Effects of some parameters affecting the crystallization rate of calcium sulfate dihydrate in sodium chloride solution

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Abstract: Crystallization of calcium sulfate dihydrate ($CaSO_4.2H_2O$) in sodium chloride solutions at different supersaturation (δ = 1.2–2), pH =3, ionic strength (I = 0.5 M) and at 80°C was studied. The influence of aluminum and magnesium nitrates having very low concentrations (10^{-7} mol dm^{-1}) on the rate of crystallization at different supersaturation was investigated. The rate of crystallization was found to be dependent of the stirring rate suggesting diffusion mechanism. The addition of Mg^{+2} or Al^{+3} retarded the rate of crystallization to an extent proportional to their amounts present. Furthermore, the retardation effect was enhanced as the supersaturation decreases. The results also revealed that the increase in both pH (3 −10) and crystallization temperature (20 −80 °C) brought about an increase in calcium sulfate crystallization rate.

1. Introduction

Calcium sulfate is frequently encountered both in nature and in industry [1–5]. It is also the most unwelcome scalant in the production of oil and gas, in water cooling systems and in hydrometallurgical processes [6]. Crystallization of calcium sulfate dihydrate (gypsum) is of importance in view of its applications in a number of industrial and environmental precipitation processes. There are three main forms of calcium sulfate: calcium sulfate dihydrate or gypsum ($CaSO_4.2H_2O$), calcium sulfate hemihydrate ($CaSO_4.0.5H_2O$), and anhydride ($CaSO_4$). The solubility of different forms of calcium sulfate dihydrate normally decreases by increasing temperature [7].

The crystallization of calcium sulfate could be initiated in presence of foreign substances or dust particles [8]. Earlier, many authors have studied the growth of seed crystals of gypsum in supersaturation solutions [3, 9–12], the crystallization of gypsum on other crystal surfaces [13], and the precipitation on heated metal surface [14]. The factors that govern this mechanism of precipitation and dissolution of the sparingly soluble salts are therefore of considerable interest, especially the influence of anions and cations which may exert a marked effect on the rate of precipitation, either through adsorption or by lattice substitution [15].

Calcium sulfate appears as an undesirable by-product in many industrial processes, mostly as scale. This results from the ubiquitous presence of the calcium ion in natural ores and is linked to the common use of sulfuric acid in industrial processing.

Phosphoric acid (H_3PO_4) is produced by two commercial methods: wet process and thermal process. Wet process phosphoric acid is used in fertilizer production. Thermal process phosphoric acid is of a much higher purity and is involved in the manufacture of high-grade chemicals, pharmaceuticals, detergents, food, and beverage products and other nonmanufacture of phosphate fertilizers products.

In a wet process, phosphoric acid is produced by reaction sulfuric acid with naturally occurring phosphate rock. The phosphate rock is dried, crushed, and then continuously fed into the reactor along with sulfuric acid. The reaction combines calcium from the phosphate rock with sulfate, forming calcium sulfate ($CaSO_4.2H_2O$), commonly referred to as gypsum. Gypsum is separated from the reaction solution by filtration. Phosphoric acid (H_3PO_4) is mainly produced by the dihydrate (DH) process, in which phosphate concentrate is leached with sulfuric acid (H_2SO_4). The reaction is fast; it takes from 2 to 10 minutes. However, the crystallization of the formed gypsum ($CaSO_4 \cdot 2H_2O$) extends from 2 to 8 hours [16].

Gypsum is either found in nature as a mineral or precipitated from aqueous solutions, as well as from the hydration of calcium sulfate hemihydrates. On the other hand, large quantities of gypsum are produced as a by-product in the production of phosphoric acid from calcium phosphate rock Eq.1

$$Ca_3\left(PO_4\right)_2 + 3H_2SO_4 + 6H_2O \longrightarrow 2H_3PO_4 + 3CaSO_4 .2H_2O \qquad (1)$$
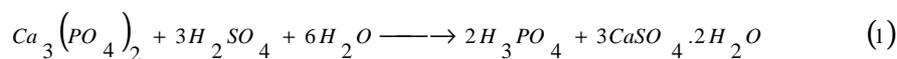
Attack of naturally occurring phosphate ores by sulfuric and/or phosphoric acid solution is the basic process for producing phosphoric acid and inorganic phosphorus fertilizers, such as superphosphate. In the wet production process, the raw phosphate ore is converted into phosphoric acid and calcium sulfate by adding solutions of sulfuric and phosphoric acids in the reactor [17]. These acids are introduced simultaneously or successively [16].

The effect of Al^{3+} and Mg^{2+} ions on calcium sulfate dihydrate (gypsum) crystallization under simulated conditions of phosphoric acid production is studied. The results showed that Al^{3+} decreases the induction time at all supersaturation ratios from 1% to 2% compared with the Mg^{2+} which increases the induction time at all supersaturation ratios. The growth efficiency increases up to 41% with addition of 1wt% Al_2O_3 and decreases by increasing Al_2O_3 content to 3wt % [18].

In contrast, the presence of 1-2 wt% MgO inhibited the crystallization process of gypsum at all supersaturation ratios. Surface energy is increased in the presence of 1% Al_2O_3 and decreased with 1 wt% MgO compared with the baseline. Nucleation rate is decreased in the presence of 1 wt% Al_2O_3 and increased with 1 wt% MgO compared with baseline. The mean diameter of the formed crystals is increased and that of the fine crystals less than 20 mm is decreased in the presence of 1% Al_2O_3 and increased in the presence of 3 wt% Al_2O_3 compared with the baseline. On the other hand, mean diameter of the formed crystals is decreased and that of the fine crystals less than 20 mm is increased in the presence of MgO. Interestingly, the majority of the formed crystals are clusters with 1 wt% Al_2O_3 and needle-like type with MgO and baseline [18].

The presence of aluminum in phosphoric acid has a positive influence on the crystal habits, size, and consequently filterability [16, 19]. Aluminum is said to promote regular crystal growth in all directions by yielding much thicker crystals. This reduces the surface to volume ratio of the crystals and hence improving the filtration rate [20–22].

Budz et al. [23] showed that aluminum reduces the nucleation and growth rates of gypsum but promoted the agglomeration of the smaller crystals. In case of magnesium, it is believed that magnesium ions hinder the gypsum filtration by either increasing the viscosity of the filtrate or affecting the gypsum crystal size [16 and 19].

However, wet process phosphoric acid could be produced from high MgO phosphate rock by accepting a weaker filter acid, higher filtration temperature, and thinner gypsum cake thickness [24 and 25]. Li et al. [26] showed that the presence of magnesium ions alone decreased the crystal size of gypsum crystals. On the other hand, Lin et al. [27] showed that the presence of Mg and Fe together during the reaction of calcium monohydrogen phosphate with sulfuric acid at 60℃ increased the width of gypsum crystals.

The present work aims at studying the crystallization of gypsum under conditions simulating the production of phosphoric acid with and without addition of $Al(NO_3)_3$ and $Mg(NO_3)_2$ using pure chemicals.

2. Materials and Methods
2.1. Materials

Calcium chloride $CaCl_2$ and sodium sulfate Na_2SO_4 (BDH, England) were used to prepare seed crystals. Hydrochloric acid HCl (MERCK, Germany) was used to adjust pH. Aluminum Nitrate $Al(NO_3)_3$ and magnesium nitrate $Mg(NO_3)_2$ (FLUKA, Switzerland) were used as a source of aluminum and magnesium ions, respectively. Sodium chloride NaCl from El-Nasr Pharmaceutical chemicals (ADWIC, Egypt) was chemical reagent grade. All solutions were prepared with deionized water of high quality (conductivity < 0.1 µS cm-1). A closed thermostatic double-walled vessel of 300 cm3 was used for all the experiments. The experiments were performed in the temperature range of 78–80 ∘C, and the systems were mechanically agitated with a flat-bladed stirrer at a constant rate (250 rpm).

2.2. Preparation of polycrystalline calcium sulfate dihydrate

Calcium sulfate dihydrate crystals were prepared by precipitation from calcium chloride and sodium sulfate solutions, as described previously by Lui and Nancollas [28]. The obtained solid was aged at least for one month before being filtered to obtain the dry crystals that were used in crystal growth experiments. The crystals were identified as gypsum by X-ray powder diffraction (Shimadzu XD-3 diffractometer) and IR analysis by scanning electron microscopy. The crystallization of calcium sulfate dihydrate carried out under various conditions was done in a thermostatted double-walled Pyrex glass vessel of 500 mL capacity and were adjusted to the required temperatures by circulating thermostatted

water through the outer jacket. Stemming was effected using a variable-space magnetic stirrer with a Teflon stirring bar. Nitrogen gas was first bubbled into a solution of the electrolyte at the temperature of the reaction for saturation with water vapor and then into the reaction vessel throughout the duration of the experiment.

2.3. Supersaturated solutions of calcium sulfate dihydrate

Supersaturated solutions of calcium sulfate dihydrate were prepared by the addition of thermostatted known volumes of calcium chloride solutions followed by careful addition of the appropriate amounts of sodium sulfate solutions in the cell which adjusted to the required ionic strength (0.5 M) with sodium chloride solutions. The reaction vessel was fitted with a Teflon cover with holes for the electrodes and sampling. At the beginning of the experiment, the pH of the supersaturated solutions was adjusted to the desired value (3) by the controlled addition of hydrochloric acid standard solutions. The pH of solutions was measured using a combination electrode (Jenway 3330) standardized before and after each experiment with NBS primary standard buffer solution.

The mineralization reactions were initiated by inoculation with dry seed crystals in the reaction vessel. The crystallization rate followed conductometry with time using Jenway 3330. The degree of supersaturation maintained at constant levels by the simultaneous addition of ionic species. Inhibitor solutions were also introduced as titrans in order to compensate for dilution effects. In addition, samples were periodically withdrawn and filtered at the reaction temperature through Millipore filters (0.22 µm), prior to solution and solid-phase analysis. The data confirmed that the lattice-ion and inhibitor concentrations were constant to within 1%.

For the calcium sulfate dihydrate crystallization growth experiments, the seed crystals of calcium sulfate dihydrate were prepared by a dropwise addition of 500 cm^3 of a 0.6 mol dm^{-3} $CaCl_2$ solution to 500 cm^3 of a 0.6 mol dm^{-3} Na_2SO_4 solution with a continuous magnetic stirring at 70°C over a period of 2 hours. The crystals obtained were filtered through a 0.22 mm membrane filter and washed repeatedly with deionized water until becoming free of NaCl. Then, the crystals were dried in an electric oven at about 105°C overnight.

3. Results and discussion

The concentrations of free ionic species in the solutions were computed by successive approximations for the ionic strength, I, as described previously [29] using activity coefficients calculated

from the extended form of the Debye–Hückel equation proposed by Davies [30]. The rate of precipitation, R, may be expressed in terms of the degree of saturation by Eq. 2:
in which m is the number of moles precipitated in

$$R = dm / dt = Rs\, d^{n} \quad ....(\ 2\ )$$

time t, R a rate constant, n the effective order of reaction, and s proportional to the number of growth sites available on the seed crystals. The degree of saturations is defined in terms of ionic products and solubility products for the calcium sulfate dihydrate salt as in Eq. 3

$$d = \frac{(IP)^{1/2} - K_{SO}^{1/2}}{K_{SO}^{1/2}} ......(\ ^{-}3) ,..... (3)$$

where the ionic products, IP, and the solubility product, K_{SO}, are expressed in terms of the appropriate activities of the ionic species $[(Ca^{2+})(SO_4^{2-})]^{1/2}$ at time t and at equilibrium, respectively.

The degree of supersaturated (δ) of the solutions, which is defined as the ratio of the activity products divided by the thermodynamic solubility product of the mineral (K_{sp}), is

$$d = \left\{ \frac{(Ca^{2+})(SO_4^{2-})}{K_{sp}} \right\}^{1/2} - 1 ,..... (4)$$

where parentheses denote activities of the respective ions and K_{sp} is the thermodynamic solubility product of the precipitating solid. The activity coefficients of divalent cations and anions were assumed equal and were obtained using the extended Debye-Huckel equation as proposed by Davies: [30]

$$-\log f_Z = 0.5115\, Z^2 \left\{ \frac{I^{1/2}}{(1+I^{1/2})} - 0.3\, I \right\} ,. (5)$$

where "f" are the activity coefficients for the Zvalent ions and I is the solution ionic strength. The value of K_{sp} was calculated as a function of temperature by means of the following relationship obtained by Marshall and Shlusher [31] for calcium sulfate dihydrate in aqueous solutions from 0 to 110°C.

Crystal growth experimental conditions are summarized in Table 1 in which $[Ca]_t$ and $[SO_4]_t$ are the total molar concentration of calcium and sulfate, respectively. Typical time plots of the amount of gypsum per moles precipitate, calculated from the titrants addition.

$$\log \left(K_{sp}\right) = 390.9619 - 152.6246 \ \log T - \frac{12,545.62}{T} + 0.0818493 \ T \ \cdots (6)$$

Table (1): Crystallization of calcium sulfate dihydrate crystals, $T_{ca} : T_{so2} = 1 : 1$ at T=80 °c, pH = 3, I = 0.5, and $\delta = 1.32$.

EXP. NO.	$Tca^{2+}/10^{-6}$ mol dm^{-1}	δ 10^{-1}	seed/Mg	R X 10^{-6} mol min^{-1} m^{-2}
1	9.48	12	50	1.86
2	9.99	13.2	50	2.09
3$_b$	9.99	13.2	100	2.11
4a	9.99	13.2	100	2.08
5	9.99	13.2	150	2.13
6	10.10	13.5	50	2.18
7	10.10	13.5	100	2.20
8	10.10	13.5	200	2.23
9	10.77	15	50	2.45
10	10.77	15	100	2.48
11	10.77	15	200	2.52
12$_b$	11.63	17	50	2.75
13a	11.63	17	50	2.79
14	11.63	17	200	2.84
15	12.39	20	50	3.16
16	12.39	20	100	3.19
17	12.39	20	200	3.24
18$_b$	9.99	13.2	50	2.10
19a	9.99	13.2	50	2.12
20c	9.99	13.2	50	3.11

Stirring speed: 300 rpm for experiments (a), 500 rpm for experiment (c) and 250 for all others.

The results cited in Table 1 show that the rate of crystal growth of calcium sulfate dihydrate was proportional to the mass of seed crystals used to initiate the reaction. The suggestion of a predominantly diffusion mechanism over a range of relative supersaturations may also be supported by the observed dependence of the experimental rate of precipitation on changes in fluid dynamics, as shown in Table 1 (compare experiments a, b and c), which conclude that the reaction is a mass transfer limited [32]. A similar mechanism for the crystal growth of calcium sulfate dihydrate has been observed [32 and 33].

The effective order of reaction was determined from the slope of typical plots of -log R against log δ, as depicted in Figure 1 which confirms a first-order dependence upon relative supersaturation (n = 1) in Eq. (2).

y = 0.9915x - 5.7902
R² = 0.9757
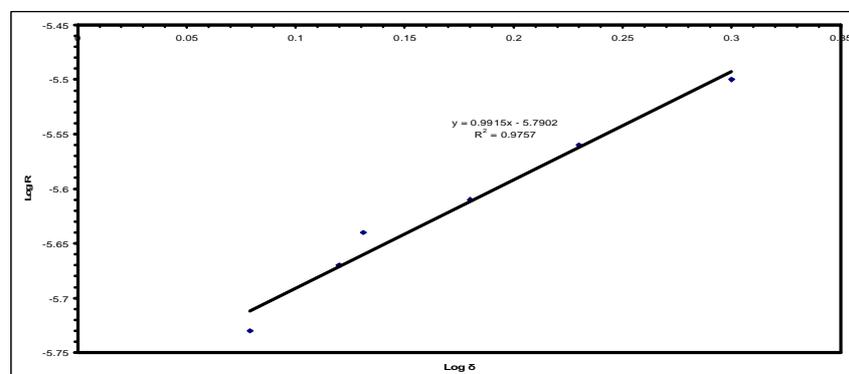
Fig (1): Plots of Log R against Log δ.

Additives play an important role in the theory of crystallization and dissolution. Recently, it is found that the presence of metal ions in the reaction medium inhibited the rate of precipitation of calcium sulfate dihydrate. The effects of Al^{+3} and Mg^{+2} on the rate of crystallization of calcium sulfate dihydrate crystals were studied. Pervious studies showed that Al^{+3} ions promote the agglomeration of small crystals of calcium sulfate dihydrate, and high Al^{+3} ions (about 3wt% Al_2O_3) increase the viscosity of the medium and inhibit the crystallization growth rate [34,35], and Mg^{+2} also retarded the crystallization rate.

3.1. Effect of concentration of the inhibitors concentration Al^{+3} and Mg^{+2} inhibitors on the crystallization process

The effect of magnesium and aluminum ions upon the rate of crystallization of gypsum in sodium chloride solution was studied at 80°C; stirring speed of 250 rpm, weight of seed crystals of gypsum 50 mg at solution (pH = 3), and a relative supersaturation (δ =1.32) results obtained are illustrated in Figure (2).

It is clear from Figure (2) that the addition of a very small amount of Al^{3+} or Mg^{2+} ions retarded the rate of crystallization to an extent proportional to the amount added. The decrease was, however, more pronounced in the case of Al^{3+} ion. In fact, the presence of 10^{-6} mol% decreased the crystallization rate to 71% and 37% for Al^{3+} and Mg^{2+}, respectively.

The presence of Al^{3+} ions may increase the viscosity of the filtrate resulting in retarding the crystallization of calcium sulfate dehydrate rate much more than Mg^{2+} [16 and 19].

The mechanism of Al^{+3} in retardation of the rate of crystallization of calcium sulfate dihydrate has been studied via carrying out the crystallization process at 80°C, pH = 3, I = 0.5 mol dm^{-3}, and δ = 1.32 in the presence of 10^{-7} mol dm^{-3} $Al(NO_3)_3$ as a source of Al^{+3} ions. Calculated volumes of $CaCl_2$, Na_2SO_4, NaCl and $Al(NO_3)_3$, respectively, are added in the same order. After the end of reaction, the solution was filtered and the produced solid was characterized using XRD and SEM techniques.

Figure (3) shows both of the diffractograms of solid left after the formation of calcium sulfate in absence of Al^{+3} ions and the diffractogram of calcium sulfate in presence of a known amount of $(Al(NO_3)_3$ 10^{-7}mol dm^{-3}).

It is seems from Figure (3) that all diffractional picks of calcite were detected in the diffractogram of the solid produced in absence of any inhibitors while the addition of Al $(NO_3)_3$ inhibitors at the beginning of the crystallization process led to the formation of Na_2SO_3 as a major phase and $NaAlCl_4$ as a minor phase.

SEM microscopic investigation of different solid left after the crystallization process in absence and in presence of $Al(NO_3)_3$ was carried out. The obtained SEM images are illustrated in Figure (4)
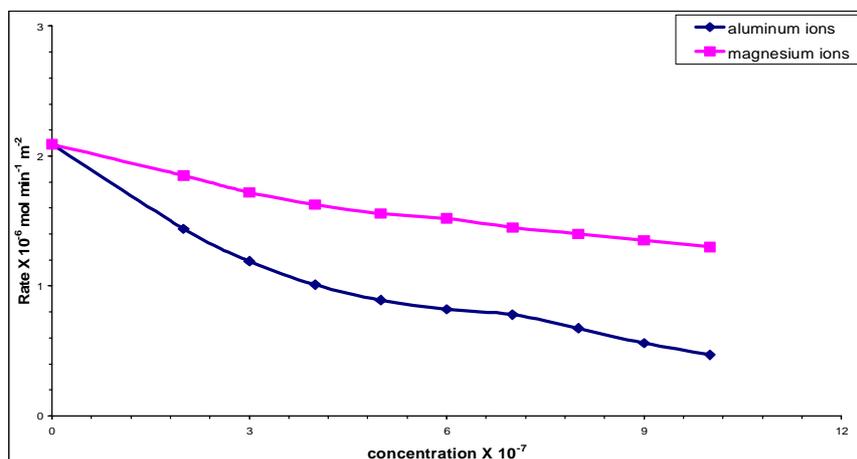
Fig (2) :Effect of Mg^{2+} and Al^{3+} on the rates of crystallization of calcium sulfate dihydrate crystals at δ = 1.32, I = 0.5 mol dm^{-3}, and 50 mg seed.
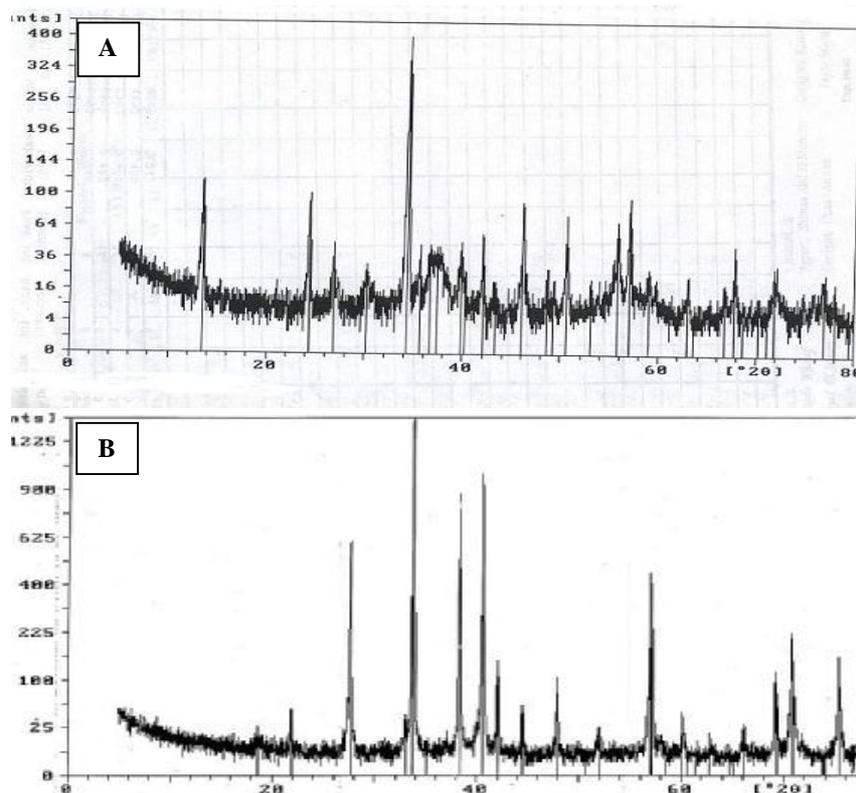
Fig (3): XRD analysis of calcium sulfate dihydrate (A) in absence of Al^{+3} (B) in the presence of 10^{-7} M of Al(NO$_3$)$_3$.
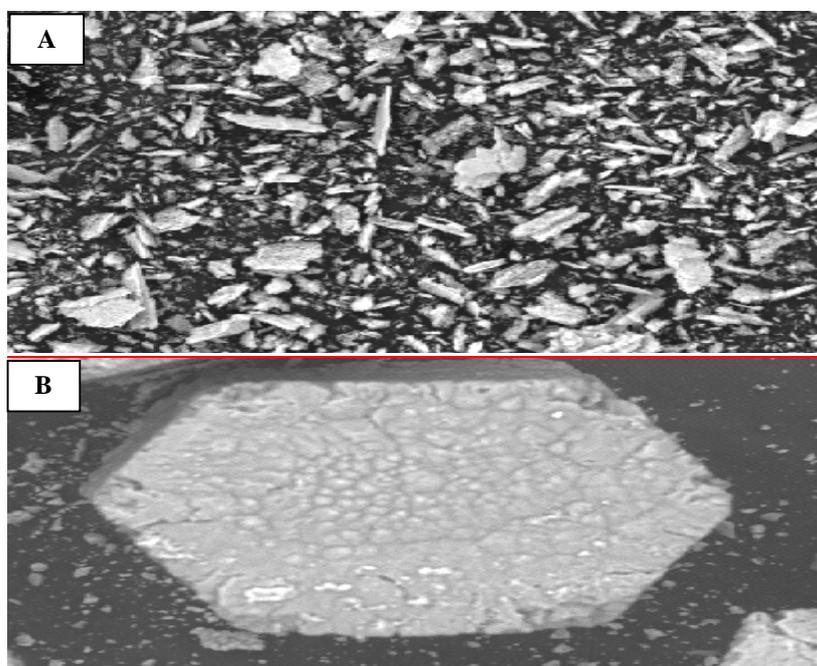
Fig (4)Scanning electron micrographs of calcium sulfate dihydrate (4a) in absence of Al^{+3} (4b) in the presence of 10^{-7} M of Al(NO$_3$)$_3$.

Scanning electron micrographs of the produced solid in the presence of Al $(NO_3)_3$ shows that only the crystals of Na_2SO_3 appeared, which means that NO_3^- ions reduce SO_4^{-2} ions to SO_3^{-2} ions in the presence of NaCl, so $NaAlCl_4$ and $CaSO_{4(aq)}$ are produced.

3.2. Effect of supersaturation degree (δ) on calcium sulfate dihydrate crystallization rate

To investigate the effect of supersaturation degree (δ) on calcium sulfate dihydrate crystallization rates in sodium chloride solution, the crystallization of calcium sulfate in absence and in the presence of Al^{3+} ions was investigated at different degrees of supersaturation from 1.2 to 2.0. The other parameters were fixed at an ionic strength solution (I) of 0.5 mol dm^{-3}, reaction temperature of 80°C, stirring speed of 250 rpm, and weight of seed crystals of gypsum of 50 mg at solution (pH = 3). The experimental results are given in Figure (5) as a relation between degree of supersaturation and calcium sulfate dihydrate crystallization rate.
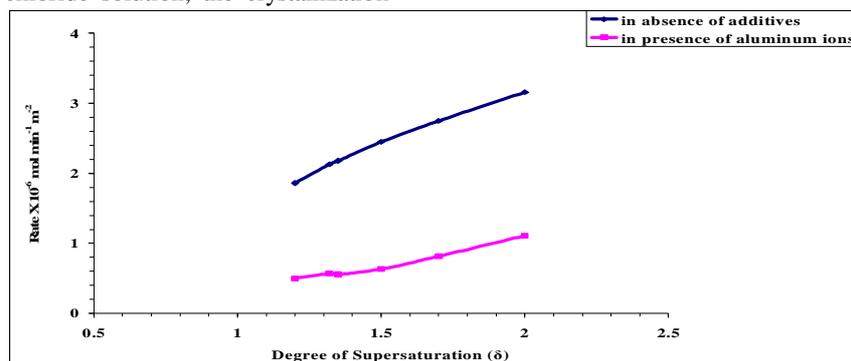
Fig (5): **Effect of supersaturation degree (δ) on the rate of crystallization of calcium sulfate dihydrate crystals at pH=3, T= 80 ºc, I = 0.5 mol dm^{-3}, and 50 mg seed in absence of inhibitors and in presence of Al^{3+} inhibitor.**

From the figure, it is clear that, as the degree of supersaturation increased from 1.2 to 2.0, the gypsum crystallization rate increased from 1.86 to 3.16 mol min^{-1} m^{-2} in absence of inhibitors and from 0.5 to 1.11 mol min^{-1} m^{-2} in presence of Al^{3+} inhibitor. The order in the presence of Al^{3+} ions was found to be equal to (n=1), which suggests diffusion mechanism.

3.3. Effect of pH on calcium sulfate dihydrate crystallization rate

The effects of solution pH on the crystallization growth of calcium sulfate dihydrate in the absence and in the presence of Al^{3+} ions were studied at different pH range (3−10). Other experiments conditions were fixed at a reaction temperature of 80°C, stirring speed of 250 rpm, weight of seed crystals of calcium sulfate dihydrate 50 mg at ionic strength (I = 0.5 M), and a relative supersaturation (δ =1.32). The experimental results are plotted in Figure (6) as a relation between pH and the rates of crystallization of calcium sulfate dihydrate crystals.
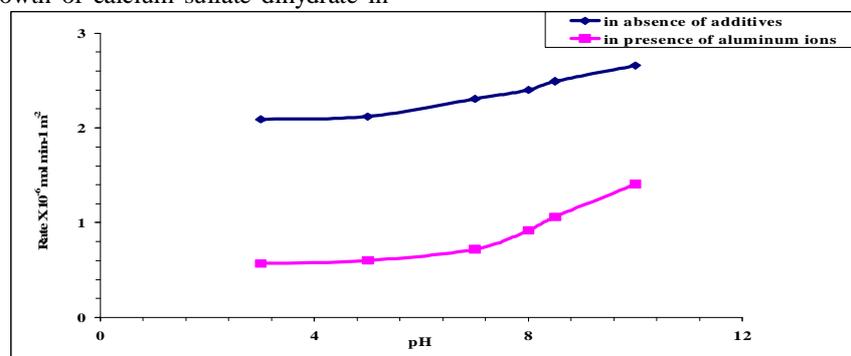
Fig (6) Effect of pH on the rate of crystallization of calcium sulfate dihydrate crystals at δ = 1.32, T = 80 ºc, I = 0.5 mol dm^{-3}, and 50 mg seed in absence of inhibitors and in presence of Al^{3+} inhibitor.

From the above figure, it is clear that with the increase of pH from 3−7, the calcium sulfate dihydrate crystallization rate slightly increased from about 2.09 to 2.3 mol min^{-1} m^{-2} in absence of inhibitors and from 0.57 to 0.72 mol min^{-1} m^{-2} in presence of Al^{3+} ions. This means that pH over a wide range (3-7) does not affect the calcium sulfate dihydrate [36, 37, and 38]. Further increase in solution pH from 7 to 10 led to increase the calcium sulfate dihydrate rates crystallization from 2.3 to 2.6 mol min^{-1} m^{-2} and from 0.72 to 1.4 mol min^{-1} m^{-2} in absence and in presence of Al^{3+} [38,39, and 40]. This may be due to the increase in degree of deprotonation [41 and 42].

3.4. Effect of ionic strength (I) on calcium sulfate dihydrate crystallization rate

The effect of ionic strength of the crystallization medium on the calcium sulfate dihydrate crystallization rate in sodium chloride solution is studied; several experiments are carried out in absence and in the presence of Al^{3+} ions at different ionic strength from 0.1 to 0.5 M. The other parameters are fixed at reaction temperature of 80°C, stirring speed of 250 rpm, weight of seed crystals of gypsum 50 mg at solution (pH = 3) and a relative supersaturation (δ =1.32). The experimental results are given in Figure (7) as a relation between ionic strength and the rates of crystallization of calcium sulfate dihydrate crystals.
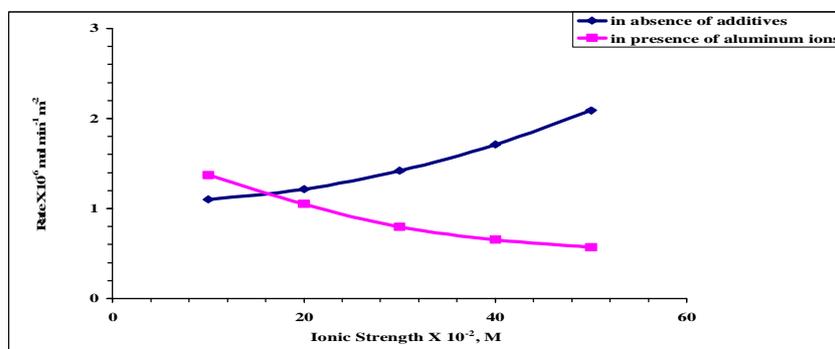
Fig (7): **Effect of ionic strength (I) on the rate of crystallization of calcium sulfate dihydrate crystals at δ = 1.32, pH=3, T = 80 °c and 50 mg seed in absence of inhibitors and in presence of Al^{3+} inhibitor.**

From the figure, it is clear that as the ionic strength increases from 0.1 to 0.5 M, the calcium sulfate dihydrate crystallization rates increased from about 1.1 to 2.09 mol min^{-1} m^{-2} in absence of inhibitors while it decreased from 1.3 to 0.57 mol min^{-1} m^{-2} in presence of Al^{3+} ions. This means that, the effect of ionic strength on the rate of crystallizations indicates that the reaction is ionic in its nature.

3.5. The effect of temperature on Calcium sulfate dihydrate crystallization rate

The rate of crystallization of calcium sulfate dihydrate is studied in absence of inhibitors and in the presence of Al^{3+} ions at temperature range of 20 to 80°C. The experimental results are given in Figure (8) as a relation between temperature and the rates of crystallization of calcium sulfate dihydrate crystals.
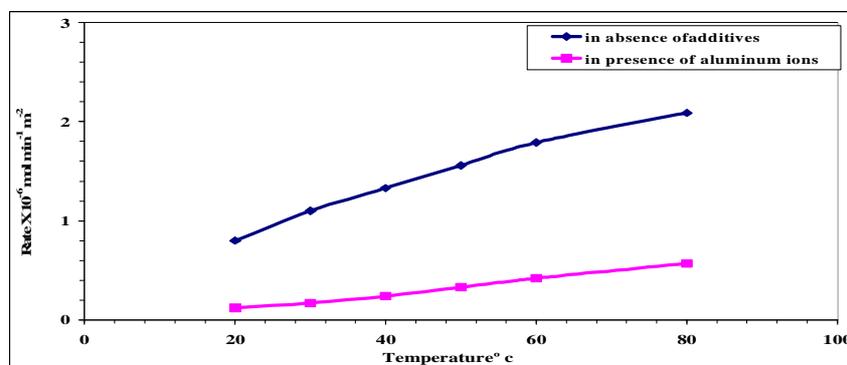
Fig (8)Effect of temperature on the rate of crystallization of calcium sulfate dihydrate crystals at δ = 1.32, pH=3, I = 0.5 mol dm^{-3} and 50 mg seed in absence of inhibitors and in presence of Al^{3+} inhibitor.

Figure (8) shows clearly that by increasing the temperature from 20 to 80 ºC, the rate of crystallization increases from 0.8 to 2.09 mol min^{-1} m^{-2} in absence of inhibitors while it increases from 0.12 to 0.57 mol min^{-1} m^{-2} in presence of Al^{3+} ions. The growth rates of calcium sulfate dihydrate crystals markedly increase with the increase in the growth temperature.

According to Arrhenius equation, the activation energies of calcium sulfate dihydrate in (Ea$_1$) and in presence of Al^{3+} ions (Ea$_2$) could be calculated at constant $\delta = 1.32$, I = 0.5 mol dm^{-3} and 50 mg seed by plotting relation between ln K against 1/T as shown in Figure (9).
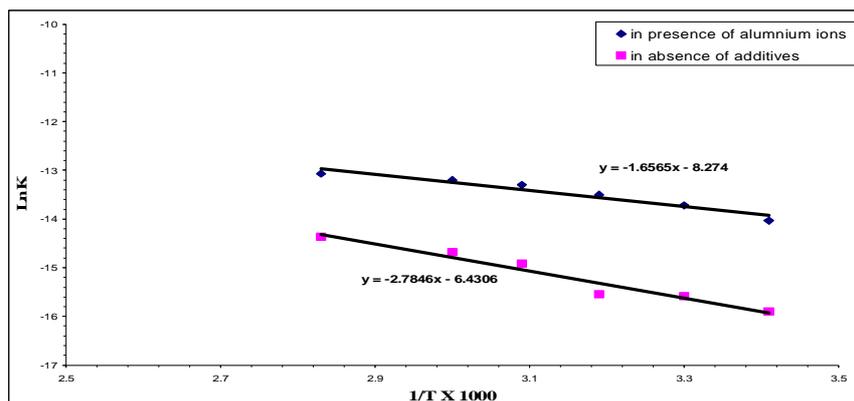
Fig (9) Arrhenius plot, for rate of crystallization of calcium sulfate dihydrate crystals at $\delta = 1.32$, pH=3, T = 80 ºc, I = 0.5 mol dm-3 and 50 mg seed in absence of inhibitors and in presence of Al^{3+} inhibitor.

From the figure, the activation energies of calcium sulfate dihydrate in absence of inhibitors (Ea$_1$) and in presence of Al^{3+} ions (Ea$_2$) were calculated and found to be equal to 13.76 and 23.14 KJ/mol. These activation energies agree with the reported activation energy for the seeded crystals growth of calcium sulfate dihydrate in salt-free solutions at a relatively lower temperature [43].

4. Conclusions

The analysis of the results shows that the presence of Al^{3+} and Mg^{2+} ions in the reaction medium inhibited the rate of precipitation of calcium sulfate dihydrate (gypsum). The degree of inhibition depends on the concentration of metal ions and degree of saturation. Precipitation is inhibited and a precipitation rate is decreased in the following order: Al^{3+} > Mg^{2+}. Complete inhibition of precipitation of gypsum was not found in any concentration of these metal ions and degree of saturations.

The inhibition of these metals was found due to reduction of NO_3^- ions of SO_4^{-2} ions to SO_3^{-2} ions. This reduction occurs only in the presence of NaCl solution. The degree of inhibition of Al^{3+} ions (as an example of inhibitors) increases in acidic medium, lower ionic strength, higher degree of supersaturation, and lower temperature.

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