



## CHAPTER III

### Foaming Property of Mixed Surfactants in the Presence of Sodium Soaps and Water Hardness

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#### ABSTRACT

This work studied the effect of ions present as hardness in tap water, *i.e.* calcium, magnesium, hydrogen carbonate and hydrogen sulfate ions, on the foaming property of three surfactant systems. The first system consisted of sodium dodecyl sulfate and coconut oil sodium soap. In the second system, a nonionic surfactant ( $C_{12}$ - $C_{15}$  alcohol with 7 moles of ethylene oxide) was additionally introduced to the first system. The third system consisted of all surfactants used in the second system together with an added co-surfactant (diethylene glycol mono-butyl ether). The results showed that a minute amount of hydrogen carbonate ions enhances defoaming in the presence of calcium and magnesium ions, the major components of hardness in tap water. Unexpectedly, hydrogen sulfate ions showed a foam-destabilizing effect. However, in the first and third systems, hydrogen carbonate ions have a greater defoaming effect than hydrogen sulfate ions. Among the three systems, the second system showed the highest foam stability whereas the first system showed the lowest.

**KEY WORDS:** Foam, Defoaming, Water hardness, Sodium soaps

Foam consists of two-phase media of gas and liquid with a particular structure which gas pockets are trapped in a network of thin liquid films. An essential ingredient in a liquid-based foam is surfactant. Surfactant residing at the interface is responsible for foaming tendency and foaming stability.

Foam has been in our daily life, for example, bubble baths, dishwasher detergent foam, and the foam head on beer. In addition to its wide occurrence, foam has important properties that may be desirable in the product formulations, such as fire extinguisher, champagne and cosmetics. On the other hand, foam is undesirable in several industrial processes, for example, paper making, textile dyeing, drug manufacturing, and detergency (1).

Detergents play an important role in laundry process. Detergents do not only remove soils and stains, but also prevent them from redeposition. Usually, consumers like to see foam in all detergent products because they believe that more foam means higher efficiency of cleaning. In fact, foam has nothing to do with the detergency. Furthermore, foam may cause the soil redeposition in cleaning process. In order to satisfy the end users, detergents must possess a high flash foam in their washing step, followed by a fast foam collapse to facilitate washing action and easy to be rinsed off.

Hence, foam controlling is very crucial in fabric washing processes. The additives to control or eliminate foam are known variously as defoamer, antifoaming agent, foam inhibitor, and foam controller. Technically, defoamer means a substance that breaks the pre-existing foam, while the antifoam or foam inhibitor is a material that prevents foam formation.

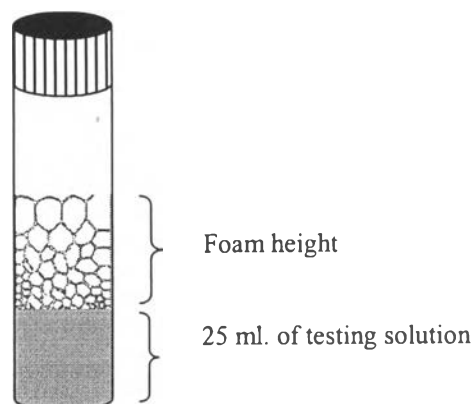
Soaps, the sodium salts of long chain carboxylic acids are traditionally main constituents as an antifoaming agent in many cleaning agents (2). An important characteristic of soaps is their tendency to precipitate in hard water (3). It has been proposed that the soap precipitate or solid calcium soaps are formed and destabilize foam film, due to their inflexible nature (4). Nevertheless, this mechanism is not universally accepted. Another mechanism proposed by Pugh and colleague, they claimed that some hydrophobic particles which are present in the system possibly cause foam rupture by dewetting mechanism (5).

The aim of this work is to study the effect of ions present as hardness in tap water on the foaming property of three surfactant systems by the shaking method. And also investigate the defoaming mechanism.

## EXPERIMENTAL PROCEDURES

*Materials.* The surfactants that used in this work consisted of three anionic surfactants and one nonionic surfactant. Anionic surfactants were Sodium dodecyl sulfate (SDS), coconut oil sodium soap and Diethylene glycol monobutyl ether (DEGMBE). SDS was obtained from Sigma Chemical Co., Ltd. (WI, USA) at a purity of at least 99% and was used without further purification. Coconut oil sodium soap was obtained from Unilever Thai Holdings, Ltd. with minimum 78% total fatty acid. DEGMBE was obtained from Carlo Erba (Milano, Italy) with purity greater than 99% and was used as co-surfactant. A nonionic surfactant, the synthetic of 12-15 carbon chain length detergent alcohol condensed with 7 moles of ethylene oxide was obtained from Huntsman Corporation Australia Pty Limited (Ascot Vale, Australia). Moreover, the materials were represented ions presenting as hardness in tap water, analytical reagent grade calcium chloride dihydrate was obtained from Scharlan Chemie S.A. (Barcelona, Spain) and was used as received. Analytical reagent grade magnesium sulfate heptahydrate obtained from Carlo Erba (Milano, Italy) with a purity no less than 99.5% . Sodium hydrogen carbonate with minimum 99.7% purity was obtained from Riedel-dettaen (Hannover, Germany) and Sodium hydrogen sulfate with minimum 99% purity was obtained from Fluka Co., Ltd. (Buchs, Switzerland).

*Method.* All experiments in this study were performed at a constant temperature of 30° C. All foaming tests were done by the shaking method. Shaking method was modified from the standard test method D3601-88. Typically, 25 ml of the testing solution was added into a 38×200 mm test tube by using pipette, and then closed with aluminium foil followed by a screw cap. The solution was placed in a water bath at 30° C for 1 hour. It was then taken out and shaken by hand 10 times in a consistent way. After that, the foam height was recorded as shown in Figure 1 and then put back to the water bath to keep the system temperature relatively constant for the whole experiments. The experiment was repeated 10 times for each testing solution.



**Figure 1.** Foam height measurement in test tube using shaking method.

The other famous technique to investigate the foaming properties, Ross-Miles method. For this study, Ross-Miles method was not suitable to observe the foaming properties because extremely high consumption of the testing solution, the large diameter of the Ross-Miles column, causing uneven foam rupture. Moreover, the behaviors of the air penetrate into the liquid is not similar to the washing action in our daily life.

## RESULTS AND DISCUSSION

The foam height of the three surfactant systems with the ions presenting as hardness in tap water was studied in this work. As shown in Table 1, the first system consisted of sodium dodecyl sulfate and coconut oil sodium soap. In the second system, a nonionic surfactant ( $C_{12}$ - $C_{15}$  alcohol with 7 moles of ethylene oxide) was added to the first system. The third system consisted of all surfactants used in the second system together with DEGMBE as a co-surfactant.

The experimental data reported in this work is the average of the data from 8 experiments selected from total 10 experiments by leaving out the maximum and minimum foam stability.

**Table 1** The surfactant ingredients in three surfactant studied systems.

<b>Surfactants</b>	<b>System 1</b>	<b>System 2</b>	<b>System 3</b>
<b>Anionic Surfactants</b>	SDS Coconut oil sodium soap	SDS Coconut oil sodium soap	SDS Coconut oil sodium soap
<b>Nonionic surfactant</b>	-	C <sub>12</sub> -C <sub>15</sub> alcohol ethoxylate	C <sub>12</sub> -C <sub>15</sub> alcohol ethoxylate
<b>Co-surfactant</b>	-	-	DEGMBE

### **Effect of bivalent cations ( $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ ) concentration on the foaming of surfactant systems in the presence of sodium soaps**

Figures 2(a), 2(b) and 2(c) show the effect of calcium ion ( $\text{Ca}^{2+}$ ) and magnesium ion ( $\text{Mg}^{2+}$ ) concentrations of 50, 150 and 300 ppm in the surfactant systems 1, 2 and 3.

#### System 1

The increasing of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration does not affect the behavior of foaming stability. Generally, for this system, the foaming stability can be divided into 3 zones. The first zone, the foam height is relatively stable from initial time to about 4 minutes and then the foam height rapidly drops in the second zone from about  $t = 4$  minutes to 14 minutes, and finally, the foam height gradually decreases from 14 to 25 minutes.

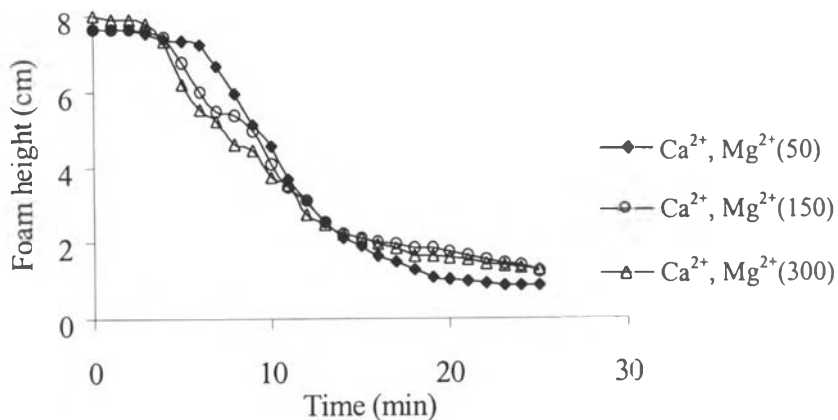
#### System 2

The foam height of the testing solution at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50 and 150 ppm is not much different. In addition, at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 50 ppm, the foam height is relatively stable which is similar as the foam height of the testing solution at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 300 ppm. However, the foam height of the testing solution at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 300 ppm is lower than the foam height of the others.

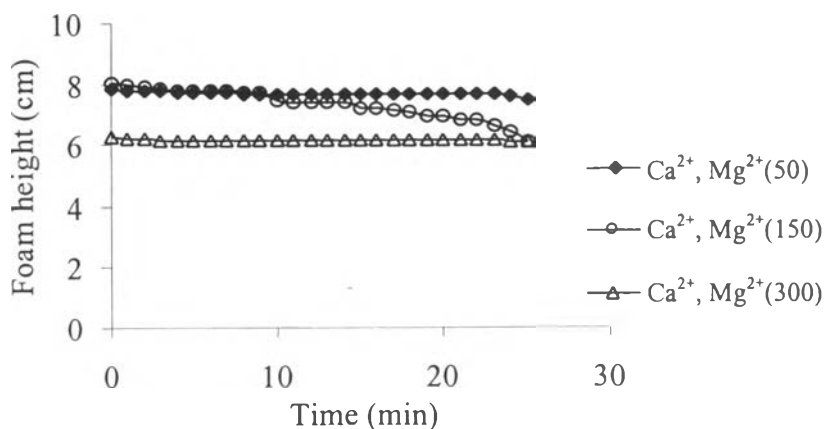
#### System 3

At  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 50 ppm, the foam height is relatively constant from the initial time to 17 minutes, after that it slightly decreases. Moreover, the foam height of the testing solutions at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 150 and 300 ppm slightly decreases for 25 minutes. For the third system, the results show that the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration has higher influence in defoaming than it has to the other systems.

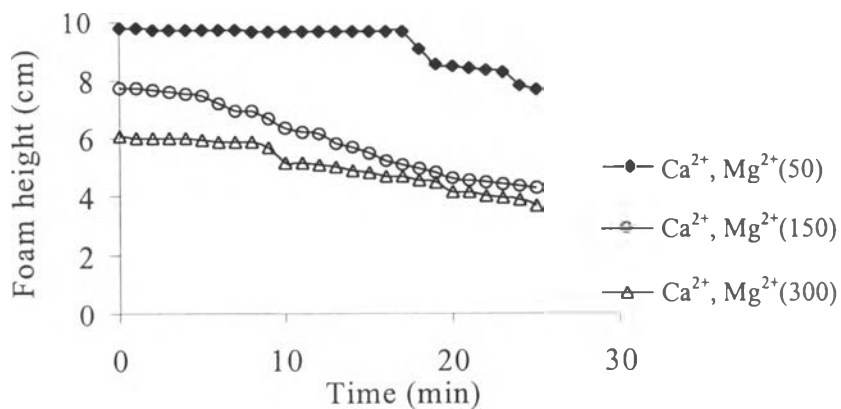
From these results, it can be observed that the foam height decreases with increasing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration. This is possibly explained by the formation of soap scum or calcium and magnesium salts of long chain fatty acids which tend to be insoluble in water and effectively remove the surfactant from the solution, leading to destabilize the foam (6).



a) The surfactant system 1



b) The surfactant system 2



c) The surfactant system 3

Figure 2. The effect of Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations at 50, 150 and 300 ppm for the surfactant systems 1, 2 and 3.

### **Effect of hydrogen carbonate ion ( $\text{HCO}_3^-$ ) concentration on the foaming of surfactant systems in the presence of bivalent cations ( $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ ) and sodium soaps**

Figures 3, 4 and 5 show the foaming stability of the testing solutions in the presence of  $\text{HCO}_3^-$  at 50 and 100 ppm and absence of  $\text{HCO}_3^-$  at the concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  50, 150 and 300 ppm of the surfactant systems 1, 2 and 3.

#### System 1

The foam height decreases with increasing  $\text{HCO}_3^-$  concentration. At  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50 and 150 ppm, the foam height of the testing solutions with and without  $\text{HCO}_3^-$  is very different. As it can be observed from the first zone of the foam height, the testing solution at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 50 ppm without  $\text{HCO}_3^-$  takes the time approximately 6 minutes, whereas the testing solutions with  $\text{HCO}_3^-$  concentration of 50 and 100 ppm take the time approximately 2 and 0 minutes, respectively. Furthermore, in the first zone of the foam height, the testing solution at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 150 ppm without  $\text{HCO}_3^-$  take the time approximately 4 minutes, whereas the testing solution with  $\text{HCO}_3^-$  concentration of 50 and 100 ppm take the time approximately 3 and 2 minutes, respectively. On the other hand, the foam heights of the testing solutions with  $\text{HCO}_3^-$  concentrations of 50 and 100 ppm are not much different. In addition, the foam heights of the testing solutions at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 300 ppm without and with  $\text{HCO}_3^-$  concentration of 50 and 100 ppm are not quite different but they are lower than the foam height at other concentrations.

#### System 2

The foam height decreases with increasing  $\text{HCO}_3^-$  concentration. The foam heights of the testing solutions at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50 and 300 ppm without and with  $\text{HCO}_3^-$  concentrations of 50 and 100 ppm are not much different. In addition, the foam height of the testing solutions at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 300 ppm is lower than other concentrations.



### System 3

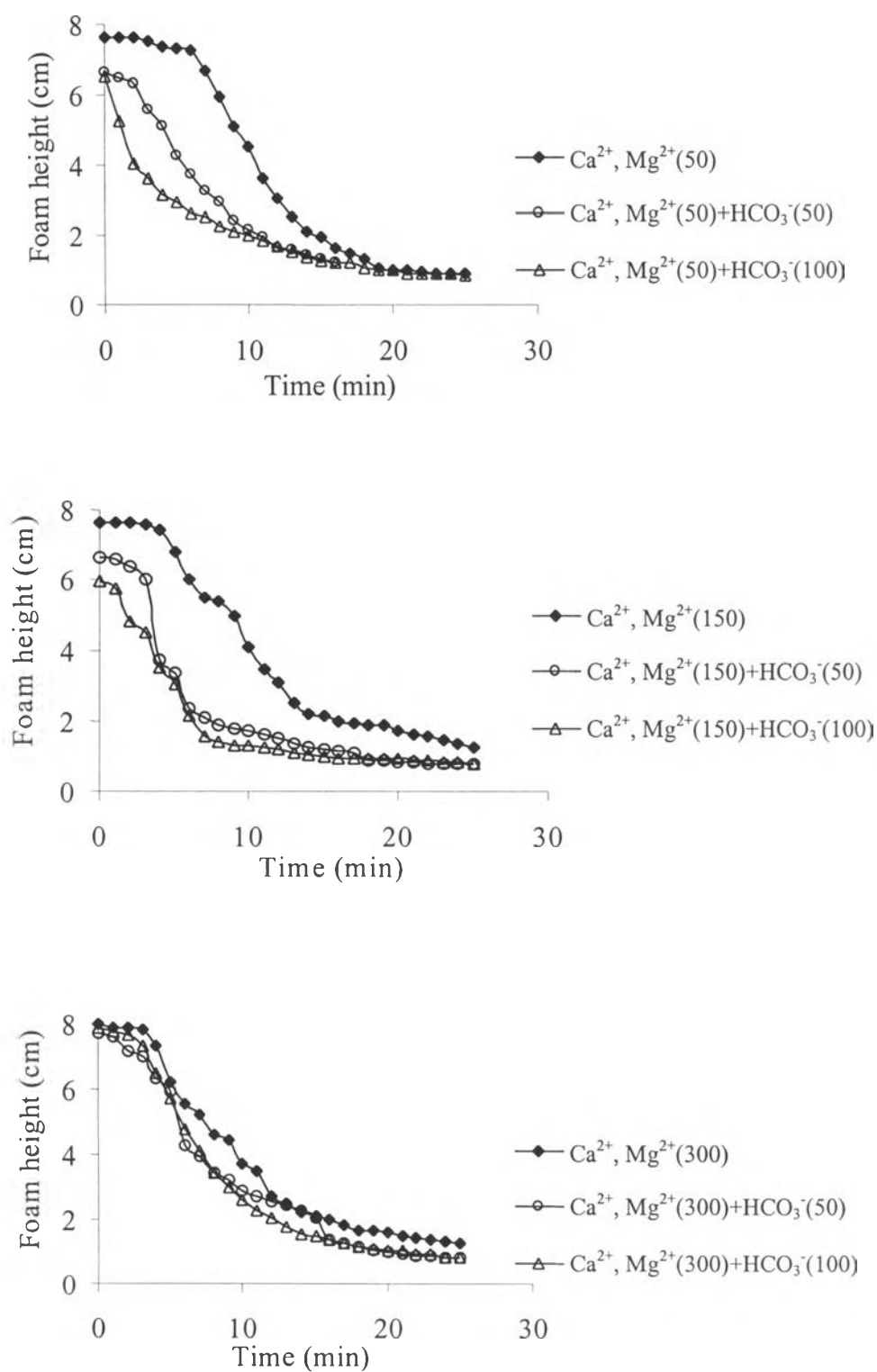
The foam height decreases with increasing  $\text{HCO}_3^-$  concentration. Particularly, at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 50 ppm, the decrease in the foam height is more pronounced than other concentrations. At  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 50 ppm without  $\text{HCO}_3^-$ , the foam height is relatively constant from the initial time to 17 minutes, after that the foam height gradually decreases. In addition, for this testing solution with  $\text{HCO}_3^-$  concentrations of 50 and 100 ppm, the foam height slightly drops together. Moreover, the foam heights of the testing solutions at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 300 ppm with  $\text{HCO}_3^-$  concentrations of 50 and 100 ppm are not much different. However, the foam height at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 300 ppm is lower than other concentrations.

The results show that the foam height decreases with increasing  $\text{HCO}_3^-$  concentration. This may be due to  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  reacting with  $\text{HCO}_3^-$  to form insoluble calcium carbonate ( $\text{CaCO}_3$ ) or magnesium carbonate ( $\text{MgCO}_3$ ) which tends to be insoluble in water, leading to foam destabilize and rupture.

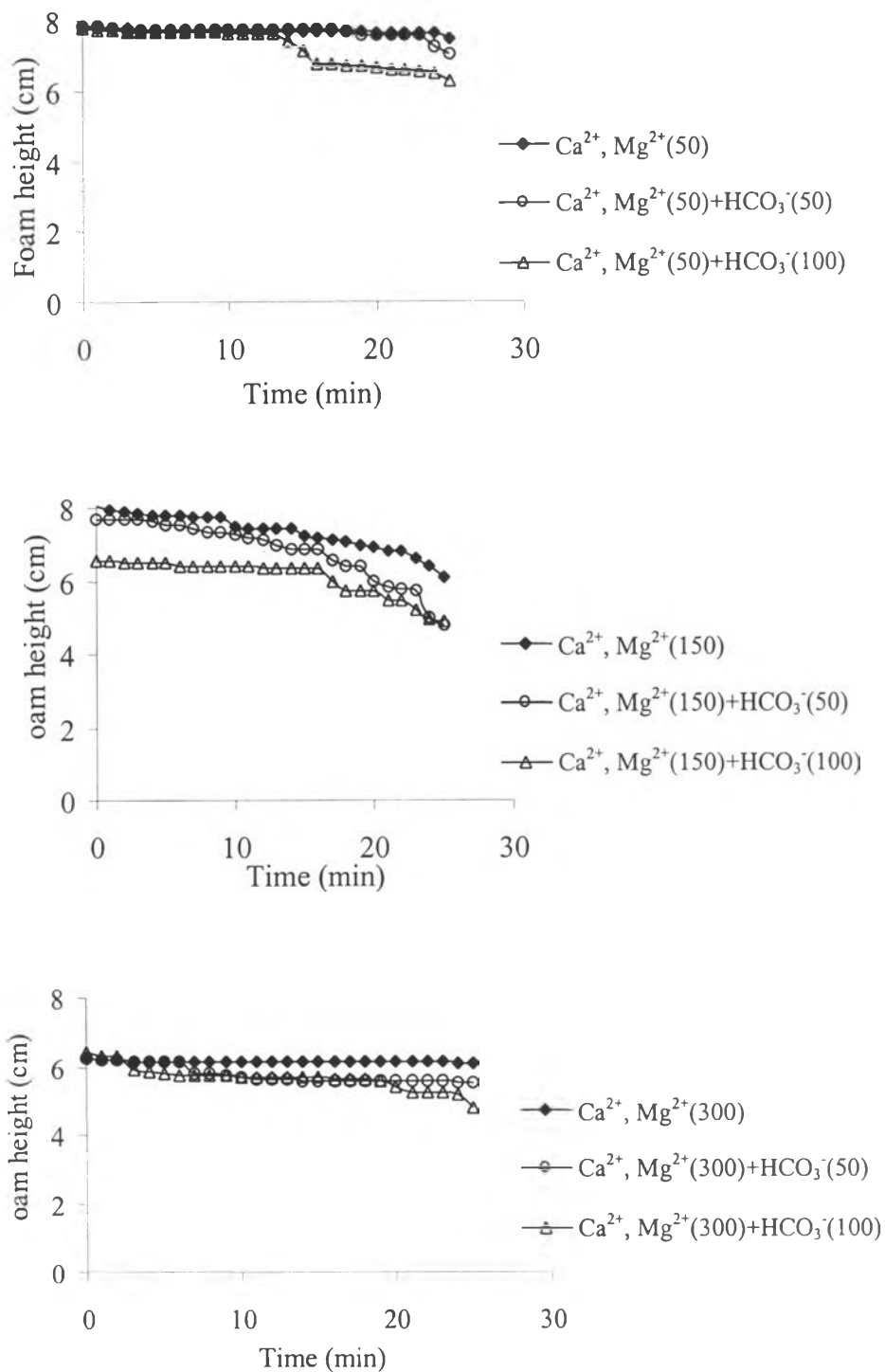
Possible reactions occurring in these systems are represented by the following equations:



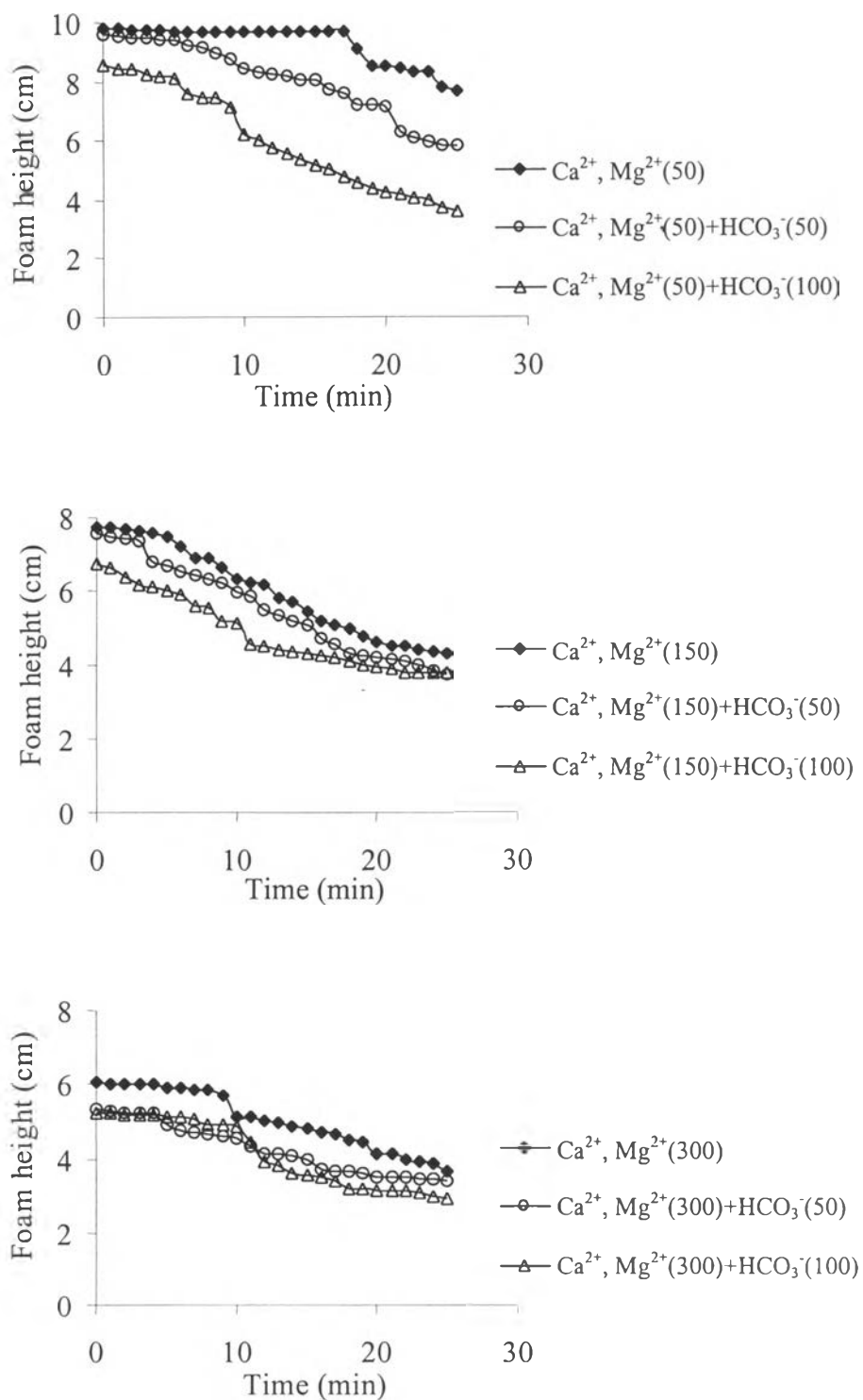
Hence, the results are possibly concluded that not only  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  but also  $\text{HCO}_3^-$  support a destabilizing effect on the foam stability.



**Figure 3.** The effect of HCO<sub>3</sub><sup>-</sup> concentration at the Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations of 50, 150 and 300 ppm for the surfactant system 1.



**Figure 4.** The effect of  $\text{HCO}_3^-$  concentration at the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50, 150 and 300 ppm for the surfactant system 2.



**Figure 5.** The effect of HCO<sub>3</sub><sup>-</sup> concentration at the Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations of 50, 150 and 300 ppm for the surfactant system 3.

### **Effect of hydrogen sulfate ion ( $\text{HSO}_4^-$ ) concentration on the foaming of surfactant systems in the presence of bivalent cations ( $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ ) and sodium soaps**

Figures 6, 7 and 8 show the change of foam height with time of the testing solutions in the presence of  $\text{HSO}_4^-$  50 and 100 ppm and in the absence of  $\text{HSO}_4^-$  at the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50, 150 and 300 ppm of the surfactant systems 1, 2 and 3.

#### System 1

The foam height decreases with increasing  $\text{HSO}_4^-$  concentration, except at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 300 ppm that shows insignificantly change of the foam height. At  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50 and 150 ppm, the difference of the foam height between the testing solutions with and without  $\text{HSO}_4^-$  is significant, but foam height of the testing solutions with  $\text{HSO}_4^-$  concentration of 50 and 100 ppm is not much different. As it can be seen from the first zone of the foam height, the testing solution at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 50 ppm take the time approximately 6 minutes, whereas the testing solution with  $\text{HSO}_4^-$  concentration of 50 and 100 ppm take time 2 and 3 minutes, respectively. Moreover, in the first zone of the foam height, the testing solution at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 150 ppm without  $\text{HCO}_3^-$  take time approximately 4 minutes, whereas the testing solution with  $\text{HCO}_3^-$  concentration of 50 and 100 ppm take the same time only 1 minute.

#### System 2

The foam height of both the testing solutions at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 150 and 300 ppm, decreases with increasing  $\text{HSO}_4^-$  concentration. Particularly, at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 150 ppm with  $\text{HSO}_4^-$  100 ppm, after 10 minutes the foam height significantly decreases. Moreover, the foam heights of the testing solutions at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 50 ppm with and without  $\text{HSO}_4^-$  are not much different.

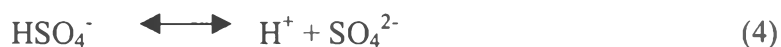
#### System 3

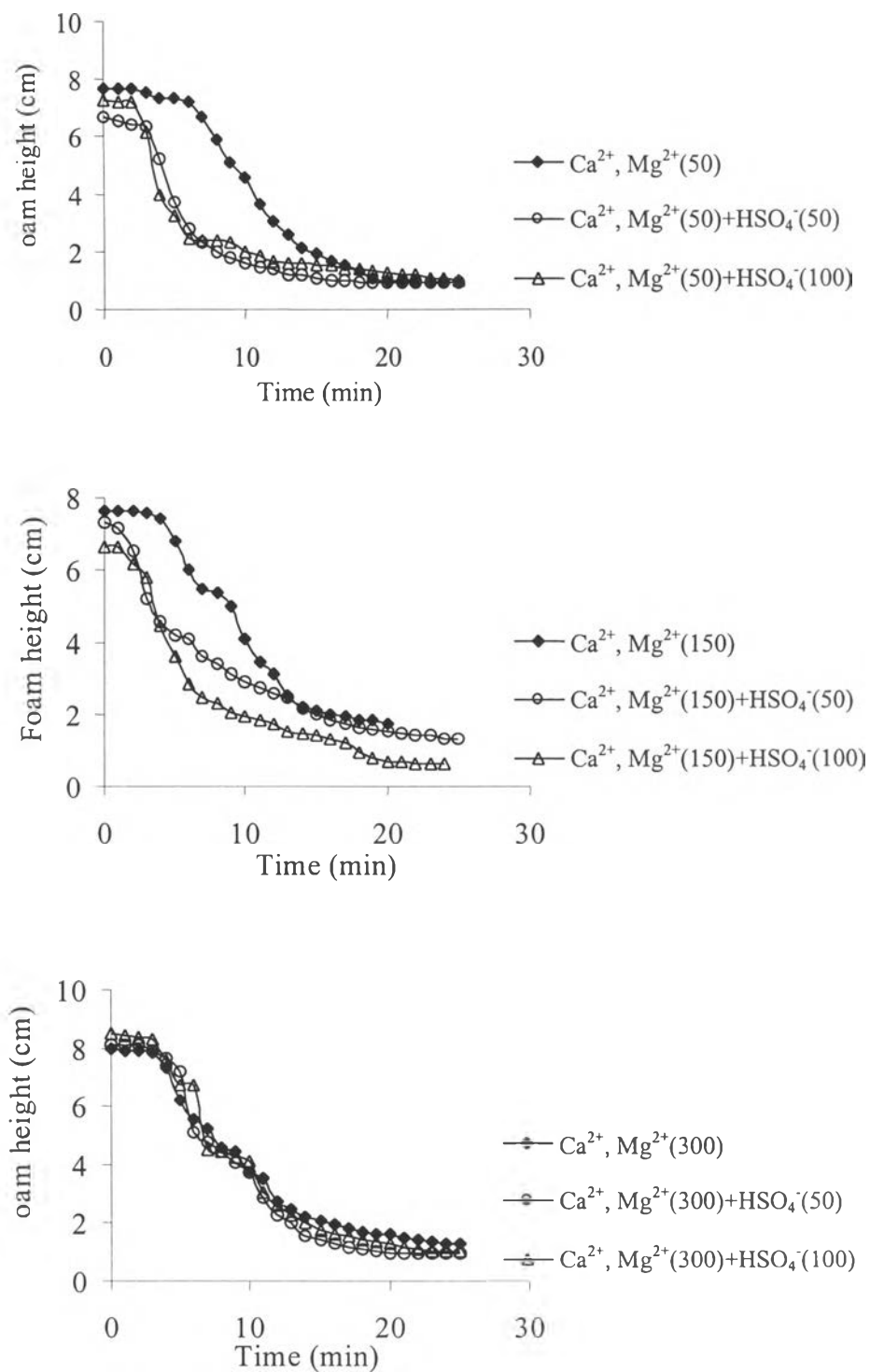
At  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50 and 150 ppm, the foam height decreases with increasing  $\text{HSO}_4^-$  concentration. The foam heights of the testing solutions at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 50 ppm with  $\text{HSO}_4^-$  concentration of 50

ppm and without  $\text{HSO}_4^-$  are not much different, whereas with  $\text{HSO}_4^-$  concentration of 100 ppm, the foam height is much lower than other concentrations. In addition, at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 150 ppm, the foam heights of the testing solutions with  $\text{HSO}_4^-$  50 and 100 ppm and without  $\text{HSO}_4^-$  are not much different. In contrast, the foam height of the testing at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 300 ppm, after 10 minutes the foam height with  $\text{HSO}_4^-$  is higher than the foam height of the testing solution without  $\text{HSO}_4^-$ .

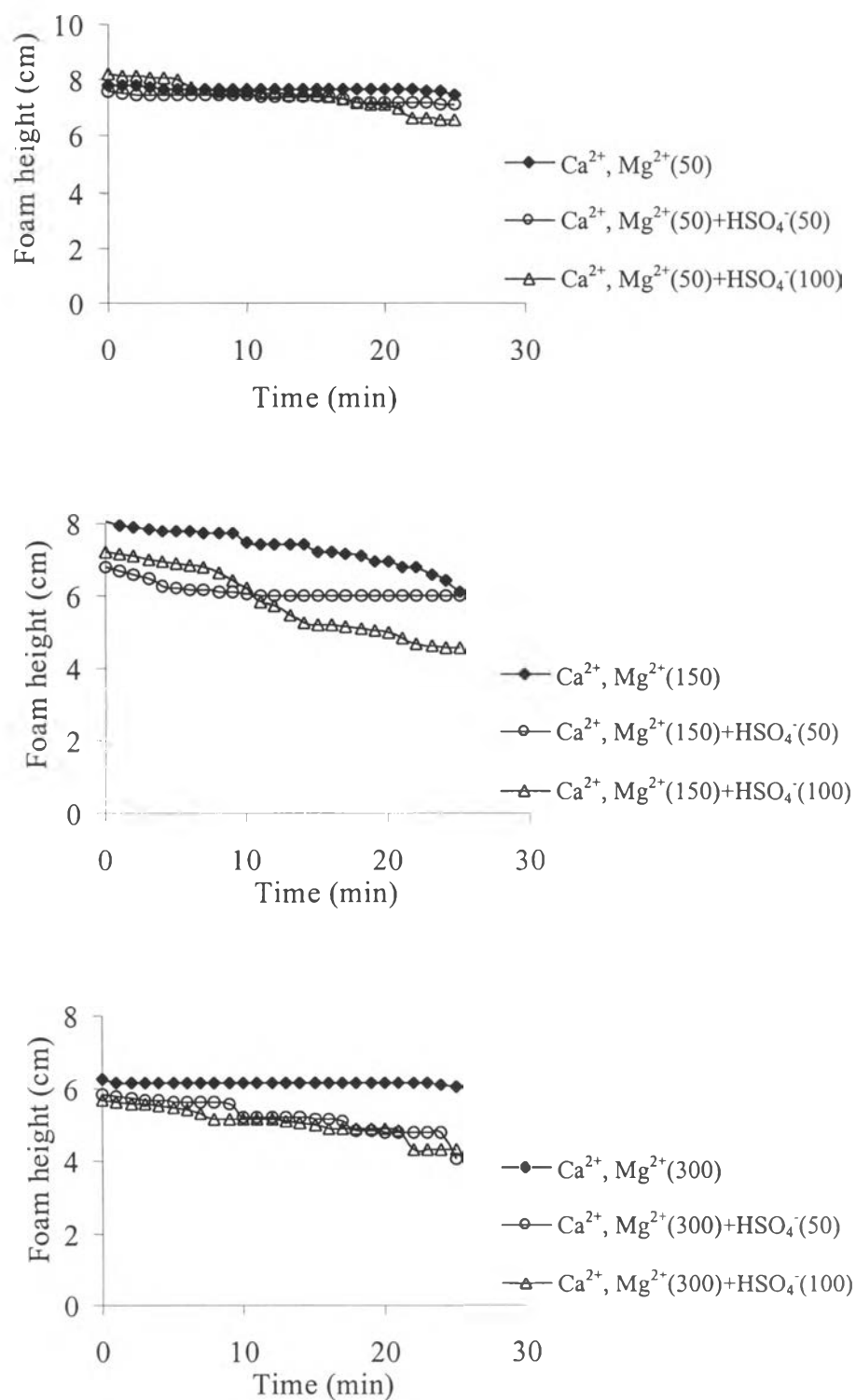
From these results, the foam height decreases with the increasing of  $\text{HSO}_4^-$  concentration. This may be because of  $\text{Ca}^{2+}$  (or  $\text{Mg}^{2+}$ ) reacts with  $\text{HSO}_4^-$  which becomes insoluble in water, leading to the inflexible film and then the foam rupture.

The possible reactions are represented by the following equations:



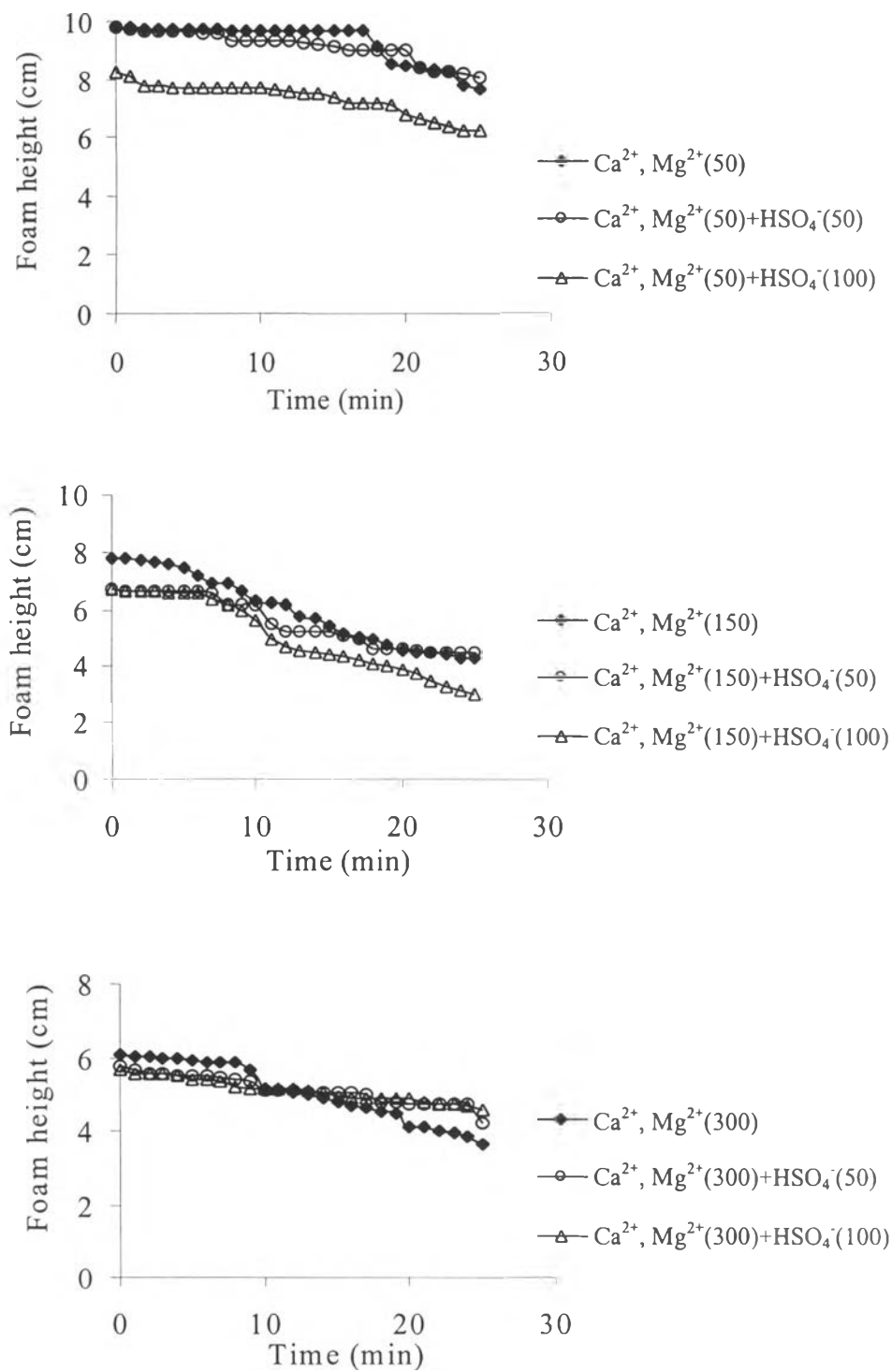


**Figure 6.** The effect of  $\text{HSO}_4^-$  concentration at the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50, 150 and 300 ppm for the surfactant system 1.



**Figure 7.** The effect of  $\text{HSO}_4^-$  concentration at the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50, 150 and 300 ppm for the surfactant system 2.





**Figure 8.** The effect of HSO<sub>4</sub><sup>-</sup> concentration at the Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations of 50, 150 and 300 ppm for the surfactant system 3.

**Comparison of the effect of hydrogen carbonate ion ( $\text{HCO}_3^-$ ) and hydrogen sulfate ion ( $\text{HSO}_4^-$ ) on the foaming of the surfactant system in the presence of bivalent cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and sodium soaps**

System 1

Figure 9 shows the change of foam height with time of the testing solutions with 50 ppm of  $\text{HCO}_3^-$  or  $\text{HSO}_4^-$  in the surfactant system 1. The results indicate that at the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 150 and 300 ppm, the foam height of the testing solution with  $\text{HCO}_3^-$  is lower than the testing solution with  $\text{HSO}_4^-$ . On the other hand, at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 50 ppm, the testing solution with  $\text{HSO}_4^-$  is lower than the testing solution with  $\text{HCO}_3^-$ .

Figure 10 shows the change of foam height with time of the testing solutions with 100 ppm of  $\text{HCO}_3^-$  or  $\text{HSO}_4^-$  in the surfactant system 1. The results indicate that the foam height of the testing solution with  $\text{HCO}_3^-$  is lower than the testing solution with  $\text{HSO}_4^-$ .

Although, the foam height of the testing solution with  $\text{HCO}_3^-$  is lower than the testing solution with  $\text{HSO}_4^-$ .

System 2

Figure 11 shows the change of foam height with time of the testing solutions with 50 ppm of  $\text{HCO}_3^-$  or  $\text{HSO}_4^-$  in the surfactant system 2. The results indicate that the foam height of the testing solution at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 150 and 300 ppm with  $\text{HSO}_4^-$  is lower than the testing solution with  $\text{HCO}_3^-$ . In addition, at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 50 ppm, the foam heights of the testing solutions with  $\text{HCO}_3^-$  or  $\text{HSO}_4^-$  are not much different.

The results in Figure 11 were confirmed by increasing the concentration of  $\text{HCO}_3^-$  or  $\text{HSO}_4^-$  to 100 ppm as shown in Figure 12. The results show that the foam height of the testing solutions with  $\text{HSO}_4^-$  is lower than the testing solution with  $\text{HCO}_3^-$ , except at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 50 ppm.

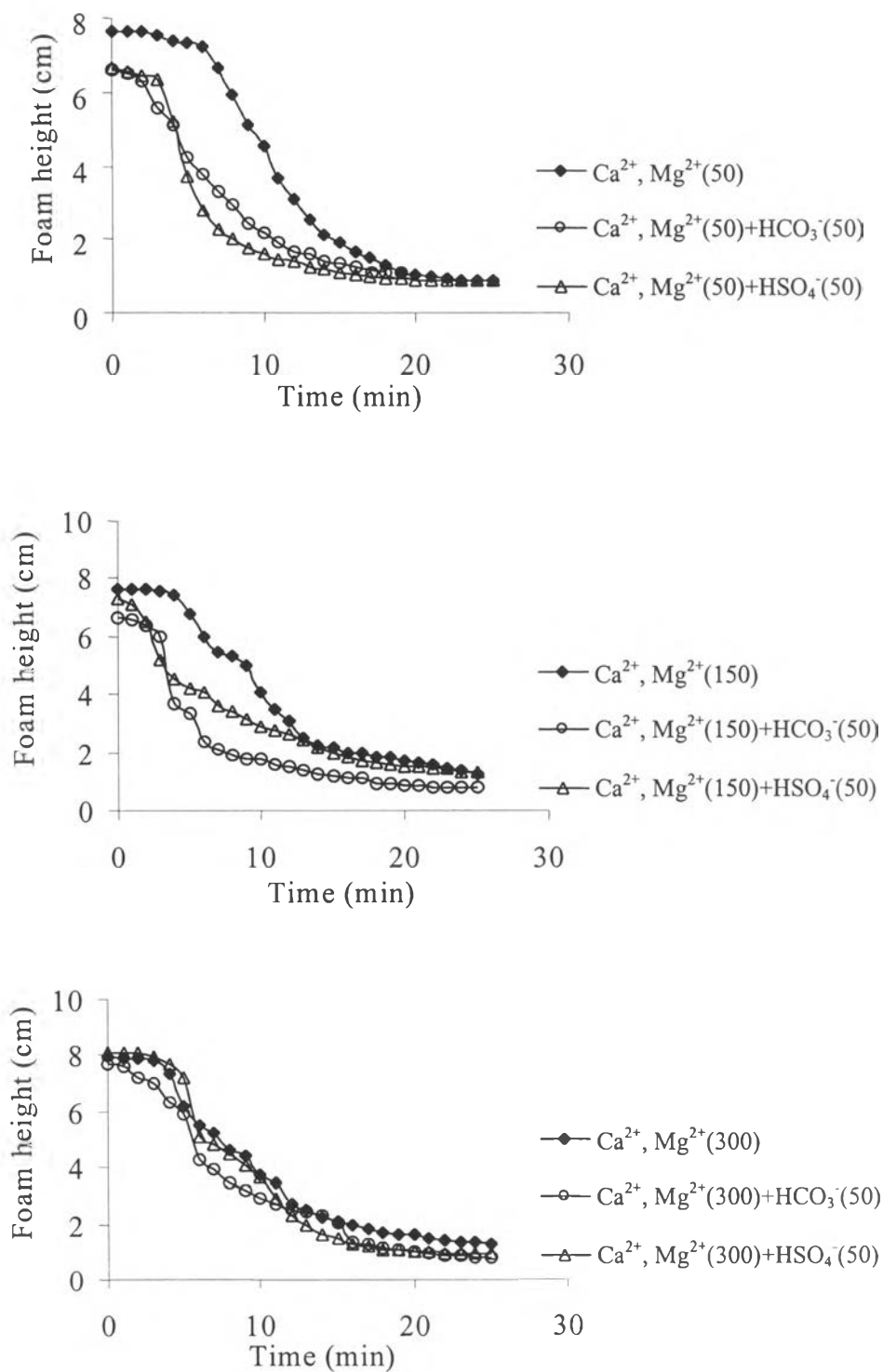
System 3

Figure 13 shows the change of foam height with time of the testing solutions with 50 ppm of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the surfactant system 3. The results indicate that the foam height of the testing solution with  $\text{HCO}_3^-$  is lower than the

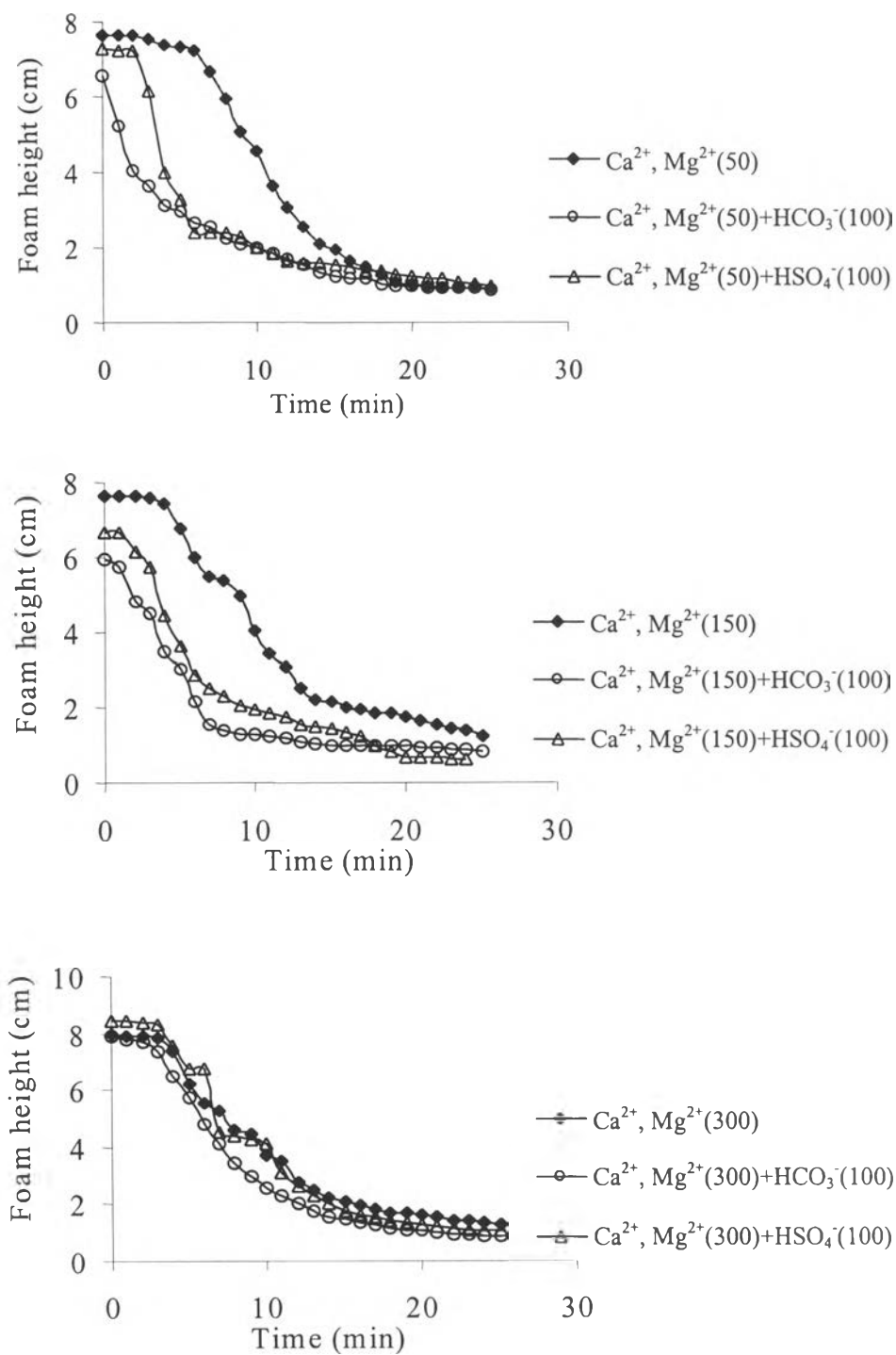
testing solution with  $\text{HSO}_4^-$ . Particularly, at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50 and 300 ppm, the effect of  $\text{HCO}_3^-$  is more pronounced than the  $\text{HSO}_4^-$ . In addition, the foam heights of the testing solutions at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 150 ppm with  $\text{HCO}_3^-$  or  $\text{HSO}_4^-$  are not much different.

Figure 14 shows the change of foam height with time of the testing solutions with 100 ppm of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the surfactant system 3. The results show that the foam height of the testing solution with  $\text{HCO}_3^-$  is lower than the testing solution with  $\text{HSO}_4^-$ . Particularly, at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50 and 300 ppm, the difference of foam heights between the testing solutions with  $\text{HCO}_3^-$  and  $\text{HSO}_4^-$  is not noticeable.

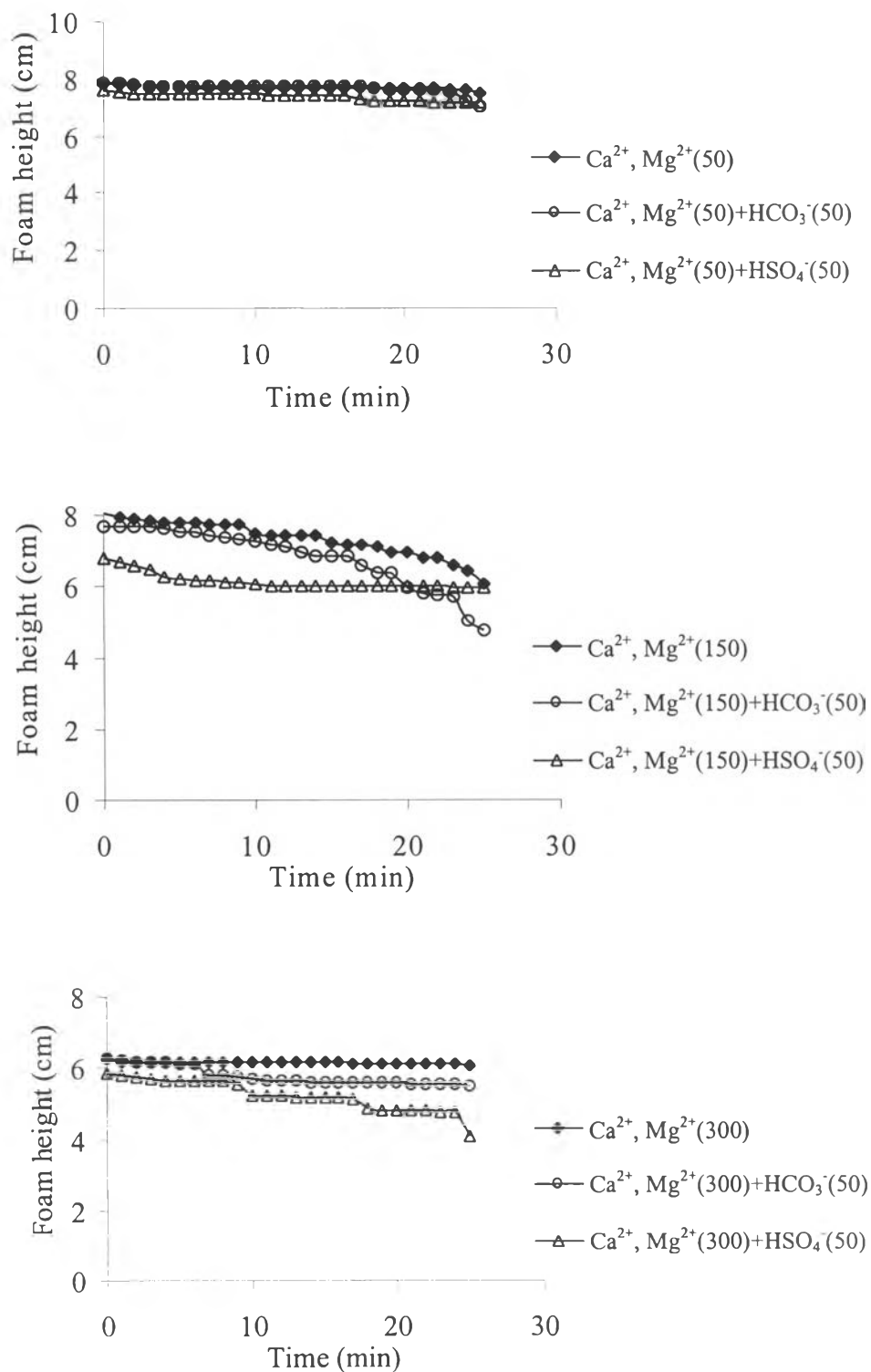
Therefore, from all of the results, it can be concluded that  $\text{HCO}_3^-$  and  $\text{HSO}_4^-$  have different defoaming effect depending on the ingredients of surfactant in each system. In the surfactant system 3, the difference of the foam height between the testing solution with  $\text{HCO}_3^-$  and  $\text{HSO}_4^-$ , is significant when compare with the system 2 and 3. This difference may be due to the effect of added co-surfactant. Therefore, it is necessary to further study of the effect of co-surfactant in the details.



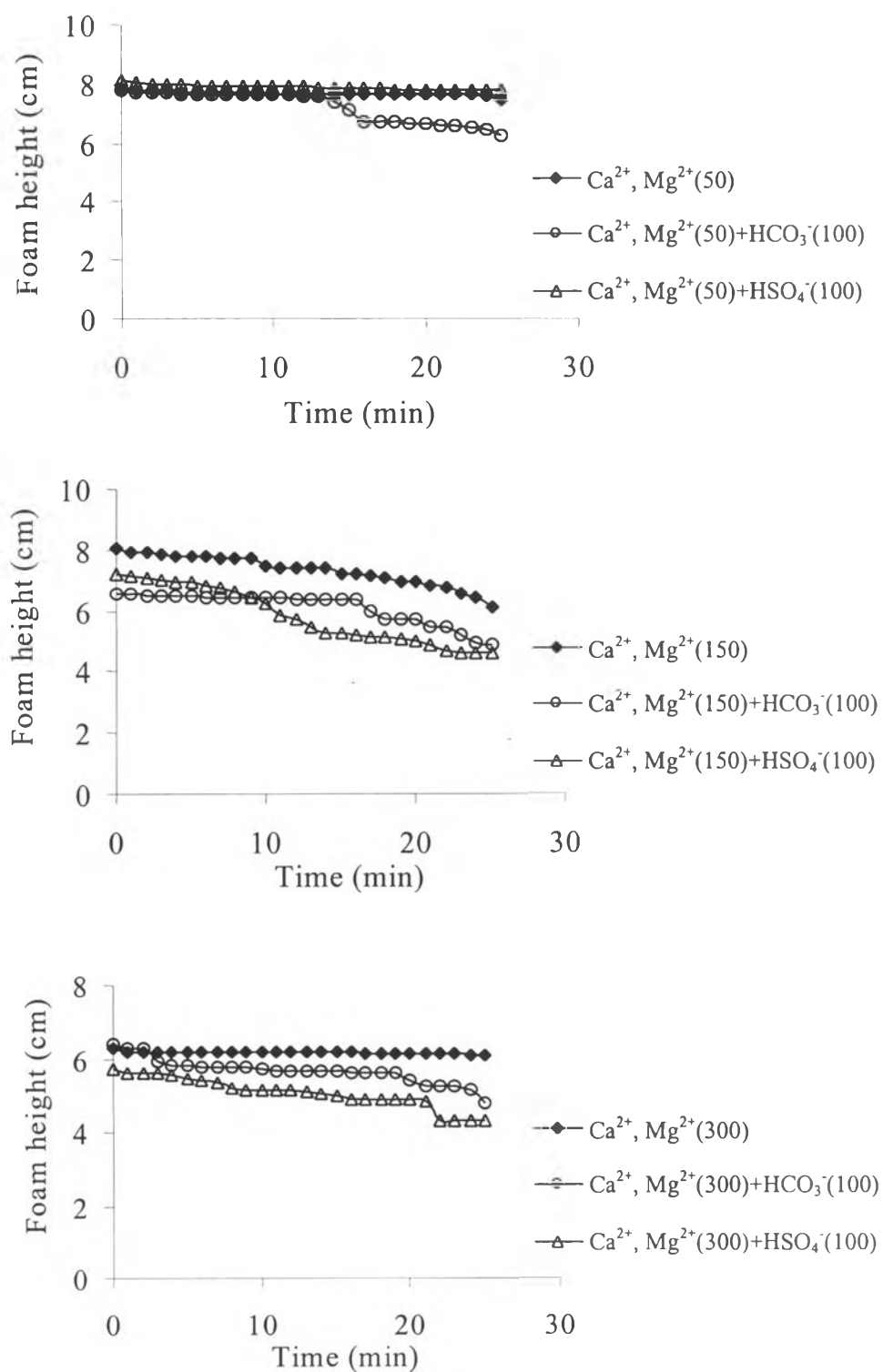
**Figure 9.** Comparison the effect of HCO<sub>3</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup> 50 ppm at the Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations of 50, 150 and 300 ppm for the surfactant system 1.



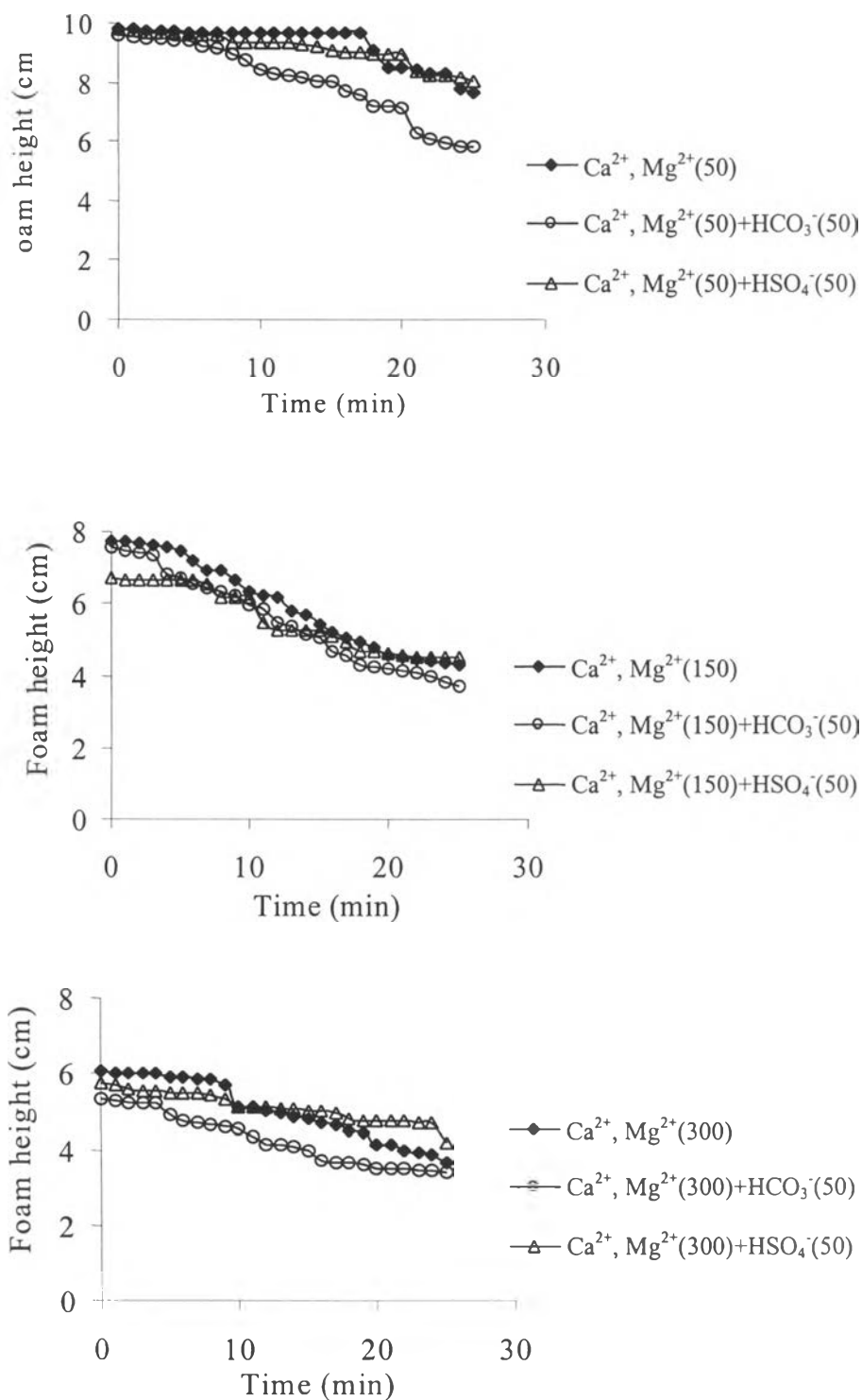
**Figure 10.** Comparison the effect of  $\text{HCO}_3^-$  and  $\text{HSO}_4^-$  100 ppm at the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50, 150 and 300 ppm for the surfactant system 1.



**Figure 11.** Comparison the effect of  $\text{HCO}_3^-$  and  $\text{HSO}_4^-$  50 ppm at the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50, 150 and 300 ppm for the surfactant system 2.

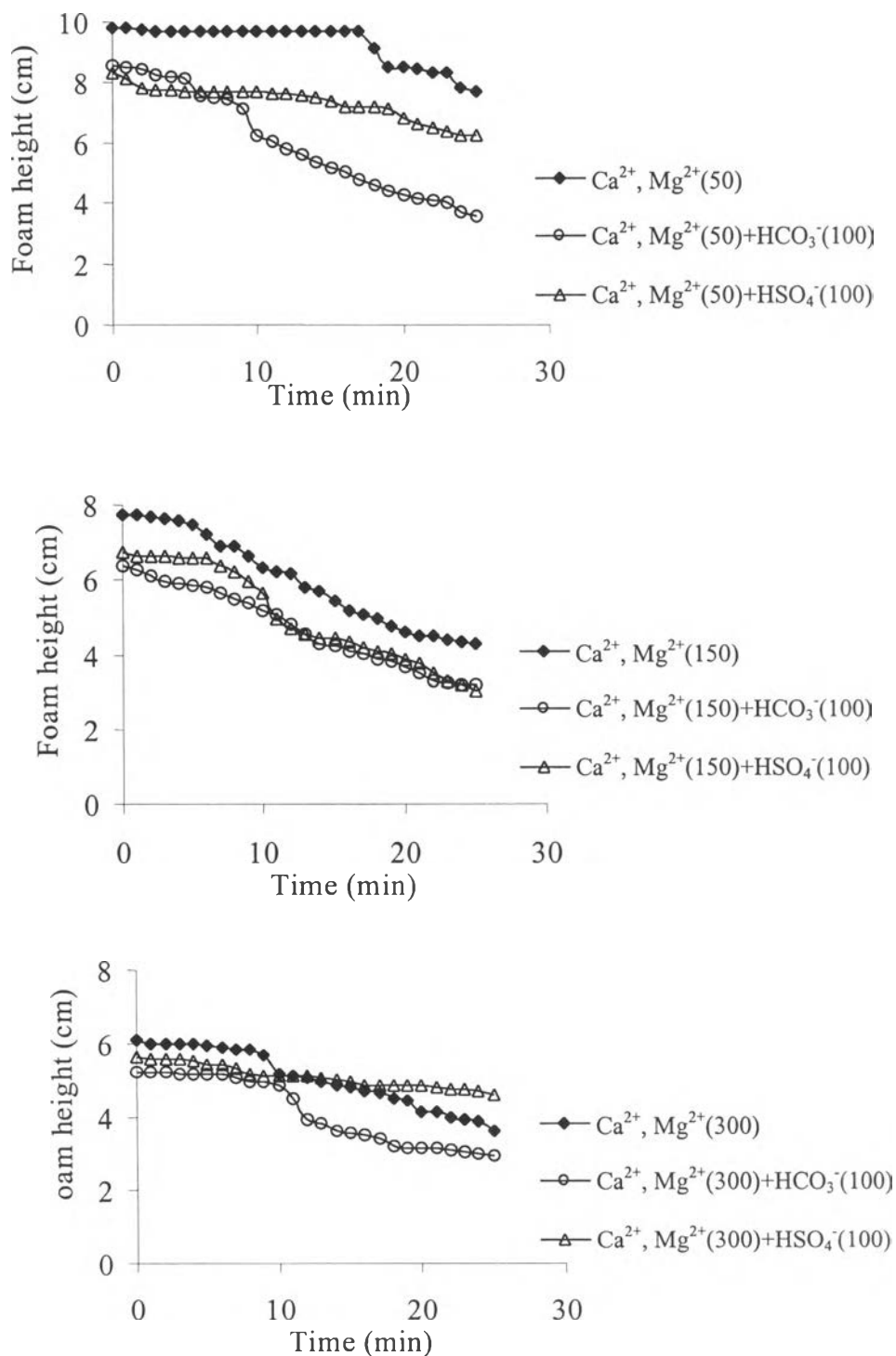


**Figure 12.** Comparison the effect of HCO<sub>3</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup> 100 ppm at the Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations of 50, 150 and 300 ppm for the surfactant system 2.



**Figure 13.** Comparison the effect of HCO<sub>3</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup> 50 ppm at the Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations of 50, 150 and 300 ppm for the surfactant system 3.





**Figure 14.** Comparison the effect of HCO<sub>3</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup> 100 ppm at the Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations of 50, 150 and 300 ppm for the surfactant system 3.

### **Comparison of the foam stability among 3 surfactant systems in the presence of bivalent cations ( $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ ) and sodium soaps**

Tables 2, 3 and 4 show the foam stability among 3 surfactant systems at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of 50, 150 and 300 ppm, respectively. In this work, foam stability can be illustrated by using the difference of foam height from initial time to 5 minutes. Therefore, the larger the difference of foam height means the lower foam stability. From these tables, it can be indicated that foam stability of the surfactant system 2 is higher than those of systems 3 and 1, respectively. However, there are some differences at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 150 ppm with  $\text{HSO}_4^-$  50 and 100 ppm and at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 300 ppm without  $\text{HCO}_3^-$  and with  $\text{HCO}_3^-$  100 ppm, in which the foam stability of the testing solution of the surfactant system 3 is higher than system 2 and 1.

In the surfactant mixtures system 2 (anionic/nonionic surfactant mixtures) and system 3 (anionic/nonionic/co-surfactant mixtures), mixed monolayer formed at the film surface increases surface viscosity due to a reduction in charge repulsion compared to the system using an anionic surfactant alone. Therefore foam stability of the surfactant systems 2 and 3 are higher than that of the surfactant system 1. Furthermore, the foam stability of the surfactant system 2 is higher than that of system 3. This may be due to the co-surfactant or DEGMBE, which is anionic surfactant forms mixed monolayer with anionic (SDS) and nonionic surfactant, leading to increase in the repulsion force of the head groups between SDS and DEGMBE. Hence, the surface viscosity is reduced, causing the foam to destabilize and rupture.

**Table 2** Comparison of the foam stability among 3 surfactant systems at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 50 ppm.

	Difference in foam height (cm)		
	System 1	System 2	System 3
Without $\text{HCO}_3^-$	0.32	0.04	0.10
$\text{HCO}_3^-$ 50 ppm	2.35	1.11	1.19
$\text{HCO}_3^-$ 100 ppm	3.60	0.11	0.45
$\text{HSO}_4^-$ 50 ppm	2.92	0.12	0.13
$\text{HSO}_4^-$ 100 ppm	4.04	0.22	0.58

**Table 3** Comparison of the foam stability among 3 surfactant systems at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 150 ppm.

	Difference in foam height (cm)		
	System 1	System 2	System 3
Without $\text{HCO}_3^-$	0.87	0.26	0.29
$\text{HCO}_3^-$ 50 ppm	3.30	0.13	0.87
$\text{HCO}_3^-$ 100 ppm	2.90	0.09	0.70
$\text{HSO}_4^-$ 50 ppm	3.10	0.55	0.05
$\text{HSO}_4^-$ 100 ppm	3.01	0.28	0.16

**Table 4** Comparison of the foam stability among 3 surfactant systems at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration of 300 ppm.

	Difference in foam height (cm)		
	System 1	System 2	System 3
Without $\text{HCO}_3^-$	1.78	1.10	0.15
$\text{HCO}_3^-$ 50 ppm	1.76	0.14	0.45
$\text{HCO}_3^-$ 100 ppm	2.16	0.60	0.08
$\text{HSO}_4^-$ 50 ppm	0.90	0.24	0.25
$\text{HSO}_4^-$ 100 ppm	1.73	0.25	0.22

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