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Inhibition of calcium carbonate ($CaCO_3$) scale formation by calix [4] resorcinarene compounds

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ABSTRACT

Inhibition effect of tetrakis{(dimethylamino)methyl}C-methyl calix [4] resorcinarene (TDMACMKR) compound on calcium carbonate ($CaCO_3$) scale formation has been studied using seeded experiment and bottle roller bath method. The effect of the addition TDMACMKR as inhibitor on $CaCO_3$ scale formation was analyzed by measuring the weight of precipitation of $CaCO_3$ formed. The morphology and particle size distribution of obtained $CaCO_3$ crystals caused by the addition of TDMACMKR were analyzed by scanning electron microscopy (SEM), and particle size analyzer. The data obtained show that the TDMACMKR inhibits formation of $CaCO_3$ scale at various inhibitor concentrations added.

Keywords: Calix [4] resorcinarene; Scale inhibitor; Calcium carbonate

1. Introduction

One of the most serious problems encountered in some industrial processes such as oil and gas, chemical industry, power generation, and geothermal industry is the formation of scale (undesired crystal growth) on surface of industrial equipment [1–6]. This scaling impact on the efficiency of the equipment, and because of this, for example, the Indonesian Oil Company (PT PERTAMINA) has spent US$ 6–7 million to renew every pipeline at the Geothermal Industry every 10 y [7].

A widespread method used to reduce the impact of scale formation is to add an inhibitor. Selection of an appropriate inhibitor can provide a cheap and effective reduction in scale formation, as low concentrations can have a large impact on acrystal growth. Research into scale inhibitors is driven by the strong industrial need for effective inhibitors [8–11].

In this report, the calix [4] resorcinarene (TDMACMKR) compound was synthesized and reported previously [12], and tested as an inhibitor of $CaCO_3$ precipitation. TDMACMKR was selected for investigation as it combines O-donor groups, with amine functional groups. While most inhibitors studied to date involve O-donor groups, such as carboxylates and phenolates, there are relatively few report where these groups are used alongside amine functional groups. Another reason the use of TDMACMKR as the inhibitor of $CaCO_3$ precipitation is the existence of amine group classified as a hard bases and the cation of Ca^{2+} classified as a hard acid. According to Person's hard soft acid base (HSAB) theory, the hard bases are more likely to pair up with the hard acids. Therefore, the existence of amine groups in TDMACMKR will inhibit growth rate of the $CaCO_3$ crystals. Previous studies of this compound focused on its use an adsorbent to bind the heavy metal ions [12–19].

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2. Experimental methods

TDMACMKR was synthesized using standard methodology reported by Sardjono [12]. Reaction scheme of TDMACMKR synthesis is shown in Fig. 1 and full details of the synthesis and characterizations were reported by Sardjono [12]. The characterization of TDMACMKR was investigated by the Fourier transform infrared spectroscopy (FTIR)(Prestige–21 Shimadzu) and ^{1}HNMR spectroscopy (JEOL MY6O 60 MHz).

2.1. Crystal seed preparation

The preparation of seed crystals was performed by mixing 1 M of Na_2CO_3 solution and 1 M of $CaCl_2$ anhydrate solution each in 50 mL of water at temperature of 80°C. The mixtures were stirred at temperature of 80°C and left for 2 h to produce seed crystals. Then, the seed crystals obtained were separated from the liquor by filtration through a 0.45 μm Millipore filter washed thoroughly with water and dried in the oven at temperature

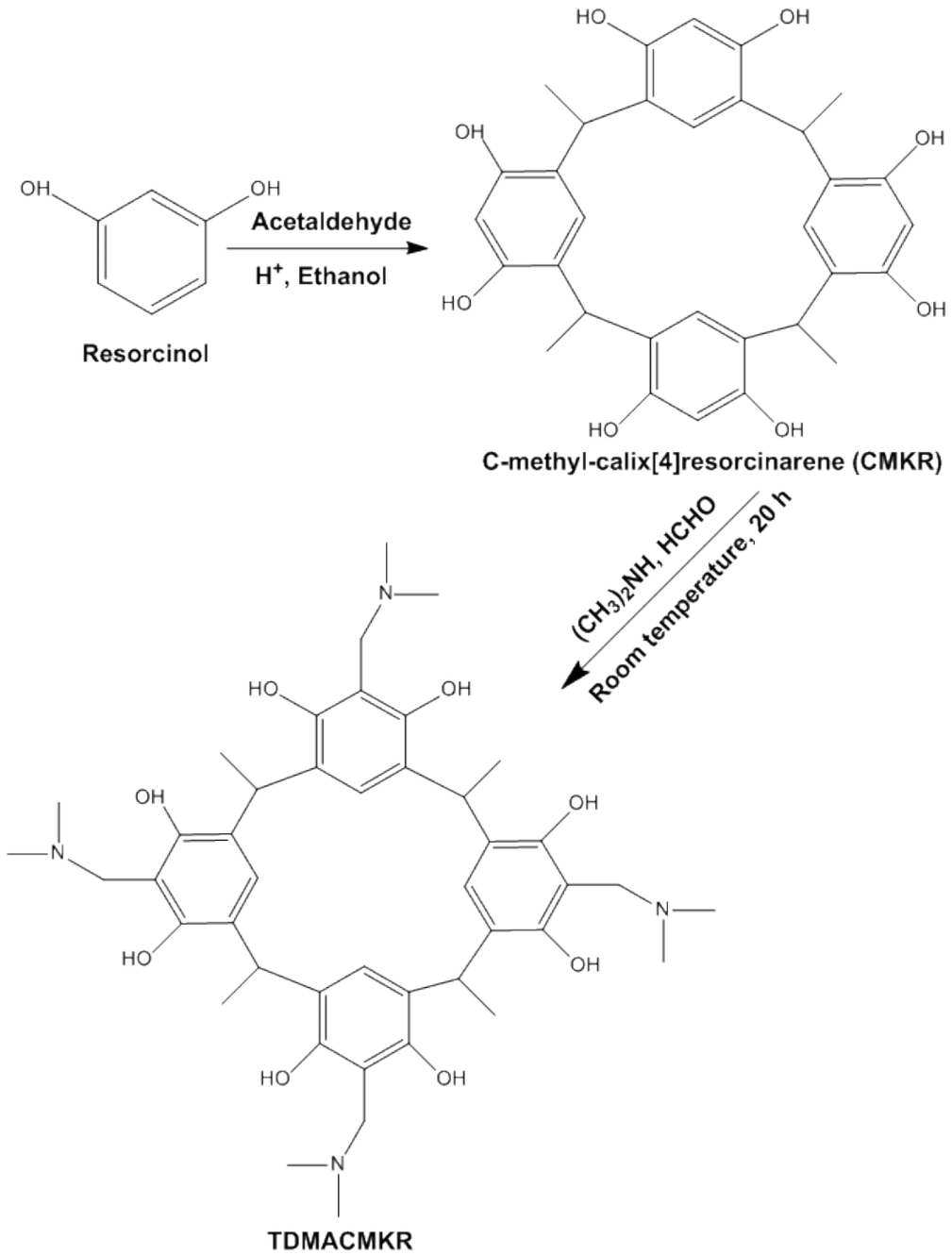

Fig. 1. Reaction scheme of TDMACMKR synthesis.

of 105ºC. These methods were repeated several times to procure the required amount of seed crystals for doing the experiments.

2.2. Crystallization experiments

The amount of 200 mL of 0.2 M $CaCl_2$ anhydrate solution and 200 mL of 0.2 M Na_2CO_3 solution were placed in 500 mL Nalgene polypropylene bottles at a temperature of 80°C, mixed, and stirred by magnetic stirrer to produce 0.1 M $CaCO_3$ growth solution up to a homogeneous solution. Then, the homogeneous solution obtained was filtered through a 0.45 µm Millipore filter. 50 mL aliquots of this stock solution were added to six 250 mL Nalgene polypropylene bottles. The bottles containing 50 mL of the $CaCO_3$ growth solution were returned to the bottle–roller bath. Into each bottle, the amount of 200 mg seed crystals was placed at an experiment temperature of 80°C. The bottle–roller was controlled automatically to rotate at 40 rpm. Over the 1.5 h experiment, a bottle was removed for every 15 min and the weight of the crystals precipitated was determined. The crystals resulted were cleaned thoroughly with water and were dried for 1 d in the oven at temperature of 105°C, and then weighed [7].

For each precipitation investigation, a blank experiment was performed in parallel with the inhibitor experiment. The same procedure was carried out for 0.3 and 0.6 M $CaCO_3$ growth solutions. Preparation of 0.3 M stock growth solution of $CaCO_3$ was performed by mixing 200 mL of 0.6 M $CaCl_2$ anhydrate solution and 200 mL of 0.6 M Na_2CO_3 solution. Preparation of 0.6 M stock growth solution of $CaCO_3$ was carried out by mixing 200 mL of 1.2 M $CaCl_2$ anhydrate solution and 200 mL of 1.2 M Na_2CO_3 solution.

2.3. Effect of TDMACMKR

In the same procedure, the influence of TDMACMKR presence at different concentrations in the $CaCO_3$ growth solution was investigated by adding different amounts of TDMACMKR (0, 25, 50, and 75 ppm). The crystal weight after TDMACMKR added as inhibitor was also calculated and analyzed. Inhibitor Effectiveness (%) can be calculated based on Eq. (1) [20].

$$\text{Inhibitor Effectiveness (\%)} = 100 \times \frac{(Cx - Cy)}{(Cz - Cy)} \quad (1)$$

where Cx = $CaCO_3$ concentration after presented inhibitor at equilibrium (g/L); Cy = $CaCO_3$ concentration without inhibitor at equilibrium (g/L); Cz = initial $CaCO_3$ concentration (g/L).

2.4. Data analysis

Using MS Excel 2007, the amount of precipitation versus time at various concentrations of TDMACMKR added and various concentrations of $CaCO_3$ growth solution were plotted as the amount of precipitation versus time for each different concentration of TDMACMKR added (0, 25, 50, and 75 ppm) in each the growth solution of $CaCO_3$ applied 0.1, 0.3, and 0.6 M. The ability of TDMACMKR in inhibiting the rate of $CaCO_3$ precipitation can be analyzed from the mass of precipitation obtained. Using SEM (JSM 6360 LA, Made in Japan), the $CaCO_3$ crystals morphology resulted from the experiment was identified to observe morphology change of $CaCO_3$ single crystal. In order to prove the effectiveness of TDMACMKR in inhibiting the rate of $CaCO_3$ precipitation, the particle size distribution of $CaCO_3$ crystals obtained from the experiments with and without inhibitor were analyzed by a particle size analyzer (Sedigraph III 5120–Micrometrics).

3. Results and discussion

3.1. Characterization of TDMACMKR

First step to synthesize TDMACMKR is synthesis of CMKR as raw material. The CMKR obtained and TDMACMKR produced were characterized by FTIR (Fig. 2). The existence of CMKR (Fig. 2a) was shown by peak band at 3425.58 1/cm as hydroxyl groups, 2877.79–2970.38 1/cm and supported clearly at 1427.32 and 1373.32 1/cm showing methine groups (=CH–) and $–CH_3$, as well as 1620.21 and 1512.19 l/cm as characteristic peaks of C=C aromatic group from condensation product. The FTIR of TDMACMKR is displayed in Fig. 2b. The characteristic change from the FTIR spectrum of CMKR can be seen clearly, but it is difficult to show the substitution has occurred because the

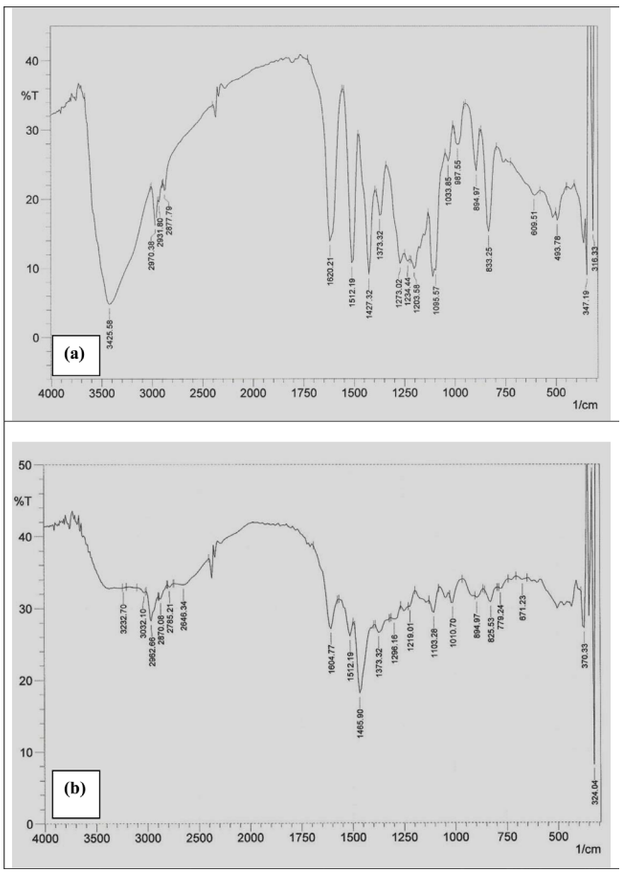

Fig. 2. FTIR spectra of (a) CMKR and (b) TDMACMKR.

existence of tertiary amine group does not give a specific peak. However, as the proof of TDMACMKR resulted from CMKR, the FTIR spectrum of TDMACMKR (Fig. 2b) shows characteristic peaks at the movement of hydroxyl existence from 3232.70–3425.58 1/cm, continued by the peak movement of C=C aromatic showing clearly the characteristic difference from first compound (CMKR). These are as the evident that the TDMACMKR synthesis was carried out successfully.

In order to prove the existence of tertiary amine group, TDMACMKR compound produced was investigated by ^{1}HNMR spectroscopy. The ^{1}HNMR spectra of TDMACMKR (Fig. 3) shows the existence of tertiary amine groups at singlet peaks of δ 2.1 dan 3.8 ppm each derived from 8 –CH_3 and 4 –CH_2-groups of N,N-dimethylamine group substituting H from CMKR. This indication was supported with the absence of proton peak at ortho position from hydroxyl group at around δ 6.0 ppm. These facts were supported with appearing peaks at δ 4.5 ppm indicating methine proton. These results are consistent with that obtained by Sardjono [12].

3.2. Influence of TDMACMKR on $CaCO_3$ scale formation

The effect of various concentrations of $CaCO_3$ growth solution on the amount of $CaCO_3$ precipitation can be seen in Fig. 4. This figure explains that the higher the concentration of the $CaCO_3$ growth solution, the bigger the amount of $CaCO_3$ precipitation obtained. Generally, the rate of $CaCO_3$ precipitation in the beginning of growth is fast and it will be relatively constant after 60 min. This obtained result is similar with the result found by Suharso et al., on the effect of Gambier extracts upon $CaCO_3$ scale formation [7].

The effect of various concentrations of TDMACMKR addition on the precipitation of $CaCO_3$ at various $CaCO_3$ growth solutions with 100 mg of $CaCO_3$ crystal seed added into growth solution can be seen in Figs. 5–7. From Figs. 5–7, it can be stated that the higher the amount of TDMACMKR (inhibitor) added, the bigger the inhibition of $CaCO_3$ precipitation over the concentration range investigated. The addition of 75 ppm of TDMACMKR in the $CaCO_3$ growth solution of 0.1 M will dramatically inhibit the growth rate of $CaCO_3$ precipitation (Fig. 5). In addition, the ability of inhibitor to inhibit the $CaCO_3$ precipitation decreases while the growth solution of $CaCO_3$ is increased from 0.1–0.6 M. The result obtained in this research can be compared to the results found by Suharso et al., on $CaCO_3$ precipitation using green inhibitor and Jones et al., [7,10] on inorganic materials using additive from calix [4] arene with the functional groups from aspartic and glutamic acid [21]. These results are also comparable to those observed for the calcium carbonate precipitation in the addition of metallocene complexes [22], green inhibitors [7,23], calixarene [24], and several inhibitors produced by industry [25].

Inhibitor effectiveness is one of parameters to investigate the ability of inhibitor to inhibit $CaCO_3$ precipitation. In this study, the value of inhibitor effectiveness (%) may be calculated based on modification of Eq. (1). Calculating data of the inhibitor effectiveness value are listed in Tables 1–3. From these tables, it can be observed that the inhibitor effectiveness to inhibit the $CaCO_3$ precipitation is around 57–94% for the growth solution of 0.1 M, 48–73% for the growth solution of 0.3 M, and 38–58% for the growth solution of 0.6 M, respectively. It is showed that the inhibitor effectiveness to inhibit the $CaCO_3$ precipitation decreases, while the growth solution concentration increases (Tables 1–3). These facts show that the growth rate of $CaCO_3$ crys-

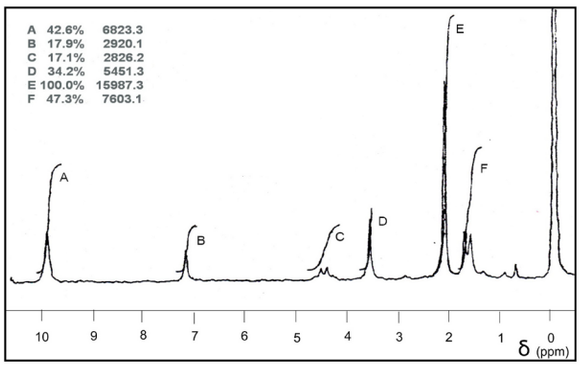

Fig. 3. ^{1}HNMR spectra of TDMACMKR.

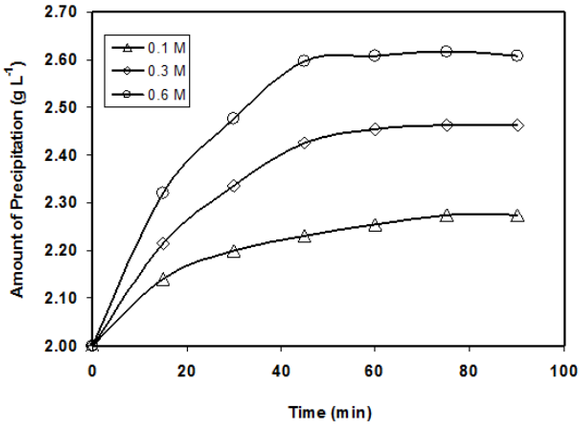

Fig. 4. The effect of various concentrations of growth solution on the precipitation of $CaCO_3$ with 100 mg of $CaCO_3$ crystal seed.

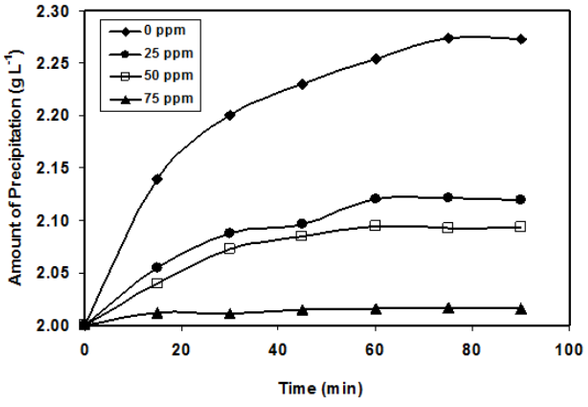

Fig. 5. The effect of TDMACMKR addition on the precipitation of $CaCO_3$ at a growth solution of 0.1 M.

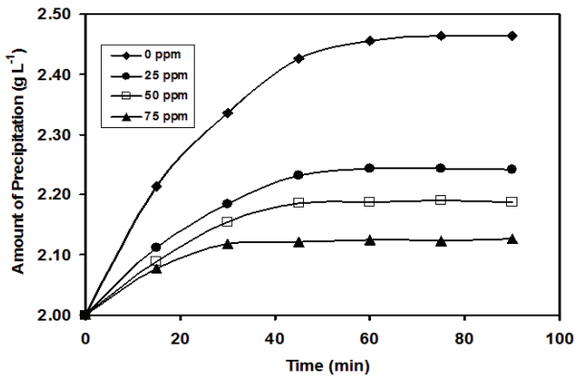

Fig. 6. The effect of TDMACMKR addition on the precipitation of $CaCO_3$ at a growth solution of 0.3 M.

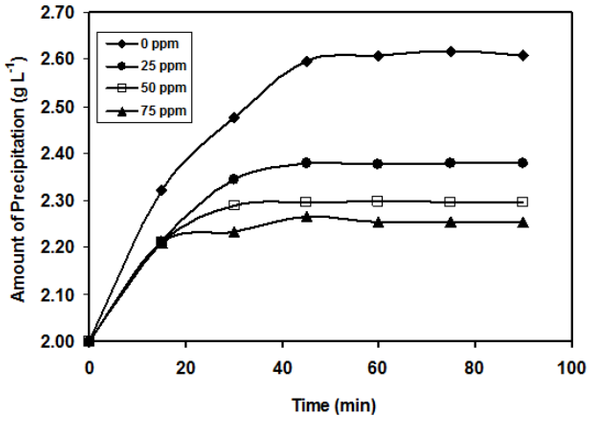

Fig. 7. The effect of TDMACMKR addition on the precipitation of $CaCO_3$ at a growth solution of 0.6 M.

tallization at the higher growth solution concentration will grow faster causing decreasing of inhibitor ability to inhibit the $CaCO_3$ precipitation or to react with Ca^{2+} ions and active sites on the crystal surface of $CaCO_3$. It can be stated that the concentration change of the growth solution affects the interaction competition among inhibitor, CO_3^{2-}, and Ca^{2+} ions in the growth solution. Therefore, in the higher growth solution concentration and at the same concentration inhibitor added (Tables 1–3), the interaction between the inhibitor and Ca^{2+} ions in the growth solution will run slower than the interaction between CO_3^{2-} and Ca^{2+} ions to form $CaCO_3$ crystal causing decreasing of the inhibitor effectiveness (%). Generally, in the growth solution concentration range studied, TDMACMKR are able to inhibit formation of $CaCO_3$ scale with the most effective (94%) of TDMACMKR concentration of 75 ppm for $CaCO_3$ growth solution of 0.1 M. The inhibitor effectiveness (%) of these results can be compared with (Table 4) the results of calcium carbonate crystal growth inhibition with addition of homopolymer of polymaleic acid (PMA-1), terpolymer of polymaleic acid (PMA-2), copolymer of polymaleic acid (PMA-3), polycarboxylic acid (EM), Polyacrylate (PAA), and Phosphonate [20]. The addition of these inhibitors derived from polyma-

Table 1
TDMACMKR effectiveness in inhibiting $CaCO_3$ scale formation on the $CaCO_3$ growth solution concentration of 0.1 M

Inhibitor concentration (ppm)	Inhibitor effectiveness (%)
0	0
25	57
50	66
75	94

Table 2
TDMACMKR effectiveness in inhibiting $CaCO_3$ scale formation on the $CaCO_3$ growth solution concentration of 0.3 M

Inhibitor concentration (ppm)	Inhibitor effectiveness (%)
0	0
25	48
50	60
75	73

Table 3
TDMACMKR effectiveness in inhibiting $CaCO_3$ scale formation on the $CaCO_3$ growth solution concentration of 0.6 M

Inhibitor concentration (ppm)	Inhibitor effectiveness (%)
0	0
25	38
50	51
75	58

Table 4
Inhibitor effectiveness in inhibiting $CaCO_3$ crystal of different inhibitors, experiment methods, and growth solution concentrations

Name of inhibitors	Inhibitor concentration (ppm)	Inhibitor effectiveness (%)	References
TDMACMKR	25–75	38–94	This work
Gambier extracts	50–250	60–100	[7]
Homopolymer of polymaleic acid	4	67	[20]
Terpolymer of polymaleic acid	4	73	[20]
Copolymer of polymaleic acid	4	18	[20]
Polycarboxylic acid	4	70	[20]
Metallocene complexes	10	27–66	[22]
Polymaleic acid	1–4	20–100	[23]
C-methyl-4, 10, 16, 22-tetrametoxy calix [4]arene	10–100	34–100	[24]

leic acid polycarboxylic acid, polyacrylate, and phosphonate groups on the calcium carbonate crystal growth gave the inhibitor effectiveness (%) around 10–70% [20].

SEM images of $CaCO_3$ crystals in the absence and presence of TDMACMKR at the growth solution of 0.1 and 0.6 M were displayed in Figs. 8 and 9. These images prove that the addition of TDMACMKR in the growth solution of $CaCO_3$ can inhibit growth rate of $CaCO_3$ crystals. The size of $CaCO_3$ crystal morphology under presence of TDMACMKR gives smaller crystal size than in the absence of TDMACMKR. At the growth solution concentration of 0.1 M, the addition of TDMACMKR changes dramatically the morphology of $CaCO_3$ crystals (Fig. 8). Crystals grown in the absence of the inhibitor (control samples) corresponding to calcite phase ($CaCO_3$ crystals) were always regular shaped rhombohedra (Figs. 8a and 9a) [9]. However, the regular shaped rhombohedrons disappeared when TDMACMKR added into the growth solution of 0.1 M (Fig. 8b) or the morphologies of the precipitates changed from the cube portion into a spherical shape. The change of morphology can be caused by interaction of inhibitor and the active sites on the surface of the crystals. The interaction between amine group from TDMACMKR and the active sites of the crystal surface change the stereochemical orientation of $CaCO_3$ growth [26], and thus the stereochemical orientation of $CaCO_3$ growth was modified. The irregular spherical shaped morphology was gained. But in the higher growth solution concentration (0.6 M), the inhibitor could not change the morphology of the crystals because the growth solution concentration affects the ability of inhibitor to change the morphology of the crystal. It is assumed that in the higher growth solution concentration (0.6 M) resulting faster growth rate of $CaCO_3$ crystal, the inhibitor adsorbs whole of the surface of the crystal so that the inhibitor can inhibit of crystal growth but it cannot alter the morphology of $CaCO_3$ crystal. As the comparison of these results, generally the bigger the concentration of the inhibitor added the smaller the particle size resulted, however, there may be exceptions and this is best to observed this explicitly [27,28]. For instance, commonly as the growth solution raises particle size decreases but this does not occur with lactose crystal [29]. The changes in morphology are able to provide an indication as to which crystal faces are preferentially adsorbing the inhibitor, as such faces are going to grow more slowly and become more dominant in the producing morphology [28]. But in the case in Fig. 9, the inhibitor does not dominate in adsorbing one

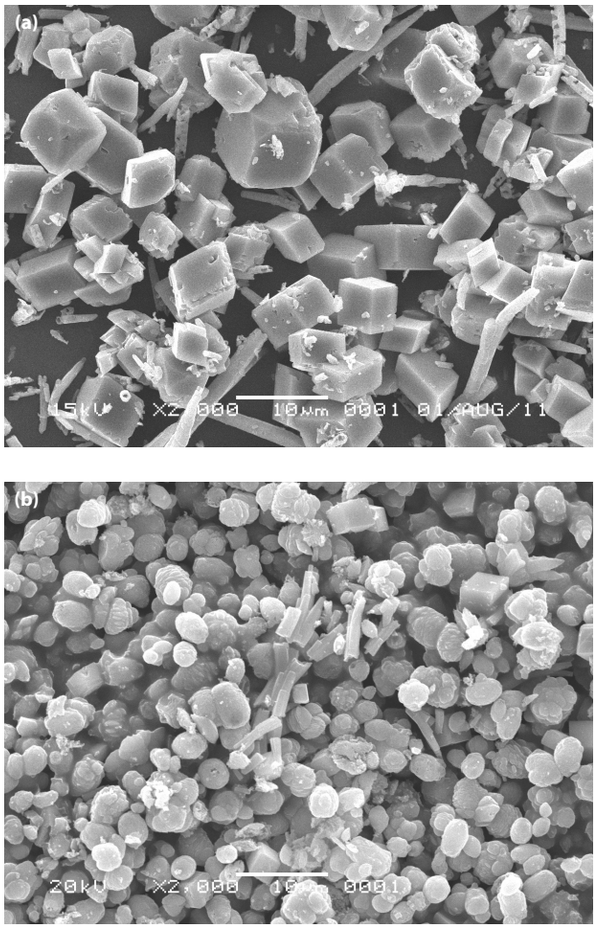

Fig. 8. SEM Images of $CaCO_3$ crystals (a) in the absence of the inhibitor (b) in the presence of 75 ppm of TDMACMKR at a growth solution of 0.1 M.

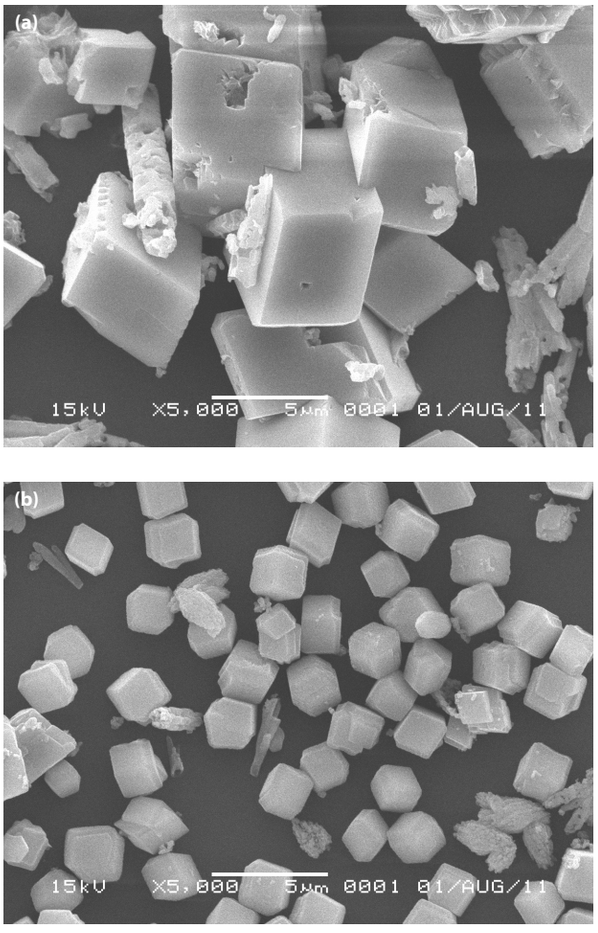

Fig. 9. SEM Images of $CaCO_3$ crystals (a) in the absence of the inhibitor (b) in the presence of 75 ppm of TDMACMKR at a growth solution of 0.6 M.

or several faces of the surface crystal, therefore the morphology of $CaCO_3$ crystal does not change as in Fig. 8.

The morphology change of $CaCO_3$ crystal may be caused by the inhibitor molecules adsorbing onto the active growth sites of the crystal surface area and inhibiting the regular outgrowth of calcium carbonate crystals. The TDMACMKR as the inhibitor molecules may also play a role as a heterogeneous nucleator controlling and stabilizing the precipitating polymorph [7,30–32]. Based on the lattice distortion happens in the addition of the TDMACMKR inhibitor, and the crystal structure and morphology are then altered dramatically (Fig. 8) [1]. From Figs. 8 and 9, it can be seen clearly the changes of the morphology and the crystal size of $CaCO_3$ and it can be concluded that the inhibitor of TDMACMKR may adsorb on the calcium carbonate crystals surface. However, Fig. 9 indicates that at higher solution concentration of 0.6 M, the additive effectiveness is low. This is evident by less modification of $CaCO_3$ crystals in Fig. 9 as compared to that in Fig. 8 at the same additive dose level of 75 ppm. TDMACMKR molecules with its amine group may react with Ca^{2+} *via* an electrostatic forces or crystal nucleus of $CaCO_3$ and then affect the growth of $CaCO_3$ crystals. The amine groups on the TDMACMKR molecules may also react with the active sites on the crystal surface and thus the TDMACMKR molecules may inhibit the $CaCO_3$ crystal growth by binding the crystal nucleus. In addition, *via* the interaction between amine groups on TDMACMKR molecules and the active sites on the crystal surface of $CaCO_3$, this inhibitor may change the stereochemical orientation of $CaCO_3$ growth. This result is consistent with the result of effect of hydrolyzed polymaleic anhydride on the crystal of calcium carbonate [33].

In order to examine the ability of TDMACMKR as inhibitor to inhibit the growth rate of $CaCO_3$ crystallization as seen in Figs. 8 and 9, the particle size distribution of $CaCO_3$ crystals obtained from the experiments with and without inhibitor added was examined by the particle size analyzer. The addition of inhibitor into the growth solution of the $CaCO_3$ precipitation should result a smaller particle size distribution of the crystal diameter than in the absence of inhibitor. Figs. 10 and 11 show the particle size distribution of $CaCO_3$ crystals in the absence and presence of 75 ppm of TDMACMKR at the growth solution of 0.1 and 0.6 M. In the growth solution of 0.1 M, the average particle size distribution of $CaCO_3$ without inhibitor is 9.15 μm and the average particle size distribution of $CaCO_3$ with inhibitor TDMACMKR decrease to be 6.12 μm. With the similar result, the mean of particle size distribution of $CaCO_3$ without inhibitor in the growth solution of 0.6 M is 14.30 μm and the mean of the particle size distribution of $CaCO_3$ with inhibitor TDMACMKR occurs decreasing to be 11.16 μm. These data obtained support the data gained from the SEM images showing $CaCO_3$ crystal size with the addition of TDMACMKR smaller than without TDMACMKR. It is also evident that TDMACMKR works as inhibitor of the $CaCO_3$ precipitation. Therefore, these results are in good agreement with those obtained by SEM. These data found show that TDMACMKR is able to play a role as inhibitor of the $CaCO_3$ precipitation under these experiment conditions. The data of the particle size distribution of $CaCO_3$ crystals obtained can be compared with the previous result using Gambier extract as inhibitor of $CaCO_3$ crystallization showing a similar trend with this study [7,34].

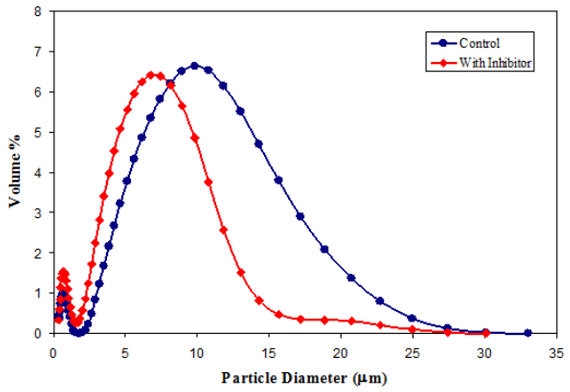

Fig. 10. Particle size distribution of $CaCO_3$ crystals in the absence and presence of 75 ppm of TDMACMKR at the growth solution of 0.1 M.

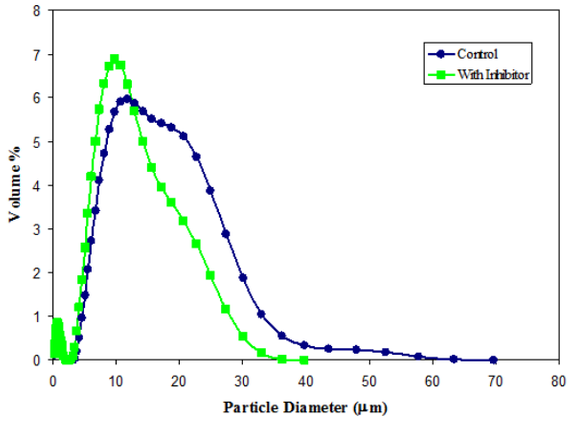

Fig. 11. Particle size distribution of $CaCO_3$ crystals in the absence and presence of 75 ppm of TDMACMKR at the growth solution.

4. Conclusions

The TDMACMKR can act as an inhibitor of the $CaCO_3$ precipitation under these operation conditions. The presence of TDMACMKR in the growth solution of 0.1 M can change significantly the morphology and size of the $CaCO_3$ crystal. But, the presence of TDMACMKR in the growth solution of 0.6 M does not change the morphology of the $CaCO_3$ crystal. The inhibitor effectiveness to inhibit the $CaCO_3$ precipitation is around 38–94% depending on the growth solution concentration and the inhibitor concentration added.

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