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Research Article/Araştırma Makalesi

The Molecular Weight Effects of Polyethylene Glycol (PEG) on the Precipitation of Barium Sulphate

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Abstract
In this work, the effect of Polyethylene glycol (PEG) polymers with different molecular weight (Mw=400, 1500 and 4000 g/mol) was investigated to explore their relative effectiveness in inhibiting crystal growth of barium sulfate ($BaSO_4$, barite). Langmuir and Temkin isotherm were utilized to evaluate the adsorption behaviour of PEG polymers on the barite crystals. It was foun that PEG polymers tested in this study are effective as growth inhibitors under the experimental conditions.

1. Introduction

Crystallization is one of the oldest separation techniques in the chemical industry. This technique used not only to separate substances, but also to produce materials with desired shape and morphology (Nývlt & Ulrich, 1995; Akyol & Oner, 2014; Mullin, 1972). It is a very complex process. The main reason for this complexity is the number of mass transfer stages involved in this process (Ilyaskarov & Bulutcu, 2003). Crystallization can sometimes be unwanted, like the formation of scaling. Scaling of inorganic compounds in water containing systems on the walls of the water distribution equipments or in pipes such as cooling and heating systems lead to significant reductions in productivity and increasing operating cost (Merdhah & Yassin, 2009; Al Rawahi & Shaik, 2017; Amjad, 1998; Oncul et all, 2006).

Crystallization process is influced from many factors such as temperature, supersaturation, pH, mixing, and the additives. Among these paremeters, additives have a very strong effect (Nývlt & Ulrich, 1995; Tavanpour et all, 2016). Research on the effect of additives on crystal properties is one of the most important research areas of industrial crystallization (Revalor et all, 2010). Studies showed that additives plays an important role in crystal shape and crystal growth. The

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inhibition mechanism for the scale was reported due to the to specific adsorbtion of the additive the crystal surface, thereby reducing the crystallization rate and changing of the crystal morphology Akyol. & Cedimagar, 2016; Dogan et all, 2017; Rodriguez-Navarro & Benning, 2013).

Barium sulphate ($BaSO_4$, barite) is one of well-known the scale-producing precipitate in many industrial and oil drilling processes. The scale of barium sulphate cannot be removed easily because this compound is highly insoluble. Solubility of barite in water is only 2 mg/L. Therefore, the control of barium sulphate formation by using inhbitors has gained a significiant importance. That's why research is done further develop and improve these inhibitors and to be more enviromentally friendly (Dera et all, 2017; Akyol et all, 2016; Van der Rosmalen et all, 1980).

In the past decades many works were published about controlling of barite crystal morphology by using additives. The effects of citric acid (Ivanto et all, 2017), vinyl sulfonic acid (Carvalhoet all, 2017), acrylamide (Amjad & Koutsoukos, 2014), EDTA (Jones et all, 2007), poly(methacrylic acid) (PMAA) (Zhao et all, 2007), formic acid, polyacrylic acid (PAA) and carboxymethyl inulin (CMI) (Akyol et all, 2016) on the growth of $BaSO_4$ crystals were given in the literature.

In this paper, prevention of barium sulfate scaling by using eco-friendly inhibitors were studied. PEG polymers with different moleculer weights were choosen as inhibitors. We investigated the effect of molecular weight of PEG and concentration of polymers on barium sulfate crystallization. Structural characteristics of pure barite were determined by FT-IR (Bruker Alpha-P). Langmuir and Temkin models were applied in order to describe the adsorption mechanism.

2. Experimental

2.1. Materials

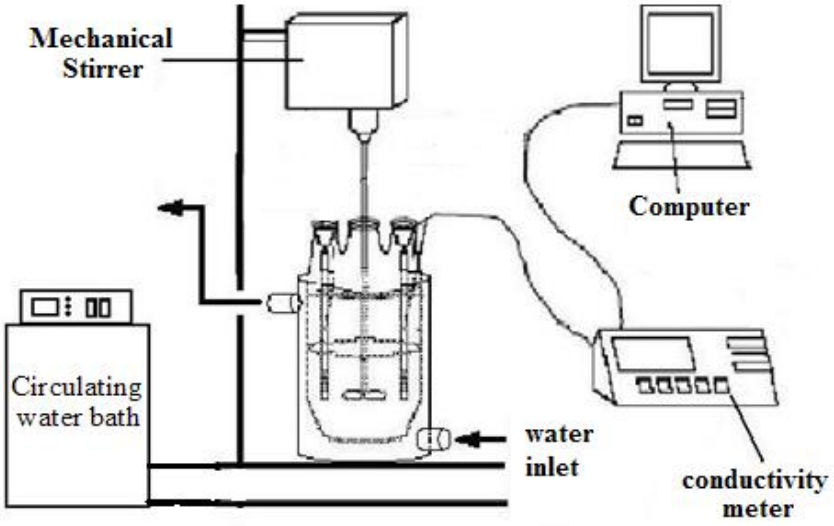
Barium chloride dehydrate (99%) were purchased from J.T Baker, sodium sulfate is obtained from Sigma-Aldrich, Polyethylene Glycol Products with different moleculer weight (PEG) (BASF-Kollisov, Mw:400), PEG (BASF-Kollisov, Mw:1500), PEG (BASF-Kollisov, Mw:4000), is supplied by BASF and all the chemicals were used without further purification. Double distilled water is used in all experiments.

2.2. Method

1 L capacity double-walled glass reactor was used in experimental studies. During the experiments, the solution in the reactor was mixed with a mechanical stirrer. All experiments were performed at a temperature of 25±0.1°C. Circulating water bath (Kerman Omron ESCSV) was used to keep the temperature constant. Experimental set-up was given in Figure 1. The effect of PEG polymers on the precipitation rate of barium sulfate was evaluated by recording the decrease in conductivity as a function of time in a solution containing equal molar solutions of barium chloride and sodium sulfate ($7x10^{-4}$M). During the experiments, WTW Inolab Series Cond-730 conductivity meter was used to determine the conductivity. The effect of PEG polymers on the rate of precipitation of barite was determined by recording the decrease, as a function of time, in conductivity of a solution [15]. Inhibition effectiveness evaluated acoording to Ro/R_i values. The

higher R_o/R_i values correspond to a better inhibition. Where, R_o is the rate of crystallization of the pure solution, R_i is the rate of crystallization in the presence of PEG polymers.

Figure 1. Experimental Set-up



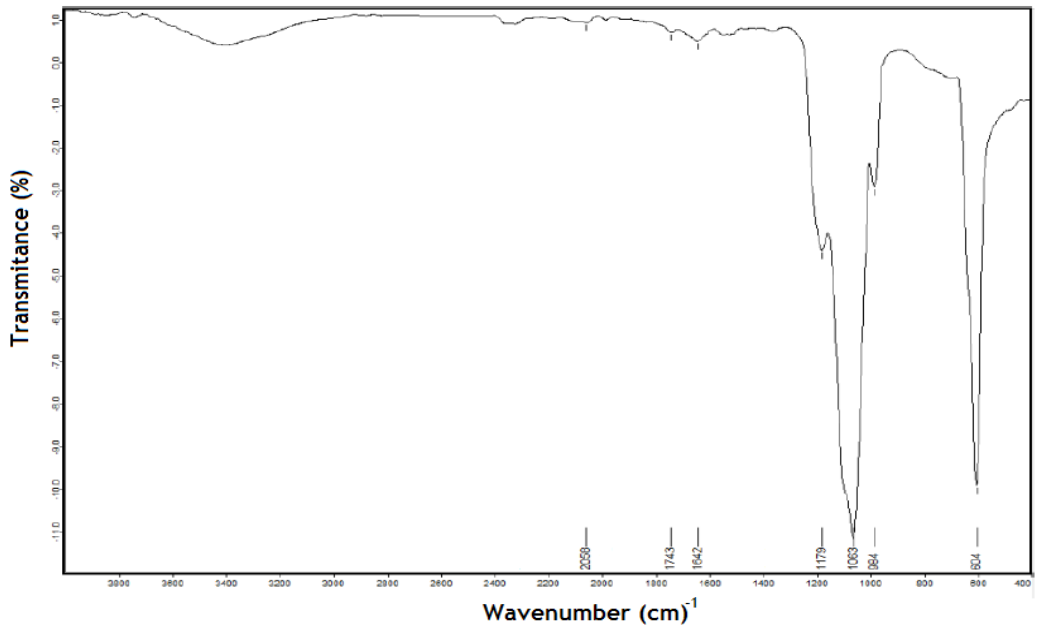
3. Results and Discussion

3.1. Characterization of $BaSO_4$ crystals by FT-IR

$BaSO_4$ crystals sentesized according to below chemical reaction;

$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl$

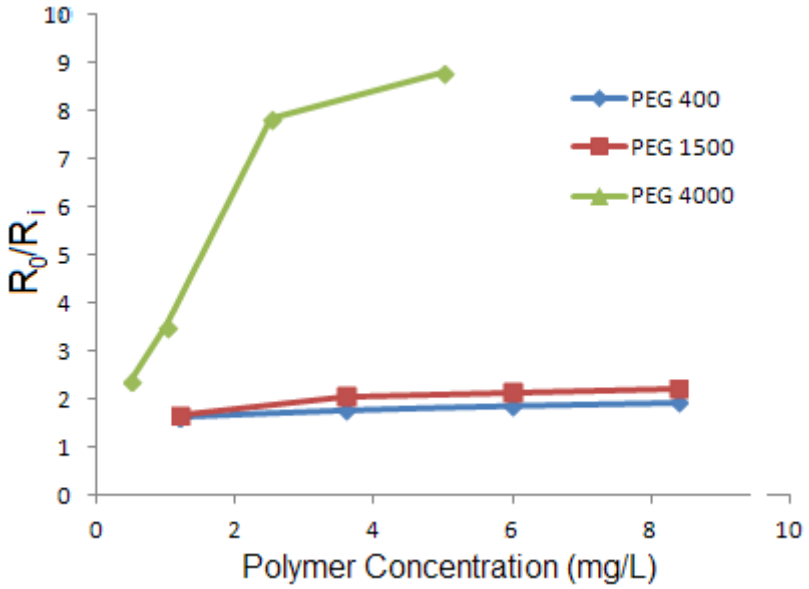
Figure 2. FT–IR spectra of $BaSO_4$



3.2. Crystal growth experiments

The influence of PEG polymers with different molecular weights on spontaneous batch crystallization of $BaSO_4$ was investigated.

Figure 3. Effect of polymer concentration on $BaSO_4$ crystallization



As shown in Figure 3 all polymers are reasonably good growth inhibitors. It is also clear that the R_0/R_i ratios increase with increasing molecular weight of PEG. According to Fig. 3, crystallization rate is decreased by increasing polymer concentration. This means that the plots of R_0/R_i values as a function of polymer concentration for PEG.

3.3. Adsorption mechanism

The adsorbate-adsorbent interactions can be easily estimated by plotting the adsorption data into equilibrium isotherm models. The Langmuir isotherm model is one of the most frequently used models in adsorption to describe the adsorption of adsorbate onto solid adsorbent surface. According to the kinetic model, there is a direct proportion between step velocity and surface coverage. If a graph is drawn between $R_0/(R_0\text{-}R_i)$ and $1/C_i$ at low polymer concentrations using equation 1, a linear relationship is observed. While the Eq. (1) represents the case at which impurity adsorption occurs at kinks in step edges as in Kubota-Mullin model, Eq. (2) represents adsorption on surface terrace as in Cabrera-Vermilyea model. When R-squared values is far from 1, the process is performed according to the Terrace method and the graph is drawn between $(R_0/(R_0-R_i))^2$ and $1/C_i$ (Kubota & Mullin, 1995; Akyol et all, 2016; Sangwal, 1999).

$$\frac{R_0}{R_0-R_i} = 1+\frac{1}{K_{aff}}\frac{1}{C_i} \quad (1)$$

$$\left(\frac{R_0}{R_0-R_i}\right)^2 = 1+\frac{1}{K_{aff}}\frac{1}{C_i} \quad (2)$$

where;

R_0= the rate of crystallization of the pure solution (R_0, mol/L.min)

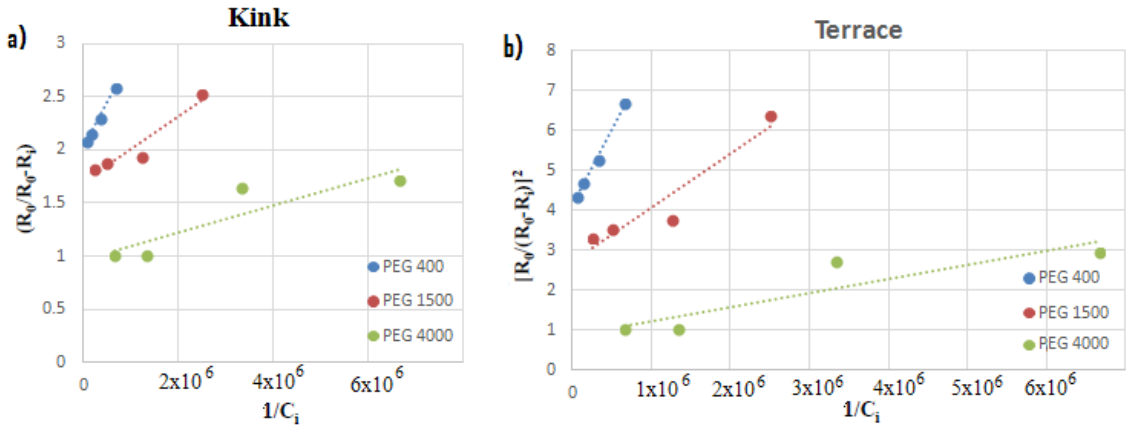
R_i= the rate of crystallization in the presence of additive (R, mol/L.min)

K_{aff} = affinity constant

C_i = is the total equilibrium concentration of the polymer.

Fig. 4a and 4b illustrate the models involving impurity adsorption of kinks and the surface terrace, respectively.

Figure 4. Isotherm models of Langmuir



From the slopes of the plots, the values of affinity constant were found (Table 1). The values of the affinity constant were calculated for PEG 400, PEG 1500, and PEG 400. The coefficient value (R^2) for the Langmuir king isotherm model was over 0.91, as shown in Table 1, higher than that for Langmuir terrace isotherm model, suggesting the adsorption isotherm of PEG polymers onto barite fits the king isotherm model. The high value of the affinity constant for PEG 4000 may reflect stronger equilibrium adsorption on the crystal surface, compared to that of PEG 1500, and PEG 400. Since PEG 4000 has the highest affinity value, it is the most effective inhibitor.

Table 1. Affinity constants for $BaSO_4$ crystallization

Polymers	King			Terrace		
	K_{aff} x (10^{-6}) (L/mol)	Q_{diff} (KJ)	R^2	K_{aff} x (10^{-6}) (L/mol)	Q_{diff} (KJ)	R^2
PEG 400	1.25	34.781	0.9967	0.25	30.794	0.9958
PEG 1500	3.33	37.209	0.9186	1	34.228	0.9075
PEG 4000	10	39.933	0.9632	2.5	36.499	0.8033

The Temkin isotherm model assumes that the heat of the adsorption of all molecules in the layer decreases linearly with the surface of adsorbent coverage due to adsorbate-adsorbent interactions [29]. The Temkin isotherm model is given by equation 3.

$$Q_{diff}=lnC_0+ZlnC_i \quad (3)$$

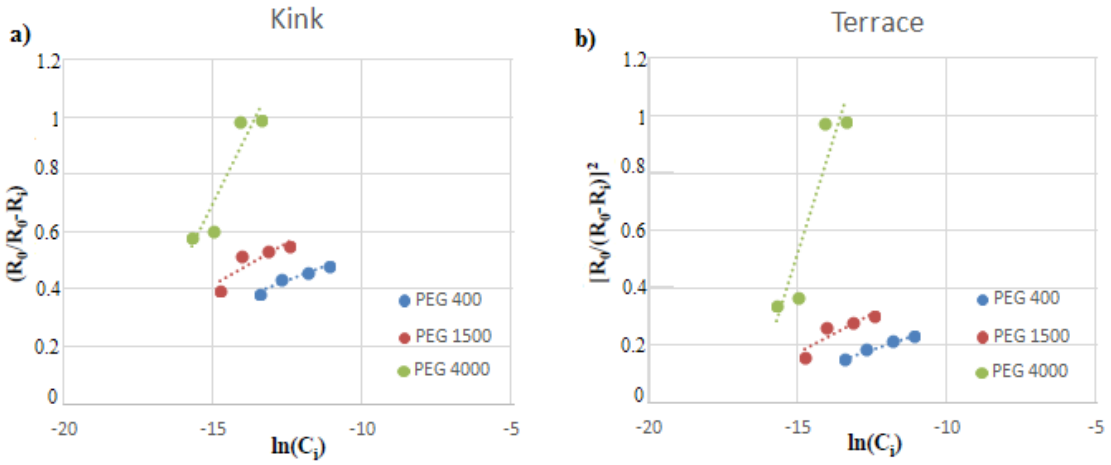
Where C_0 , Z are constants and C_i is the amount of additive in solution, Q_{diff} (kJ/mol) the initial heat of adsorption.

Constant C_0 is expressed as,

$$C_0=\frac{exp Q_{diff}}{RT} \quad (4)$$

Temkin adsorption parameters for PEG polymers are presented in Figure 5. In the figure, a) and b) illustrate the models involving impurity adsorption of kinks and the surface terrace, respectively.

Figure 5. Isotherm models of Temkin



The value of Q_{diff} for kinks and terrace were calculated from Equation 4. The results were shown in Table 2. The value of Q_{diff} predicted from Temkin model were higher during adsorption at kinks than those involved in adsorption The value of Q_{diff} predicted from Temkin model were higher during adsorption at kinks than those involved in adsorption at the surface terraces. Therefore, it is concluded that the mechanism of the inhibitory effect of PEG poymers best follows the Temkin kink model.

Table 2. Estimated values of Q_{diff} for crystal growth of $BaSO_4$

Polymers	King			Terrace		
	C_0x10^{-10}	Q_{diff} (KJ)	R^2	C_0x10^{-10}	Q_{diff} (KJ)	R^2
PEG 400	1.6461	58.283	0.9466	0.0066	44.609	0.9593
PEG 1500	0.3264	54.274	0.7636	0,0065	44.571	0.7869
PEG 4000	0.0092	45.431	0.8642	0,0015	41.062	0.8599

4. Conclusion

PEG polymers tested in this study are effective as growth inhibitors for $BaSO_4$ crystallization under the experimental conditions. Crystallization rate decreased with the increasing molecular weight of the polymer. Increasing the concentration of polymers resulted in higher inhibition efficiency. Our results show that inhibition by PEG is caused mainly by adsorption barite steps, which blocks kink nucleation. The inhibition increases with acid content of the polymer.

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