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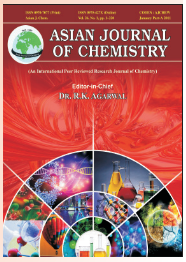

Influence of Calix[4]arene Derived Compound on Calcium Sulphate Scale Formation

SUHARSO*, BUHANI and L. APRILIA

Department of Chemistry, Faculty of Mathematic and Natural Sciences, University of Lampung, Jl. Soemantri Brojonegoro No. 1, Bandar Lampung, Indonesia

*Corresponding author: Tel/Fax: +62 721 704625; E-mail: suharso_s@yahoo.com

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Influence of C-methyl-4,10,16,22-tetramethoxy calix[4]arene compound as inhibitor of calcium sulphate scale formation has been studied using seeded experiment method. The results show that C-methyl-4,10,16,22-tetramethoxy calix[4]arene as calix[4]arene derived compound inhibits a formation of calcium sulphate crystals at a concentration of growth solution of 0.1 M and at various inhibitor concentrations of 0-150 ppm. The ability of C-methyl-4,10,16,22-tetramethoxy calix[4]arene as inhibitor of the formation of calcium sulphate scale is optimum in inhibiting growth rate of $CaSO_4$ scale formation is 50 ppm at 80 °C.

Keywords: Tetramethoxycalixarene, $CaSO_4$, Inhibitor, Scaling.

INTRODUCTION

Serious problem on several industries such as oil and gas industry, chemical industry, water cooler system in nuclear reactor is formation of scaling on their instruments. The scaling formation is undesired because its deposit causes appearing of hard scaling deposit and it can reduce efficiency of thermal transfer and disturb fluid flow process. In addition, scale deposit can cause corrosion and sudden damage of production process instrument[1-4]. These cause high cost for instrument maintenance to control scale deposit.

As a calcium carbonate, calcium sulphate is one of scale deposits which are to be serious problem at some industrial processes. In order to control this problem, several methods to control scale deposit such as decreasing of pH and water treatment which have been performed are not effective solution because they can cause corrosion and high cost of production. The low-cost and effective solution are use of anti scaling inhibitor from inorganic compounds, amino acid compounds and water soluble polymer such as polyaspartate, phosphonate and carboxylate[5-10]. The use of calix[4]arene compound derivative, C-methyl-4,10,16,22-tetramethoxy calix[4]arene as innovative scale inhibitor of $CaSO_4$, is not yet reported by researchers, whereas it has potency to be effective alternative inhibitor as it was performed by Suharso *et al.*[11] on $CaCO_3$ scale.

This research studied the effect of inhibitor use from calixarene compound (C-methyl-4,10,16,22-tetramethoxy calix[4]arene) on $CaSO_4$ scale. This inhibitor was synthesized based on procedure carried out by Jumina *et al.*[12] to be applied as inhibitor of $CaSO_4$ scale formation. This compound was selected because of several reasons such as strong ability to be applied as a ligand, extractant, adsorbent, or ionophore for metal cations[13-21]. In addition, this compound has four methoxy groups playing a role as strong ligand compared from other inhibitors used by several researchers. The advantage of calixarene is caused by its characteristics which has active sites adsorbing metal cations in aqueous solution. Derivative of this compound which has functional group as ester, ketone, carboxylic acid and ether is very effective as adsorbent and ligand of alkaline (Group-I) and earth alkaline group metal ions (Group-II)[17].

EXPERIMENTAL

Reagents used in this work consist of C-methyl-4,10,16,22-tetramethoxy calix[4]arene resulted from synthesis in laboratory based on procedure published by Jumino *et al.*[12], $CaCl_2$ anhidrat p.a. (Merck), Na_2SO_4 p.a. (Merck), deionized water, membrane cellulose nitrate 0.45 μm and acetone p.a. (Merck).

Preparation of seed crystals: Seed crystals were prepared with mixing anhydrous $CaCl_2$ solution 1 M and Na_2SO_4 solution 1 M each in 50 mL water at 80 °C. The mixture was stirred to produce deposit crystal. The seed crystals obtained were separated by membrane cellulose, cleaned by water and acetone. Then, it was dried in oven at 105 °C. This procedure was repeated for several times to obtain seed crystal as much as 50 g for preparation of crystal growth experiment.

Determination of $CaSO_4$ growth rate without inhibitor at various concentrations: Growth solution was made with mixing 200 mL of 0.1 M $CaCl_2$ and 200 mL of 0.1 M Na_2SO_4 solution into beaker glass with magnetic stirrer at 80 °C. The mixture was stirred and filtered by membrane filter. The mixture was kept in water bath for 10 min at 80 °C continued with placing the solution into 6-7 plastic bottles for each 50 mL in water bath at 80 °C. At the same time, 200 mg of seed crystal was added into the solution for each bottle. Investigation was carried out for 1 h and every 10 min one bottle was taken. The crystals of $CaSO_4$ obtained were filtered, washed by water and acetone and dried in oven at 105 ºC. The crystals were weighted to be observed its growth rate. The morphology of crystal produced was identified by Scanning Electron Microscopy (SEM), Jeol JSM-6510la.

Determination of $CaSO_4$ growth rate at various inhibitor concentrations: Influence of inhibitor addition with different concentrations was observed with applying the same procedure as the experiment of determination of $CaSO_4$ growth rate without inhibitor. In this experiment, the inhibitor concentration added in the growth solution is 0, 10, 50, 100, and 150 ppm.

RESULTS AND DISCUSSION

Data of $CaSO_4$ precipitation mass change with addition of different inhibitor concentrations were listed in Table-1, while graph of $CaSO_4$ growth rate *versus* time is displayed in Fig. 1. Data in Table-1 show that growth rate of $CaSO_4$ crystal without addition of inhibitor increases together with increasing of growth time. Increasing of precipitation mass in interval of 0-60 min is around 2.71 g L^{-1}. Thus, growth rate of $CaSO_4$ crystal in the absence of inhibitor in interval of 0-60 min is 0.045 g L^{-1} min^{-1}.

TABLE –1
CHANGE OF $CaSO_4$ PRECIPITATION MASS WITH THE ADDITION OF VARIOUS INHIBITOR CONCENTRATIONS

Time (min)	Precipitation mass change (g L^{-1})				
	0 ppm	10 ppm	50 ppm	100 ppm	150 ppm
0	4.00	4.00	4.00	4.00	4.00
10	5.15	2.11	1.32	2.15	2.76
20	5.49	4.33	2.91	3.56	3.68
30	6.12	5.22	3.52	3.83	4.34
40	6.39	5.82	3.92	4.21	4.83
50	6.42	5.82	4.01	4.22	4.83
60	6.41	5.82	4.01	4.22	4.84

The growth rate of $CaSO_4$ precipitation decreases consistently together with presence of inhibitor. C-methyl-4,10,16,22-tetramethoxy calix[4]arene inhibitor presence at various concentrations in time interval of 0-60 min indicates increase of precipitation mass of 1.82, 0.22 and 0.84 g L^{-1} for inhibitor concentrations of 10, 100 and 150 ppm, respectively, whereas at inhibitor concentration of 50 ppm does not occur significantly precipitation increase. In fact, at this inhibitor concentration, seed crystal added looses approximately 2.68 g L^{-1} at first 10 min. This fact shows that optimum inhibitor concentration occurs at C-methyl-4,10,16,22-tetramethoxy calix[4]arene presence of 50 ppm. At this inhibitor concentration, C-methyl-4,10,16,22-tetramethoxy calix[4]arene not only inhibits totally growth rate of $CaSO_4$ crystal but also it dissolves seed crystal added in the growth solution. This result is in accordance with previous result with applying this inhibitor upon $CaCO_3$ crystal[11]. The same results were also reported by Jones *et al.*[9] using calix[4]arene from aspartic acid and glutamic acid functional groups on inorganic material and Suharso *et al.*[22] using extract Gambier as inhibitor of $CaCO_3$ crystal.

Fig. 1 shows that growth rate at first 10 min decreases drastically at addition of inhibitor concentration of 10-150 ppm. Almost all data of inhibitor addition at this condition indicate consistently that mass of calcium sulphate precipitation decreases. This indicates that some of seed crystals added dissolve in growth solution. Thus at interval of first 10 min, C-methyl-4,10,16,22-tetramethoxy calix[4]arene added in growth solution is able to increase $CaSO_4$ solubility level in growth solution. Together with increasing of time, $CaSO_4$ crystals grew slowly as C-methyl-4,10,16,22-tetramethoxy calix[4]arene inhibitor was added at different concentrations in growth solution.

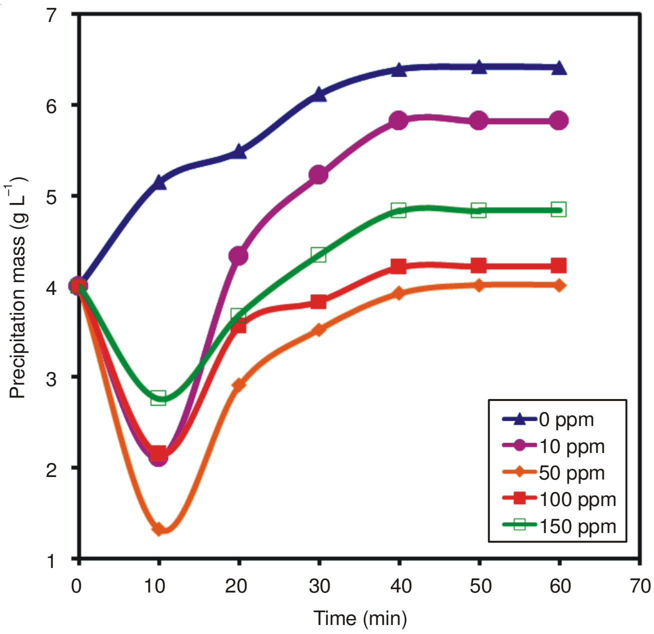

Fig. 1. Change of $CaSO_4$ precipitation mass in 0.1 M growth solution *versus* time with addition of inhibitor at various concentrations

In order to prove that C-methyl-4,10,16,22-tetramethoxy calix[4]arene inhibitor is able to inhibit $CaSO_4$ crystal growth physically, so $CaSO_4$ precipitation obtained from this experiment was observed by its morphology using SEM. Observation results using SEM upon $CaSO_4$ crystal morphology with and without inhibitor are displayed in Fig. 2. Fig. 2 gives a proof that $CaSO_4$ crystals resulted by inhibitor presence are relatively smaller in size of crystal (Fig. 2b) than inhibitor absence (Fig. 2a).

Inhibitor is an active surface material disturbing precipitation reaction. Inhibition mechanism of C-methyl-4,10,16,22-tetramethoxy calix[4]arene inhibitor in inhibiting growth rate of $CaSO_4$ crystal can be occurred because inhibitor ability controls solubility of salt in solution. In this research, crystal starts to grow at submicroscopic level, negative group on inhibitor molecules, C-methyl-4,10,16,22-tetramethoxy calix[4]arene, attacks a crystal positive charge causing damage of electronic equilibrium needed on crystal growth. Besides, C-methyl-4,10,16,22-tetramethoxy calix[4]arene also can trap calcium ions having positive charge. This mechanism can run *via* complex formation with a molecule or ion. Complex formed is a host-guest complex system, C-methyl-4,10, 16,22-tetramethoxy calix[4]arene as a host and calcium cation as guest [23-24]. Complex resulted, when it interacts with calcium cation, it can be exo and endo-calix complexes. In the endo-calix complex, calcium cations are trapped on C-methyl-4,10,16,22-tetramethoxy calix[4]arene molecule, while in the exo-calix complex, calcium cations trapped exist on between C-methyl-4,10,16,22-tetramethoxy calix[4]arene molecules.

Crystal modification mechanism is one of mechanisms that can explained this result. Modification of crystal morphology can produce soft and non-stick crystals. In this work, C-methyl-4,10,16,22-tetramethoxy calix[4]arene added in the growth solution of $CaSO_4$ causes change of crystal morphology of $CaSO_4$. This change can be seen in Fig. 2.

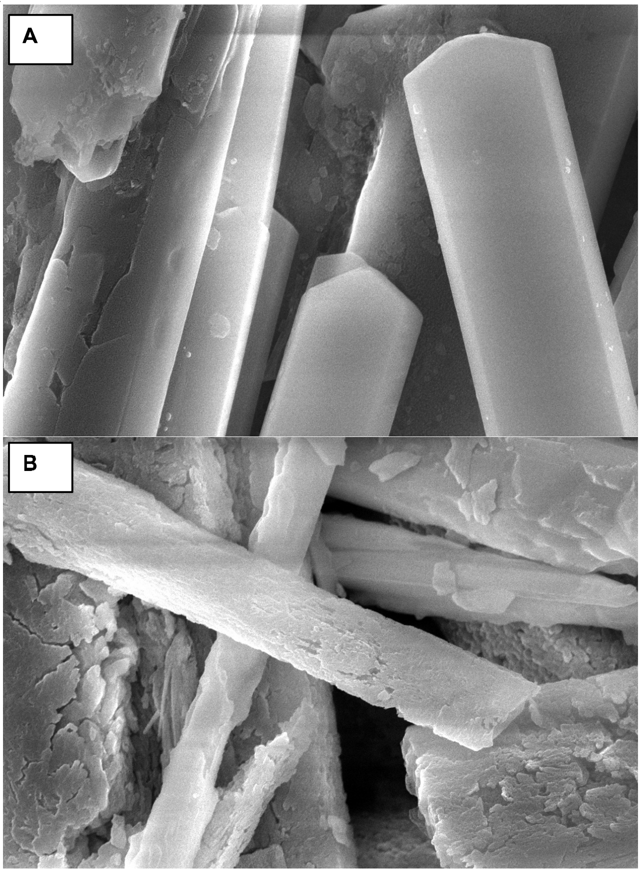

Fig. 2. SEM Images of $CaSO_4$ crystal morphology with 5000x magnification (a) without inhibitor, (b) with 50 ppm of inhibitor

Inhibitor can also adsorb the crystal or colloidal and give a big anionic charge. C-methyl-4,10,16,22-tetramethoxy calix[4]arene can also act as scale inhibitor with adsorbing scale surface when the crystal starts to grow. This compound is a big molecule that can be covered small crystals and obstruct nucleation of $CaSO_4$ crystals. Thus, with the addition of this compound, growth rate of $CaSO_4$ precipitation decreases.

Fig. 3 shows this mechanism. Blocking of crystal growth units by inhibitor causes $CaSO_4$ crystal growth rate to be slow. Blocking of crystal growth by inhibitor molecule can cause crystal morphology change. Crystal faces adsorbed by C-methyl-4,10,16,22-tetramethoxy calix[4]arene inhibitor, their growth is being hampered resulting $CaSO_4$ morphology to be irregular growth. This result is consistent with the result obtained by Sikiric dan Milhofer[25] investigating about effect of organic molecule on crystallization of biomineral in solution as well as reported by Suharso *et al.*[11] in $CaCO_3$ scale. Their research results show that change of growth rate and crystal morphology on biomineral crystals resulted by addition of organic molecules with specific functional groups.

Inhibitor mechanism in inhibiting crystal growth rate[11,21] according to this mechanism may be illustrated in Fig. 3. Fig. 3 indicates how inhibitor work in adsorbing on crystal growth faces from seed crystals (signed on crystals given black colors) producing slow crystal growth. On the contrary on the seed crystals are not adsorbed by inhibitors (signed on crystals given white colors) to be normal growth. On these both cases are showed by SEM results in Fig. 2.

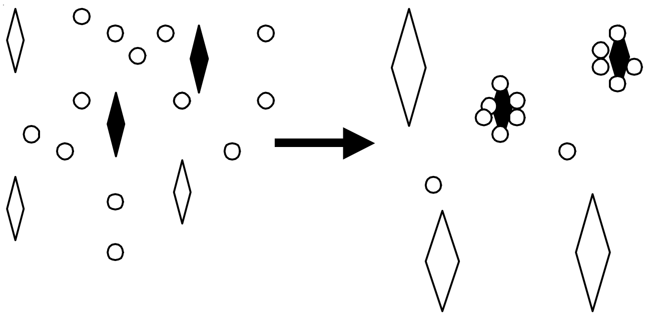

Fig. 3. Inhibitor mechanism in inhibiting crystal growth rate in growth solution (◇ = inhibitor molecule, ○ = seed crystal)

Conclusion

C-methyl-4,10,16,22-tetramethoxy calix[4]arene compound plays a role as inhibitor of calcium sulphate scale formation at concentration of growth solution 0.1 M and temperature of 80 ºC. The ability of C-methyl-4,10,16,22-tetramethoxy calix[4]arene as inhibitor of calcium sulphate scale formation is optimum at concentration of 50 ppm.

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