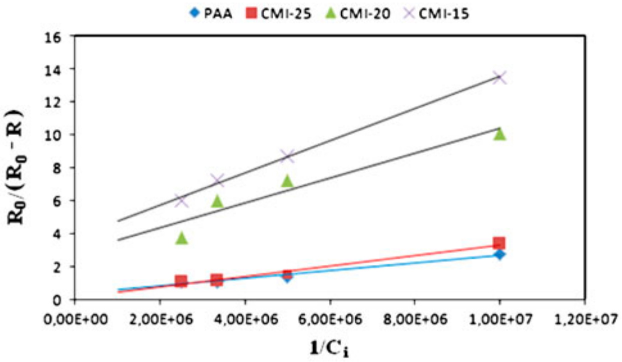

Fig. 1. Langmuir-type adsorption isotherm for the effect of inhibitors.

The relative solution SS with respect to $BaSO_4$, σ, is defined as

$$\sigma = \frac{\text{IP}^{1/2} - K_{\text{sp}}^{1/2}}{K_{\text{sp}}^{1/2}} = S^{1/2} - 1 \tag{4}$$

in which IP is the ionic activity product and K_{sp} represent the thermodynamic solubility product and was taken as 1.20×10^{-10} mol^2/L^2 for $BaSO_4$ at 30°C [35,36]. The ratio IP/K_{sp} represents the degree of SS, S, and was computed by using MINEQL + chemical equilibrium modeling software [37], which is free energy minimization program taking into account all equilibria in the solution, mass balance, and electroneutrality conditions. The considered equilibria with the related values of the thermodynamics constants are given in Table 2.

Table 2
Equilibria of barium sulfate in aqueous and the corresponding equilibrium constants K [38]

Equilibrium	log K
$H_2O \rightleftharpoons H^+ + OH^-$	−13.999
$Ba^{2+} + SO_4^{2-} \rightleftharpoons BaSO_4^{2-}$	2.342
$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^{2-}$	1.987
$BaSO_4^{2-}$ (solid) $\rightleftharpoons Ba^{2+} + SO_4^{2-}$	−9.992

The rate of barium sulfate crystallization can be expressed in terms of semiempirical kinetics equation:

$$R = k\sigma^n \tag{5}$$

where k is the rate constant for crystal growth and n is the apparent order of the crystal growth. The values of n are 1 for adsorbtion control, 2 for spiral growth, and >2 for polynuclear growth.

Logarithmic plots of the rates of $BaSO_4$ formation as a function of the relative SS yielded a straight line as shown in Fig. 2. The value of n, the effective order of the reaction, is calculated from the slope of the line. The effective order of the reaction was found as 2.48 for $BaSO_4$ growth in the presence of 1 mg/L PAA. When the deviation is taken into account, this value suggests a predominantly spiral dislocation, surface controlled process. This value is in agreement with earlier reports on the seeded growth of $BaSO_4$ [39–41].

3.2. Effect of the ratio $[Ba^{2+}]_t/[SO_4^{2-}]_t$

A series of experiments were carried out in order to investigate the influence of the $[Ba^{2+}]_t/[SO_4^{2-}]_t$ molar ratio on the kinetics of crystal growth of barium sulfate. The comparison of the $BaSO_4$ growth rate in three different RR, are given Fig. 3. The faster growth rates were obtained in the presence of excess sulfate ions. Rate increased from 3×10^{-6} to 6×10^{-6} when the RR decreased from 2/1 to 1/2 in the presence of PAA at 2×10^{-7} mol/L. Varying the $[Ba^{2+}]_t/[SO_4^{2-}]_t$ ratio could change the surface electrostatics of crystals and thus influence the PAA–$BaSO_4$ crystal interaction, leading to a increasing crystallization rate $BaSO_4$. This result indicates that the presence of excess sulfate ions at the surfaces of $BaSO_4$ crystals could impair the interaction of the PAA with crystal surfaces. barium ions increase the adsorption of PAA.

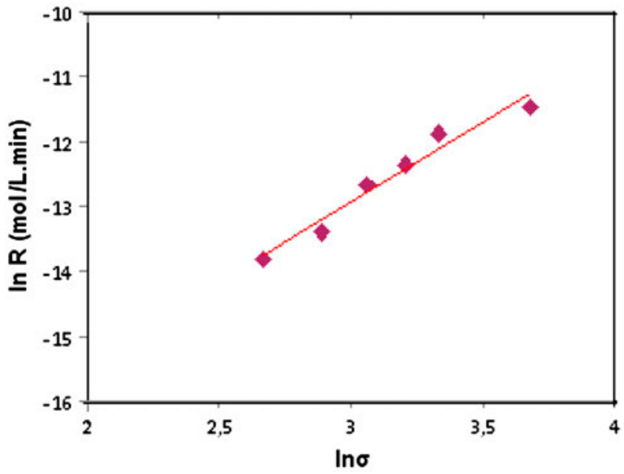

Fig. 2. Logaritmic plot of rate of precipitation of $BaSO_4$ vs. the relative solution SS ($T = 30$°C, 2×10^{-7} mol/L PAA, pH = 5.5).

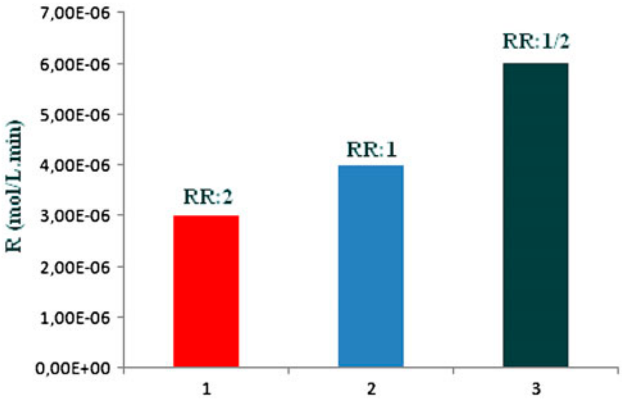

Fig. 3. The comparison of the $BaSO_4$ growth rate in three different RR.

3.3. Effect of additives on barium sulfate size and morphology

Since additives have great influence on crystal size and shape, we investigated the selective effect of the polymers on the crystal morphology and size using SEM. On examination of the SEM images, it was clear that the presence of additives in supersaturated solutions affects not only the kinetics of crystal growth but especially morphology and size of barium sulfate crystals, as shown in Fig. 4 and Table 3. The characteristic morphology of barium sulfate precipitated in the absence of additives is shown in Fig. 4(a). Examination of the morphology of the precipitated barium sulfate crystals by SEM showed the formation of the characteristic rectangular tablets. As shown in Fig. 4(a), the crystals were an average side length of 9.53 m and average side width of 5.79 m. The crystal habit of the precipitated barium sulfate crystals was affected by presence of additives, as may be seen in the scanning electron photographs shown in Fig. 4(b)–(d). The products comprised round tablets or flower-like aggregates of tablets in the presence of CMI. It was noteworthy that the as-prepared flower-like aggregates comprised many round tablets randomly grown from the central part of certain mother tablet. It was observed that the crystals have gained a spherical form in the presence of PAA. It could be concluded that the inhibition action of PAA on the crystallization of barium sulfate led to the controlled aggregation or growth of flower-like aggregate particles toward spherical

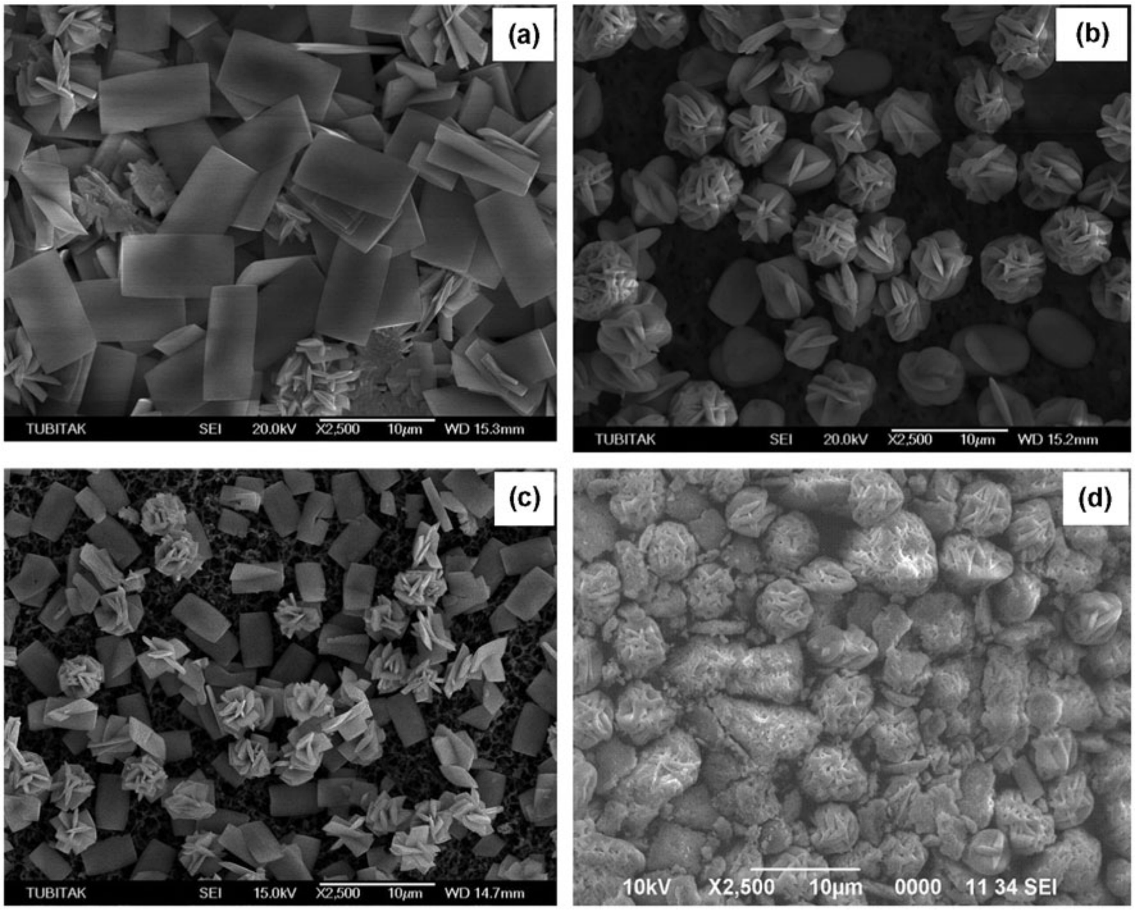

Fig. 4. SEM of formed barium sulfate crystals in the presence of (a) no additives, (b) 2×10^{-7} mol/L CMI-20, (c) 2×10^{-7} mol/L CMI-25, and (d) 2×10^{-7} mol/L PAA.

morphology. The average diameter of spherical particles is 3.65 m. The shape or morphology of a crystal is determined by the relative growth rate along different crystallographic directions. Hence, altering of the crystal morphology can be achieved by changing the relative crystal growth rate with specific inhibition. The interaction between inhibitors and crystal surfaces can be either specific or nonspecific. Specific interaction arises between a certain structural group of an inhibitor and a particular crystal face of inorganic crystals. The inhibitor can then be preferentially adsorbed into the corresponding crystal plane. Nonspecific inhibition, on the other hand, is less useful for modifying crystal habit in a specific way. In this work, the formation of spherical particles showed that PAA caused higher surface coverage of the particles and finally non-selective adsorption on all crystal faces of $BaSO_4$ particles. This resulted in the formation of spherical particles.

3.4. Effect of pH

In present experiments, we varied pH to investigate the effect of pH on the $BaSO_4$ crystal morphology in the absence and presence of PAA at 2×10^{-7} mol/L. Fig. 5 shows the SEM pictures of the particles obtained under the same conditions but at different pH values. It was seen that the variation of pH also affected the crystal morphology in the presence of PAA. Without any additives rectangular crystals were obtained when pH 3 and 9 (Fig. 5(a) and (b)). With PAA at 2×10^{-7} mol/L and at pH 3, the rectangular particles (as shown in Fig. 5(c)), which were somewhat similar to the products obtained in the absence of polymer were produced. PAA does not show any influence at pH = 3. When the pH was increased to pH 9, the crystals have gained a spherical form in the presence of PAA at 2×10^{-7} mol/L (Fig. 5(d)). This showed that PAA was more effective inhibitor in

Table 3
Comparison of barium sulfate crystal characteristics based on SEM results in the presence of additives at a concentration of 2×10^{-7} mol/L

Polymer	Rectangular-shaped			Spherical-shaped
	L (SD) (μm)	W (SD) (μm)	L/W	D (SD) (μm)
No additive	9.53 (±0.73)	5.79 (±0.50)	1.65	–
CMI-15	7.26 (±0.96)	5.59 (±0.63)	1.30	8.87 (±3.45)
CMI-20	6.88 (±3.96)	4.62 (±0.16)	1.49	6.13 (±3.88)
CMI-25	6.83 (±0.49)	4.37 (±0.57)	1.56	4.20 (±0.17)
PAA	–	–	–	3.65 (±0.60)

Note: W = width. L = length. D: Diameter SD = standard deviation.

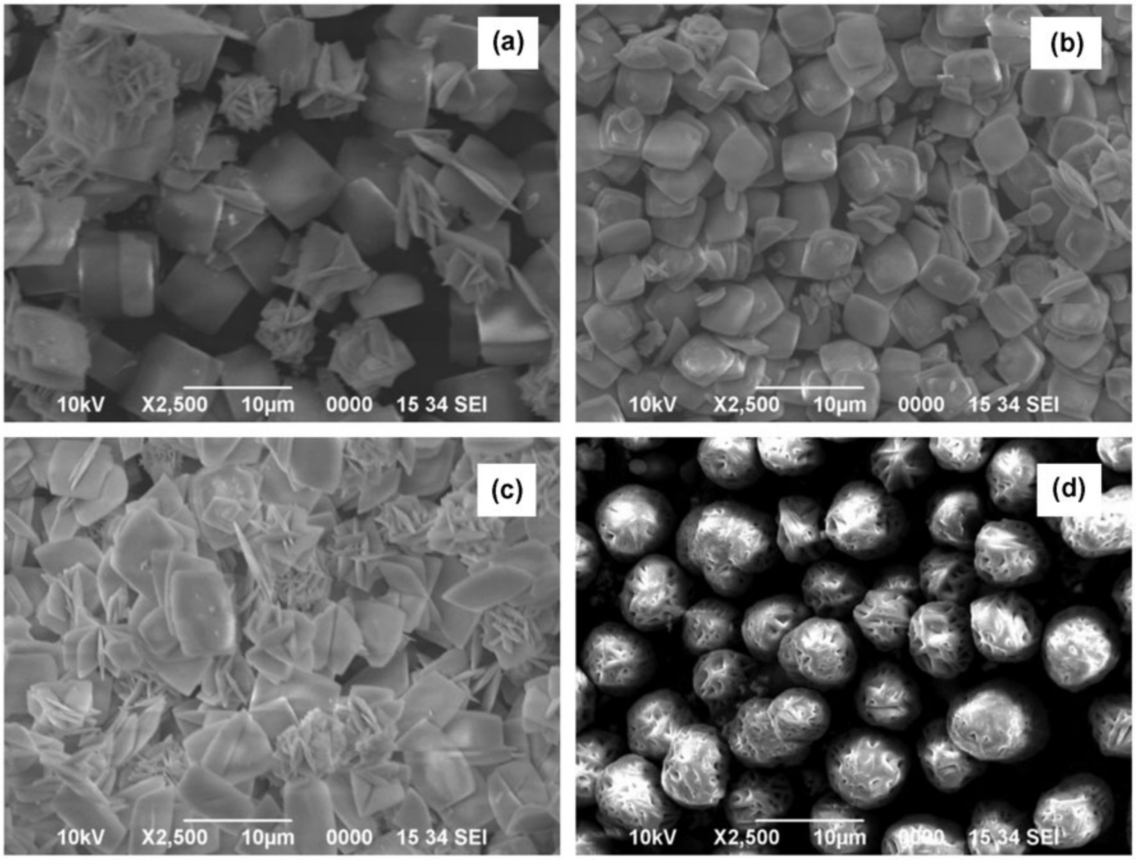

Fig. 5. SEM of formed barium sulfate crystals (a) no additives and pH 3, (b) 1 mg/L PAA and pH 3, (c) no additives and pH 9, (d) 1 mg/L PAA and pH 9.

higher pH levels. The same type of morphology was also reported in literature [42,43].

It is known that the pH of the solution influences the protonation degree of the carboxylic acid groups of PAA and low pH generally reduces protonation degree. Therefore, the interaction between PAA and $BaSO_4$ crystal was weakened at low pH, the inhibition effect of PAA on the crystallization of $BaSO_4$ at low

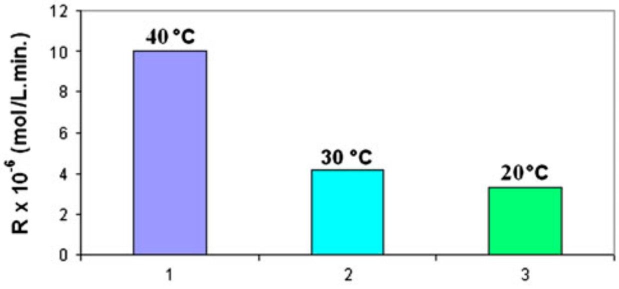

Fig. 6. The Comparison of the $BaSO_4$ growth rate in three different temperature.

pH was impaired and the morphology of the crystals was similar to that of the crystals prepared in the absence of polymer. When the pH of the solution was increased to 9 the spherical particles were obtained. This result showed that the increase of pH of the solution led to the increase of the protonation degree of the carboxylic acid groups of PAA.

3.5. *Effect of temperature*

The effect of temperature on growth rate was investigated at 20, 30, and 40˚C in the presence of PAA at 2×10^{-7} mol/L. It can be seen in Fig. 6 that the faster growth rates were obtained at 40˚C. Rate increased from 3.3×10^{-6} to 1×10^{-5} mol/L.min. when the temperature increased from 20 to 40˚C in the presence of PAA at 2×10^{-7} mol/L. Higher temperatures provided enough energy to the molecules to overcome the activation energy of the precipitation reaction and sped up the transport of scale components from the bulk solution to the surface. This result is consistent with expectations and in a good agreement with the values reported in the literature [44].

4. Conclusion

In this study polymers were added in solution as an additive, in concentrations ranging from 1×10^{-7} to 1×10^{-6} g/L. The results have shown that very low concentrations of polymers are capable of retarding barium sulfate crystallization. The micron-sized barium sulfate particles with different morphologies were obtained via a simple precipitation of sodium sulfate with barium chloride in the absence and presence of PAA and CMI. The concentration of polymers, the ratio of $[Ba^{2+}]/[SO_4^{2-}]$, temperature and pH were found to be important parameters for the control of morphologies and growth rate of $BaSO_4$ crystals. We present a result in this work that the all additives tested in this study are effective inhibitors for the formation of barium sulfate scale under the described experimental conditions. Additional results indicate that experimental parameters have significant influence on barium sulfate crystallization process. While rectangular crystals were obtained in the absence of additive, the spherical crystals were obtained in the presence of PAA. The morphology change was explained in terms of crystal growth retardation by nonspesific adsorbtion. Nonspecific inhibition can be described as blanket blocking of crystal steps and kinks over the entire surface of the growing crystals.

The pH can influence the morphology of the produced particles significantly with rectangular particles formed at pH 3; spherical particles or conjoined spheres were mainly produced at pH 9. The effect of pH on the crystallization can be interpreted in terms of the influence of pH on the protonation degree of the carboxylic groups of polymers. An appropriate pH might be beneficial to adjust the morphology control of $BaSO_4$. It was also found that the presence of excess barium ions at the crystal surfaces could promote the interaction of PAA with $BaSO_4$ crystal. Higher temperatures are favorable for increasing the growth rate. The results described herein indicate that the effectiveness of anionic polymers was ascribed to their relative ability to adsorb on the crystal surface and such inhibition is directly linked to fractional coverage of adsorption sites.

Acknowledgment

We appreciate the support of B.A.P.K. (Project No: 28-07-01-04) for the accomplishment of this work.

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