CHAPTER IV
RESULTS AND DISCUSSION

4.1 Critical Micelle Concentration (CMC)

4.1.1 CMC of SOAP/SDS Solutions

The experimental data of all CMC measurements are given in Appendix A. The mixture CMC values for both ideal (The ideal mixed CMC values were obtained by calculating from Equation 1) and measured Soap/SDS mixture systems were plotted as a function of mole fraction of soap at different pH as shown in Fig. 4.1. According to this plot, it can be observed that the mixture CMC values exhibit a negative deviation from ideality, i.e., the values of the mixture CMC are lower than expected from the ideal mixture. A negative deviation from ideality normally occurs due to a decrease in electrostatic repulsion between the charged head groups in the micelle.

4.1.2 Effect of Calcium

The mixture CMC values for the SDS/SO system are plotted in Fig. 4.1 as a function of mole fraction of soap and in Fig. 4.2 as a function of calcium concentration. Following these plots, it can be observed that both the pure component and mixture CMC values decrease when the calcium concentration increases. The explanation of this phenomenon is that calcium acts as the counter ion to the negatively charged head groups in the micelle reducing the repulsion between the head groups. The micelles are then easier to form and hence the CMC is lowered(Scamehorn, 1986)

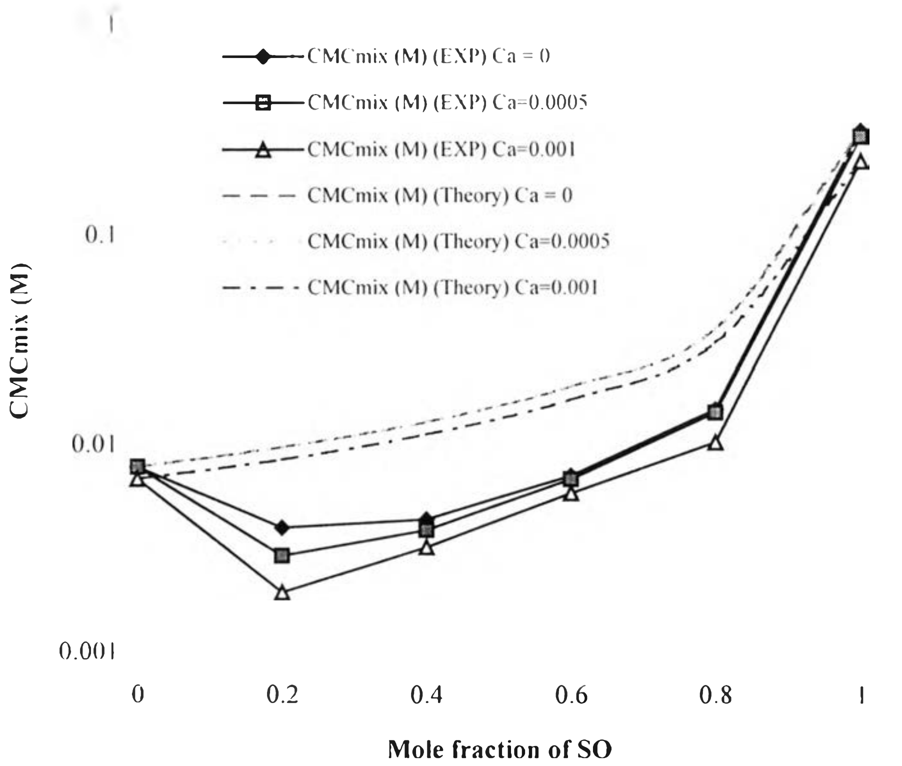


Fig.4.1 Plot between CMC of mixture system and mole fraction of soap at pH = 7, T=30 C

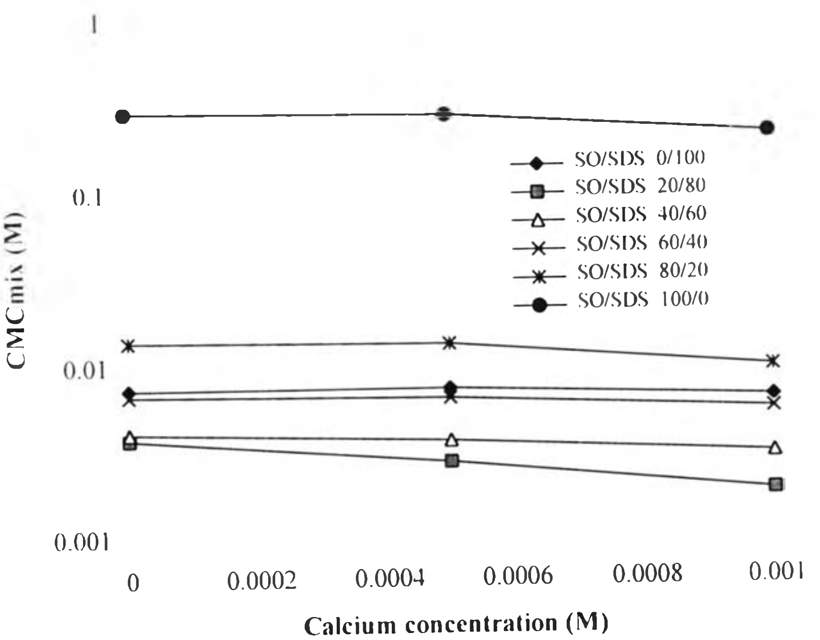


Figure 4.2 CMCmix at different calcium concentrations at pH = 7, T = 30 °C (EXP.).

4.2 Foaming of SDS, Soap and their Mixture

4.2.1 Foaming of SDS

Ross-Miles Method

Fig. 4.3 shows the foam height of SDS at t = 0 min in the concentration range of 0.00086 M to 0.0798 M with the Ross-Miles method. The concentration range covers roughly an order of magnitude below to an order of magnitude above the CMC of SDS at 0.008 M. It can be seen that at t=0 min, foam height increased with an increase in concentration and reached the maximum of 200 mm in the neighborhood of CMC. Above the CMC, foam height remained constant regardless of concentration.

At t=5 min, there was only a slight decrease in foam height throughout the whole concentration range showing that the foam stability was high.

Fig. 4.4 shows the stability index of SDS foam after 5 min. The stability index is defined as foam height at t=5 min devided by foam height at t=0 min, thus the stability index has the value in range of 0-1 and the higher the stability index, the higher the foam stability. It can be seen that foam stability of SDS at low concentration started at around 0.7, it then rose to the maximum of 1 before declining slightly beyond the CMC.

Mixing Method

The Mixing method used here was developed to roughly simulate the fairly gentle swirling motion of a solution in a top-loaded washing machine. Fig.4.5 shows the foamability of SDS solutions by the Mixing method. Similar results were obtained as in the case of the Ross-Miles tests, i.e. the foam height at t= 0 increased with concentration up to 100 mm at the CMC and remained constant after the CMC.

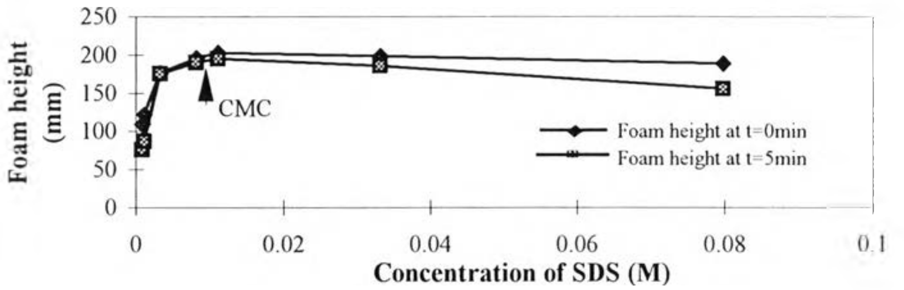


Figure 4.3 Relationship between foam height and SDS concentration by the Ross-Miles method.

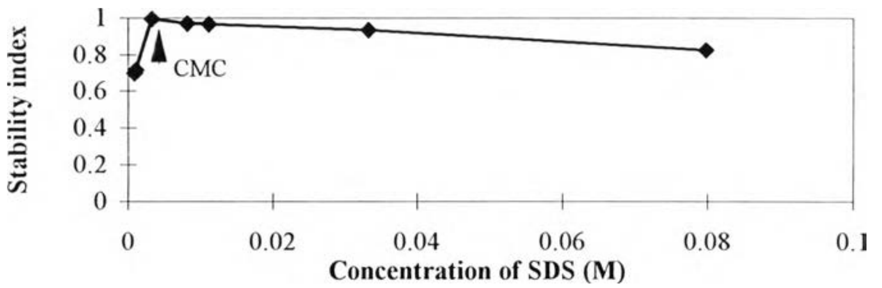


Figure 4.4 Relationship between stability index and SDS concentration by the Ross-Miles method.

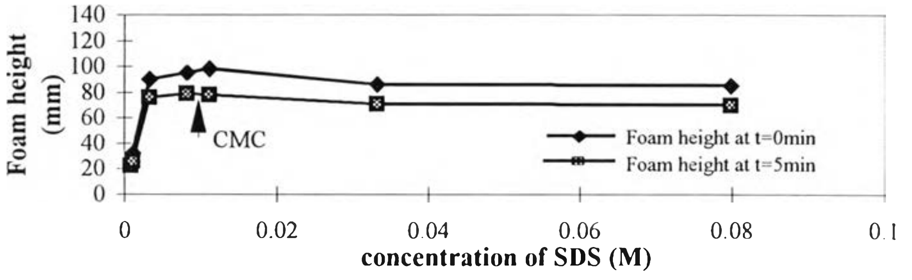


Figure 4.5 Relationship between foam height and SDS concentration by the Mixing method.

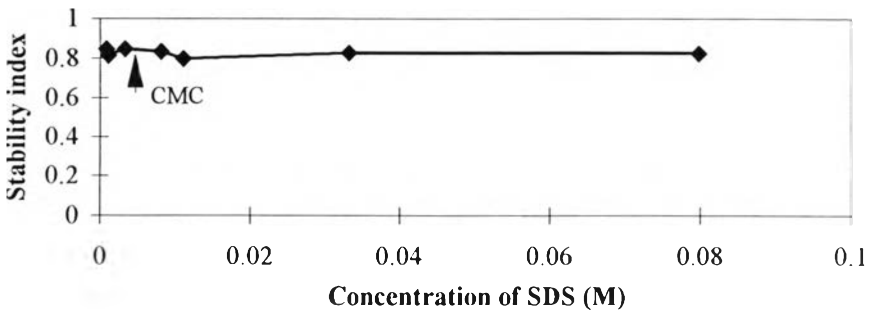


Figure 4.6 Relationship between stability index and SDS concentration by the Mixing method.

Fig.4.6 shows the stability index of SDS foam by the Mixing method. It can be seen that, unlike in the case of Ross-Mile method, the foam stability index remained high at around 0.8 throughout the whole concentration range. The results show that foam stability after 5 min was not effected by surfactant concentration in the Mixing method.

Cohen, et al.(1993) studied the foamability of LAS with the Ross-Miles method and obtained a foam height in the range of 20 - 200 mm. Using the Ross-Miles method, Weil (Rosen, 1988) gave a foam height of 220 mm for SDS around its CMC(0.0087 M) at 60 ^{O}C and a foam height at t = 5 min of 200 mm, which is consistent with the results obtained in this work. A maximum in initial foam formation is often observed around the CMC(Cohen, 1993).

4.2.2 Foaming of Soap

Fig. 4.7 shows the results of a foaming test by the Ross-Miles method for soap solutions. The results were similar to those for SDS, foam height increased with an increase in soap concentration until it reached the maximum around the CMC; after that, foam height remained relatively constant.

At t= 5 min, foam stability improves initially as soap concentration increases. There is however a dramatic decrease in foam height after 5 min above a concentration around the CMC, leading to a maximum in the stability index around the CMC as seen in Fig. 4.8.

On the other hand, as seen in Figs. 4.9 and 4.10, results from the Mixing method exhibited a plateau in foaming above the CMC initially and after 5 min and a high stability index above the CMC. A low stability index is observed below the CMC. So, low foaming and foam stability is observed in both tests below the CMC. The decrease in foam stability observed in the Ross-

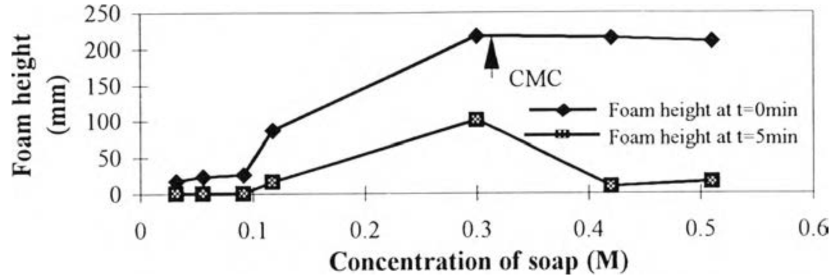


Figure 4.7 Relationship between foam height and soap concentration by the Ross-Miles method.

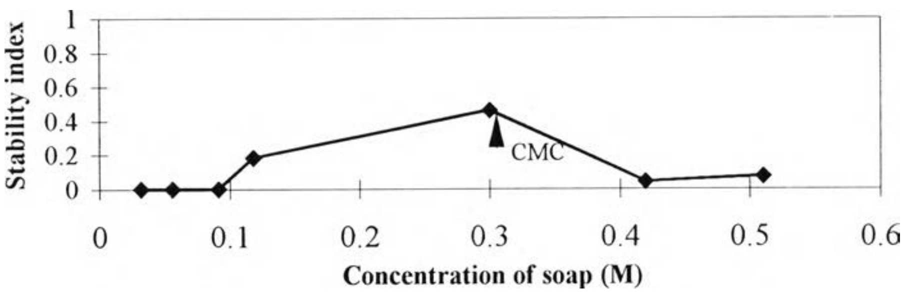


Figure 4.8 Relationship between stability index and soap concentration by the Ross-Miles method.

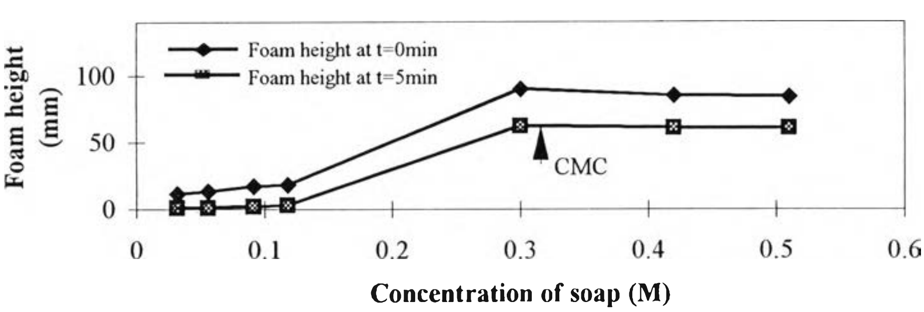


Figure 4.9 Relationship between foam height and soap concentration by the Mixing method

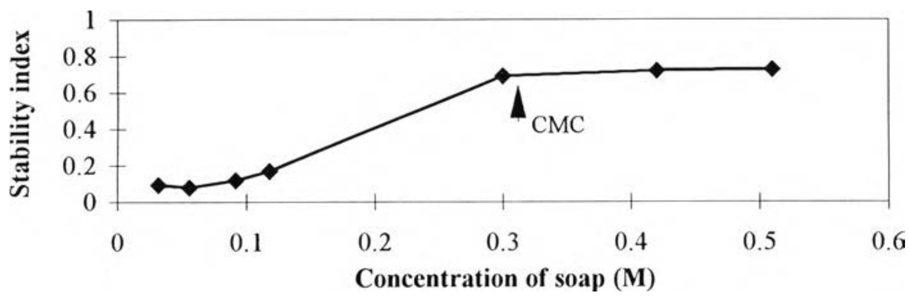


Figure 4.10 Relationship between stability index and soap concentration by the Mixing method

Miles test above the CMC is dramatic and is not observed in the Mixing method.

It is also interesting to note that the foam height of soap solutions below the CMC was much lower than in the case of SDS . The results show that, below the CMC, soap is a poorer foaming agent than SDS. This may be because the soap used in this work has a much shorter hydrophobic portion than SDS and therefore is less surface active than SDS. Above the CMC, there is not much different in foam height. This may be due to the fact that the solution is fully saturated above the CMC and the CMC of soap(0.3 M) is much higher than that of SDS (0.008 M), so both solutions generate about the same amount of foam.

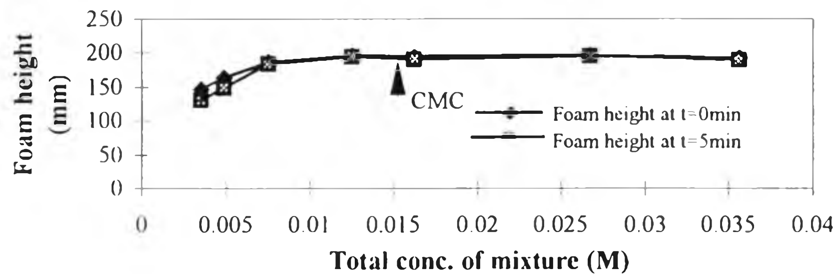
In the case of foam stability, SDS generally has higher stability index than soap indicating that SDS foams are more persistent. The difference is greastest below the CMC.

4.2.3 Foaming of SDS/SO systems

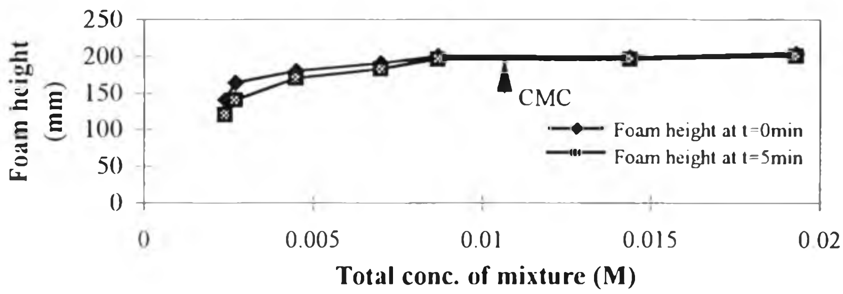
In this work, the mole ratio of SDS/SO was varied from 80/20, 60/40, 40/60, to 20/80. The concentrations in each mixture was chosen to cover the regions above and below the SDS precipitation boundary regions as determined by Chintanasathien(1995).

Ross-Miles Method

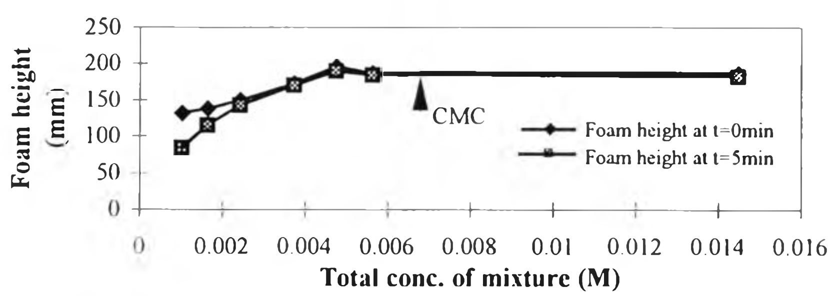
Fig.4.11 shows the foam height of solutions containing different ratios of SO/SDS by the Ross-Miles method. It was found that foam height increased with an increase in the total concentration of surfactant mixtures until it reached the maximum in the neighborhood of the mixture's CMC. Above the CMC, foam height remained constant.



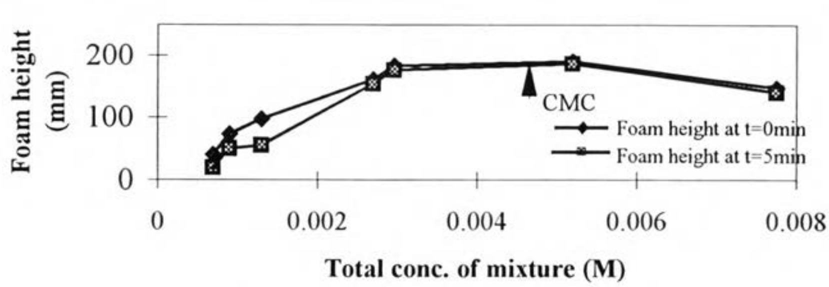
a) Mole ratio of SDS/SO = 20/80



b) Mole ratio of SDS/SO=40/60



c) Mole ratio of SDS/SO = 60/40



d) Mole ratio of SDS/SO = 80/20

Figure 4.11 Relationship between foam height and mixture concentration by the Ross-Miles method.

Foam height at t = 5 min was found to decrease slightly below the CMC but remained unchanged after the CMC. Fig. 4.12 shows the stability index of the SDS/SO mixtures after 5 min by the Ross-Miles method. It can be seen that foamability was low below the CMC but rose to the maximum of close to 1 and remained constant after that. Since the points for each molar ratio fall more or less on the same line, the results show that the different compositions do not affect the foam stability of mixtures. They behave similarly to pure SDS (Fig. 4.4) even at a SDS/SO molar ratio at 20/80.

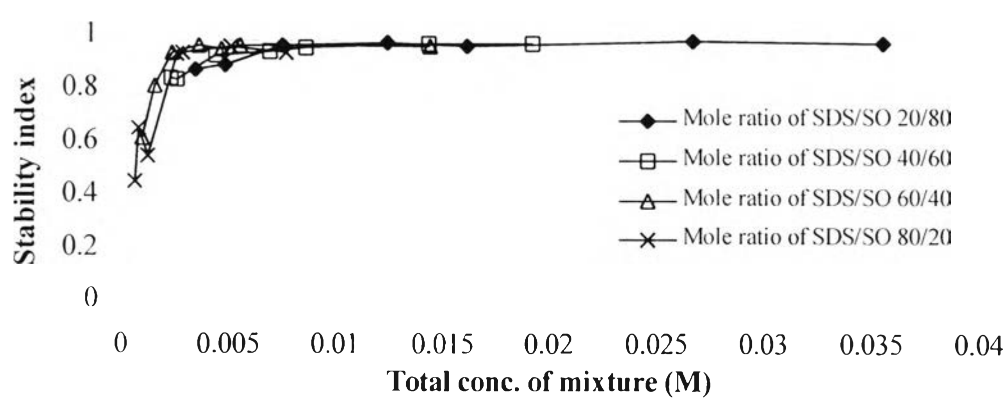


Figure 4.12 Relationship between stability index and mixture concentration by the Ross-Miles method.

Mixing Method

In the Mixing method, foam height (Fig. 4.13) was found to increase with an increase in concentration until it reached the maximum in the neigborhood of CMC. Above the CMC, foam height remained constant regardless of concentration.

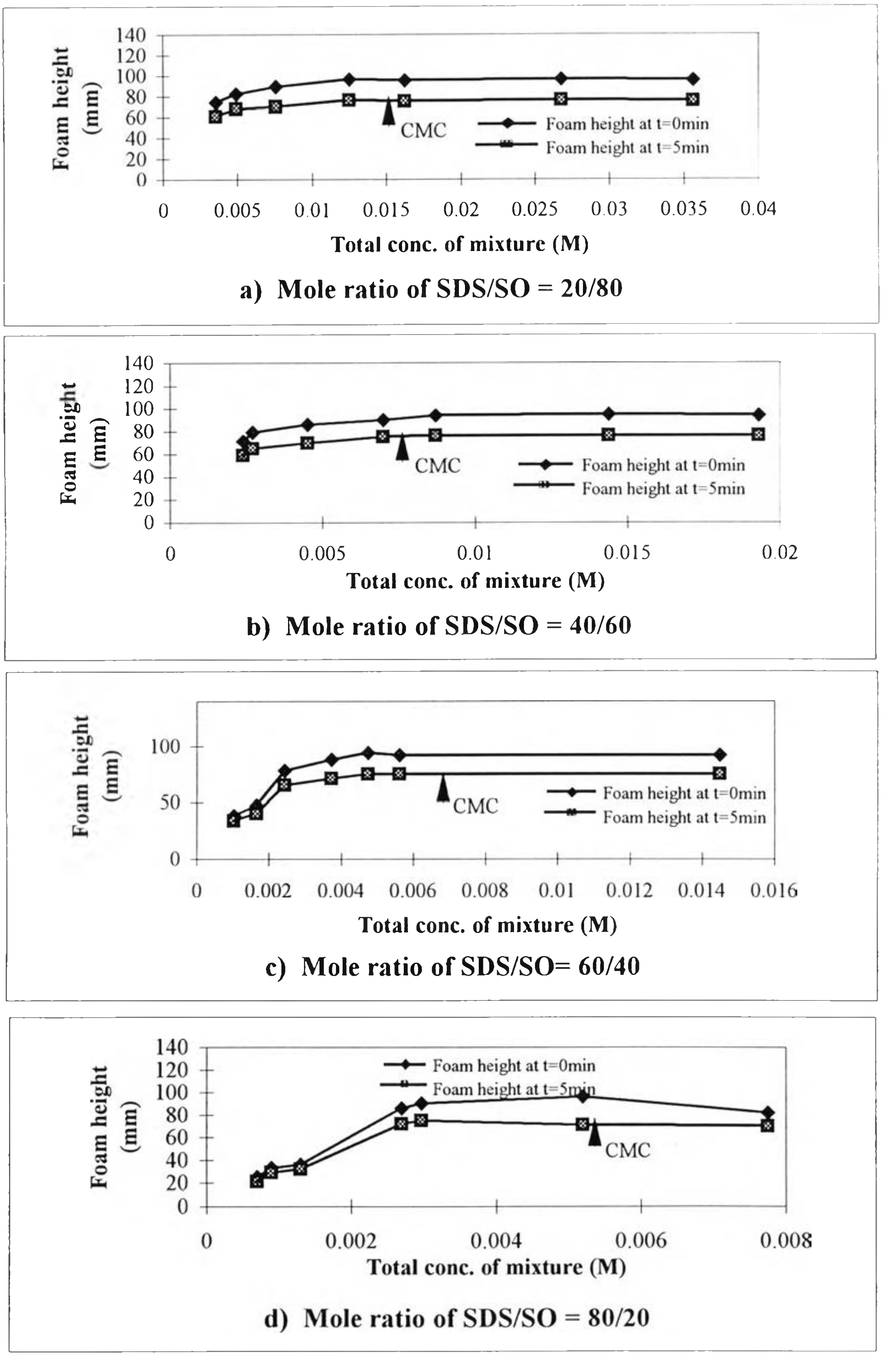


Figure 4.13 Relationship between foam height and mixture concentration by the Mixing method.

Fig. 4.14 shows the stability index of the SO/SDS mixtures after 5 min by the Mixing method. It can be seen that stability index was high at around 0.8 throughout the whole concentration range. The results show that foam stability remained constant at high level regardless of mixture concentration. The results are again similar to those of pure SDS (Fig. 4.6) indicating that SDS plays a predominant role in the mixture even at the SDS/SO ratio of 20/80.

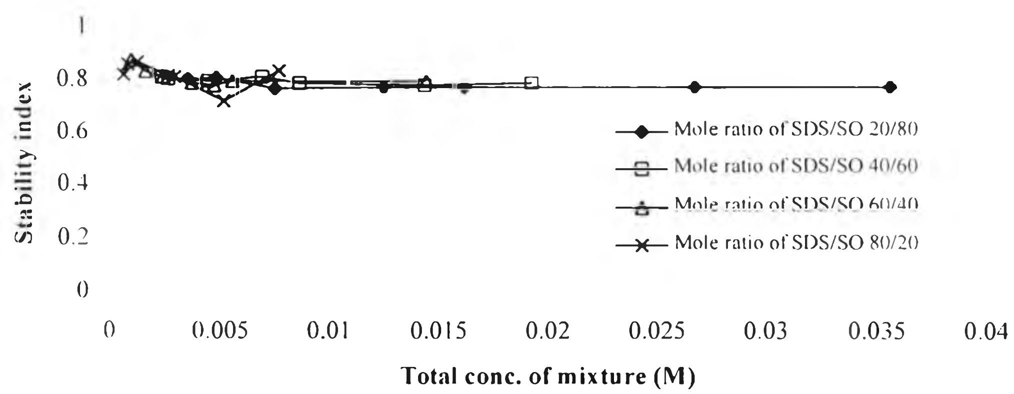


Figure 4.14 Relationship between stability index and mixture concentration by the Mixing method.

4.3 Effect of Calcium on the Foaming of SDS, Soap and their Mixture

4.3.1 <u>Effect of Calcium on the Foaming of SDS</u>

Foamability

Fig. 4.15 shows the foamability of SDS solutions in the presence of calcium salt with the Ross-Miles method. It can be seen that at t=0 foam height increased with an increase in concentration of SDS until it reached the maximum after CMC. Beyond the CMC foam height remained constant. At t= 5 min, There is little change in foam height throughout the concentration range.

Fig. 4.16 compares the foam height of SDS at different calcium levels by the Ross-Miles method. One noticeable effect of calcium was that the foam height below the CMC was significantly reduced when compared to the system with no calcium. This is probably due to the binding of calcium ion with the surfactant molecule leading to lower solubility and hence lower foamability. It is interesting to note that these regions of reduced foam height fall within the precipitation boundary of the system enclosed by the dotted lines.

Qualitatively similar results were obtained with the Mixing method as shown in Fig.4.17 and Fig. 4.18. Addition of calcium salt also led to a decrease in the initial foam height.

Foam stability

Fig.4.19 compares the stability index of SDS foam at different calcium levels after 5 min in the Ross-Miles method. It can be seen that addition of calcium reduced the stability index below the CMC from 0.7 down to 0.4, but above the CMC, calcium had little effect on the foam stability.

In the Mixing method (Fig.4.20), the reduction in foam stability below the CMC was very slight with no noticeable effect above the CMC.

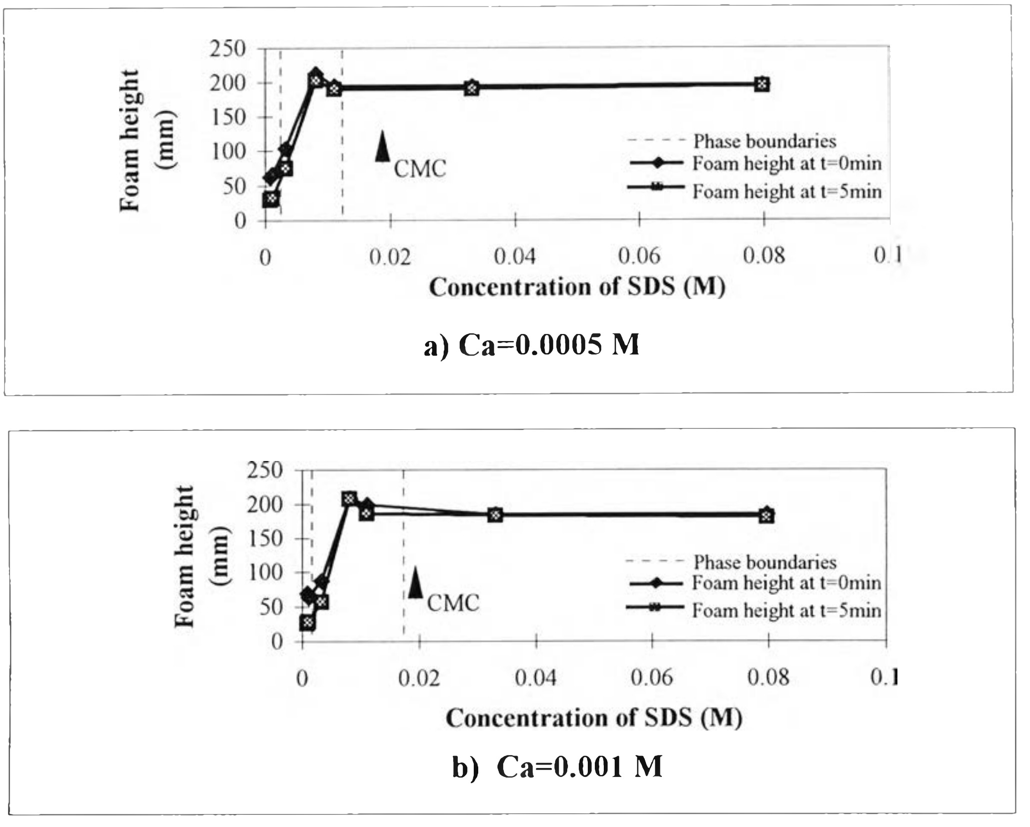
The results show that calcium reduced foam stability below CMC in the Ross-Mile method but the effect was less pronounced in the Mixing method. Above the CMC, calcium had no effect on the foam stability.

4.3.2 Effect of Calcium on the Foaming of Soap

Foamability

Figs. 4.21 and 4.22 show the foaming of soap in the presence of calcium by the Ross-Miles method. It can be seen that addition of calcium salt reduced the initial foam height below the CMC but it had little effect above the CMC.

The same qualitative results were obtained with the Mixing method as shown in Fig. 4.23 and Fig. 4.24.



a) Ca=0.0005 M

b) Ca=0.001 M

Figure 4.15 Relationship between foam height and SDS concentration in the presence of calcium by the Ross-Miles method.

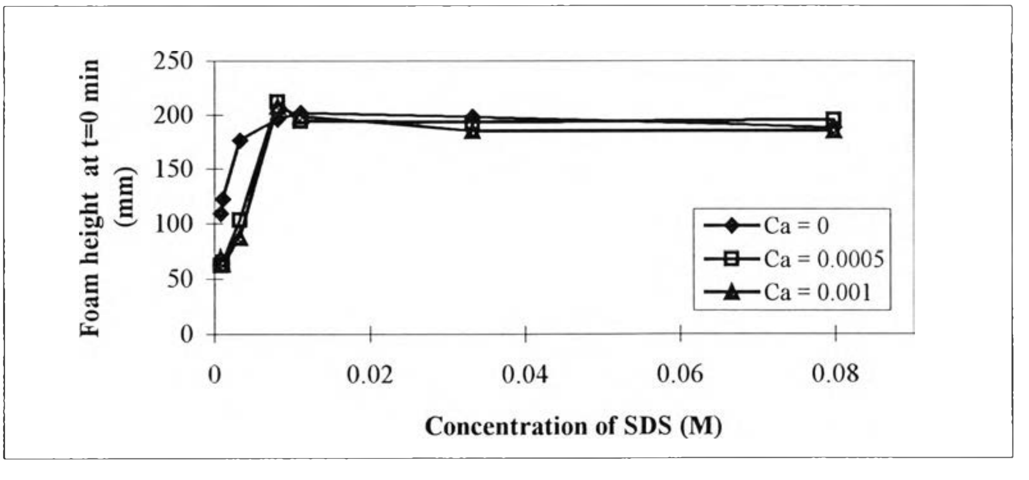
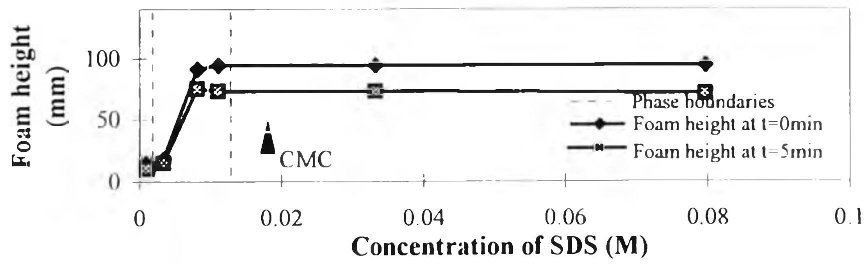
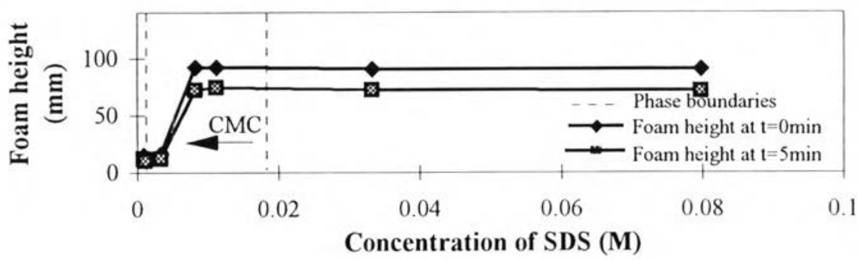


Figure 4.16 Relation between foam height at t=0 min and SDS concentration at different calcium concentrations by the Ross-Miles method.



a) Ca=0.0005 M



b) Ca=0.001M

Figure4.17 Relationship between foam height and SDS concentration in the presence of calcium by the Mixing method.

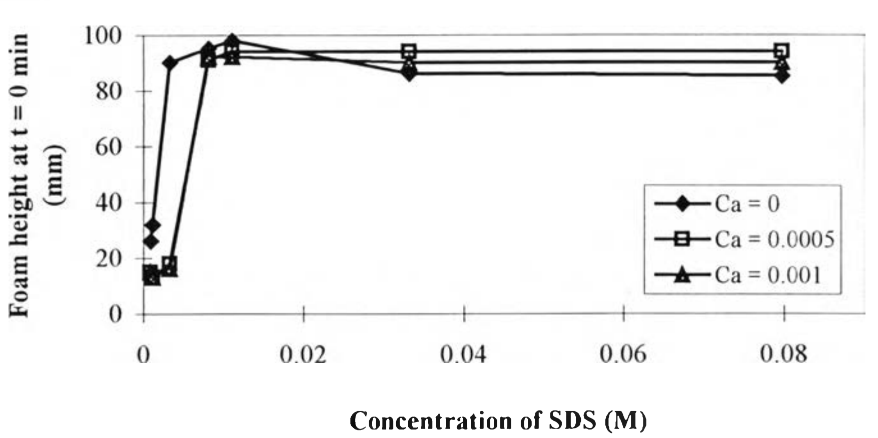


Figure4.18 Relation between foam height at t=0 min and SDS concentration at different calcium concentrations by theMixing method.

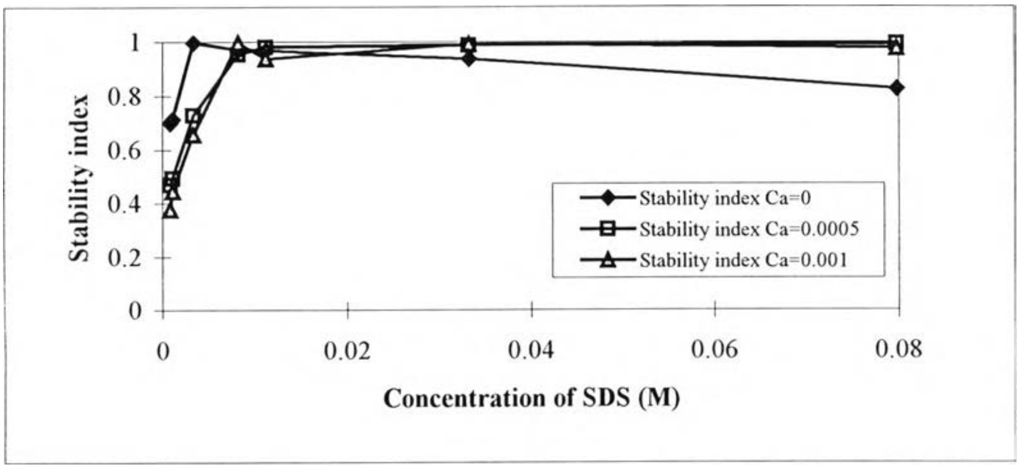


Figure 4.19 Relation between stability index and SDS concentration at different calcium concentrations by the Ross-Miles method.

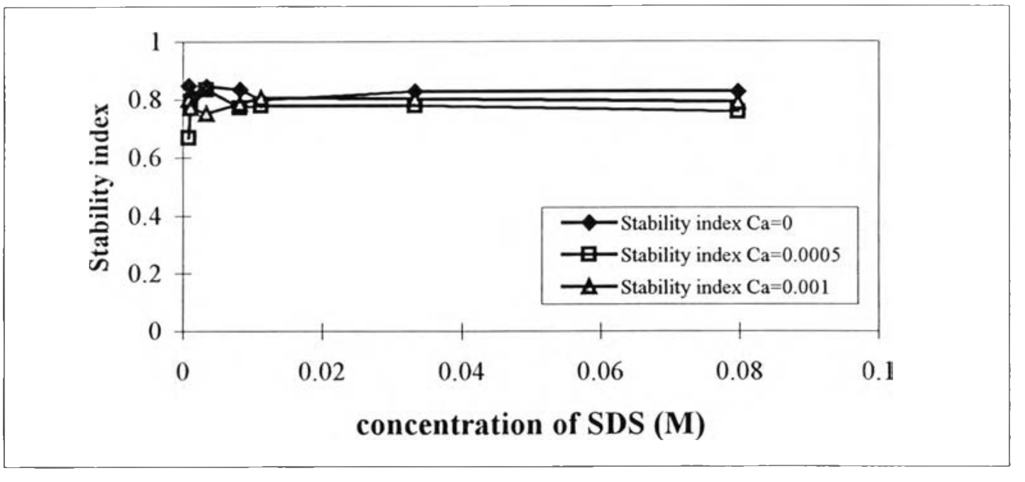
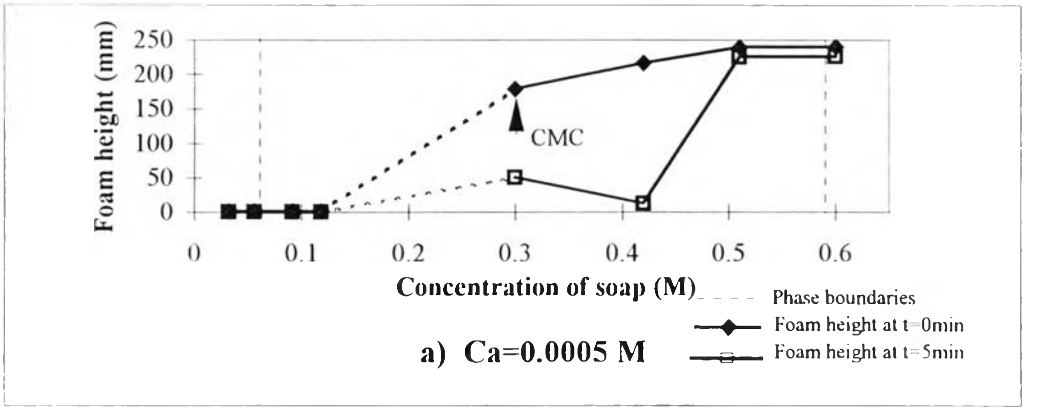


Figure 4.20 Relation between stability index and SDS concentration at different calcium concentrations by the Mixing method.



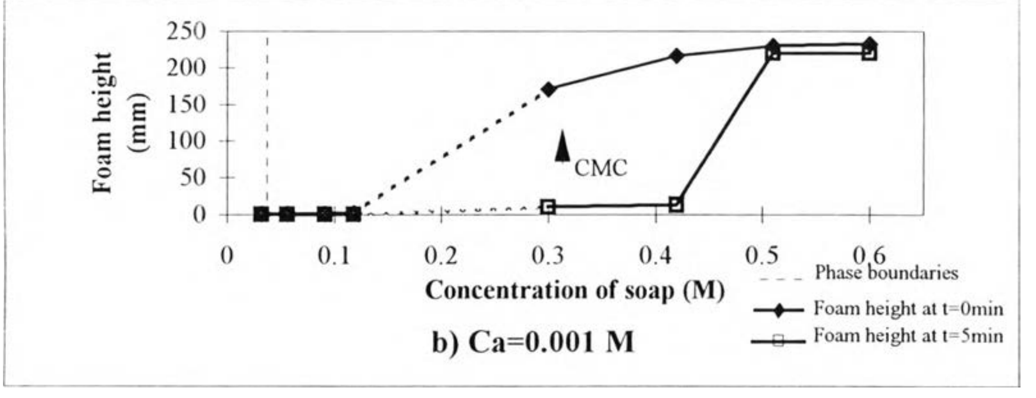


Figure 4.21 Relationship between foam height and soap concentration in the presence of calcium by the Ross-Miles method.

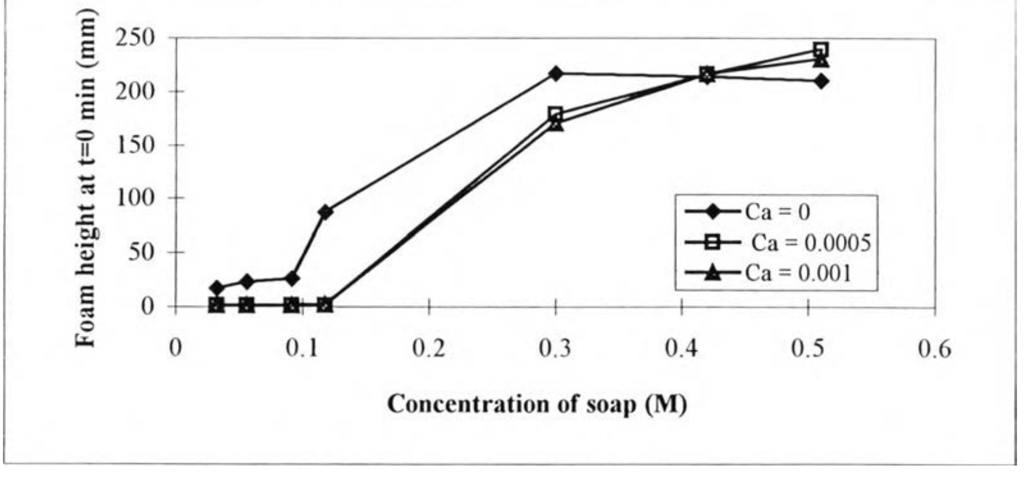
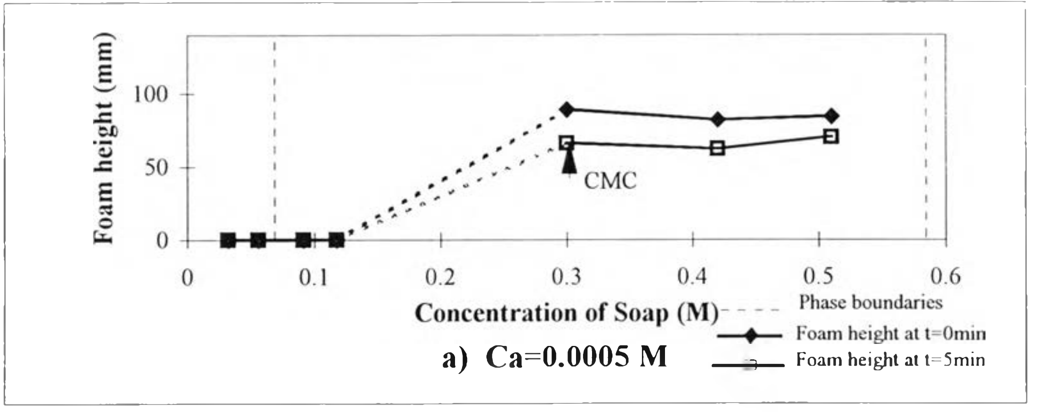


Figure 4.22 Relation between foam height at t=0 min and soap concentration at different calcium concentrations by the Ross-Mile method.



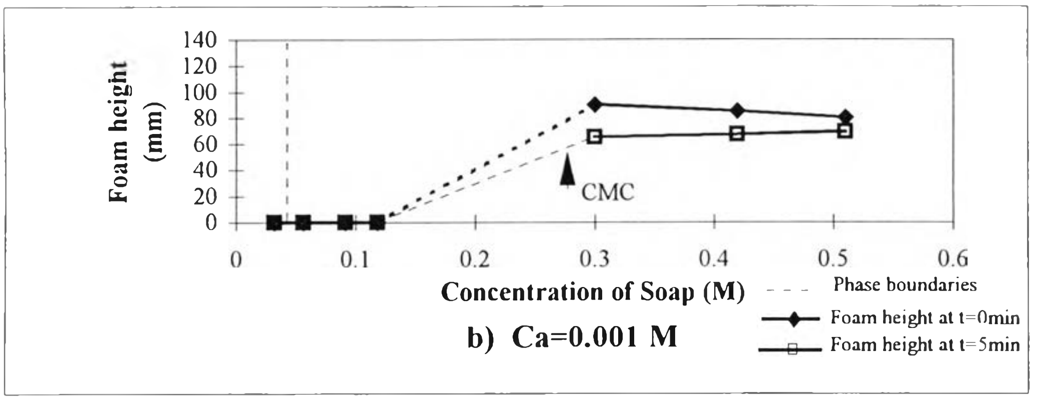


Fig. 4.23 Relationship between foam height and soap concentration in the presence of calcium by the Mixing method.

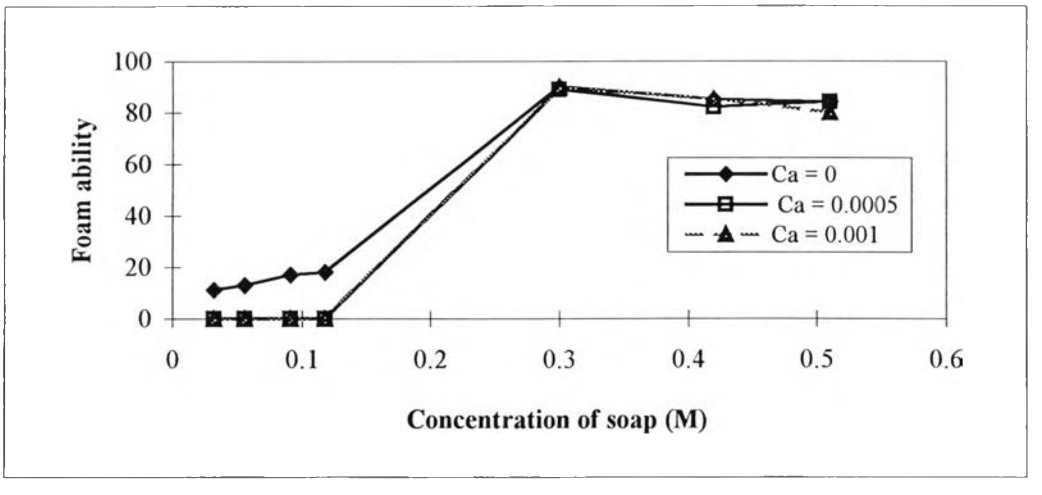


Figure 4.24 Relation between foam height at t=0 min and soap concentration at different calcium concentrations by the Mixing method.

Foam stability

Fig. 4.25 and Fig.4.26 compare the stability index of soap solution at different calcium levels by the Ross-Miles and Mixing methods respectively. Since the foam heights below the CMC were very low, the stability index was close to 0 in this concentration range. Above the CMC, the stability index was high and calcium was found to have little effect on the foam stability in both methods.

The results show that calcium depressed foam stability below CMC but had little effect above the CMC.

4.3.3 Effect of Calcium on the Foaming of SDS/SO Mixtures

Foamability

Fig. 4.27 shows the foaming of the mixtures with 0.0005 M calcium salt by the Ross-Miles method. It was found that foam height increased with an increase in the mixture concentration until it reached the maximum slightly above the CMC, after which it remained constant. Similar results were obtained with calcium concentration of 0.001 M and from the Mixing method as shown in Fig. 4.28. 4.29, 4.30.

Fig. 4.31 compares the foamability of the SDS/SO mixtures at different calcium levels by the Ross-Miles method. It can be seen that the addition of calcium depressed the foam height below the CMC at all SDS/SO ratios. Above the CMC, calcium had little effect on foam height. The increase in calcium level from 0.0005 to 0.001 M further decreased foaming only very slightly.

Similar results were obtained by the Mixing method as shown in Fig. 4.32. It can be seen that addition of calcium reduced the foam height below the CMC to as low as 20 mm.

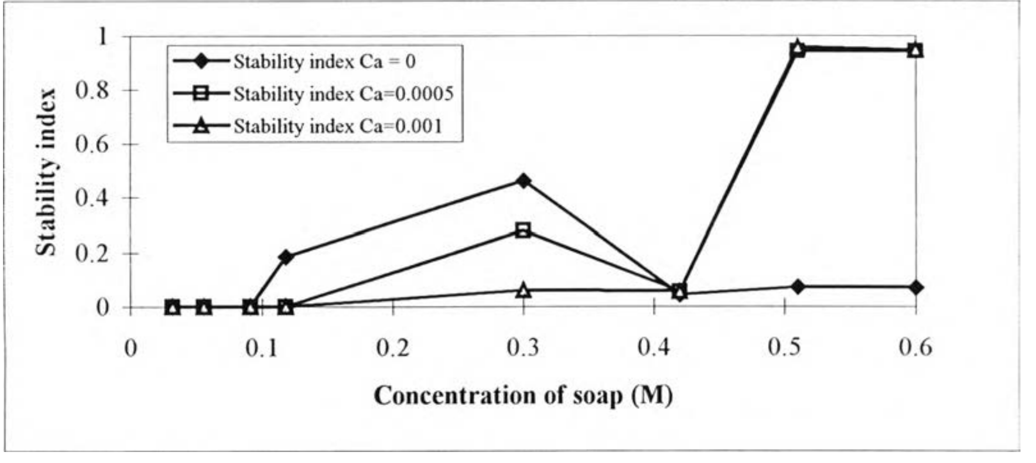


Figure 4.25 Relation between stability index and soap concentration at different calcium concentrations by the Ross-Miles method.

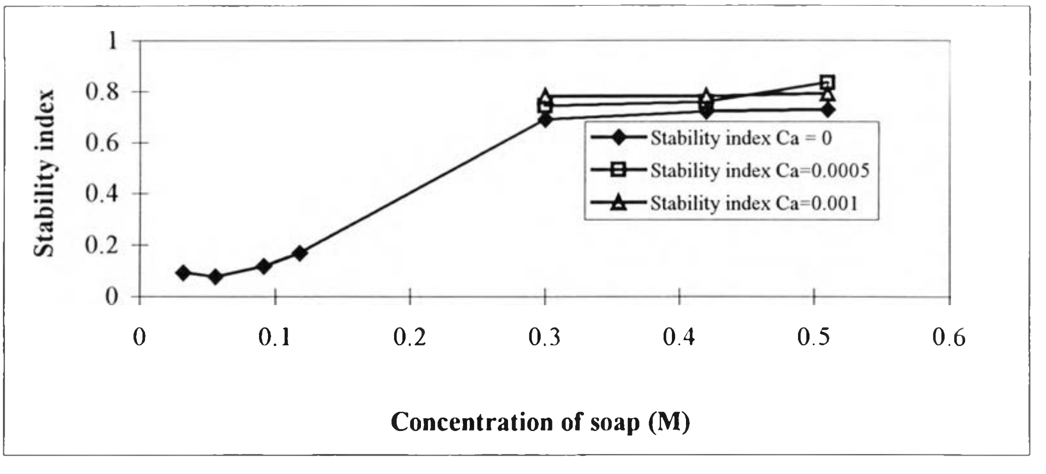


Figure4.26 Relation between stability index and soap concentration at different calcium concentrations by the Mixing method.

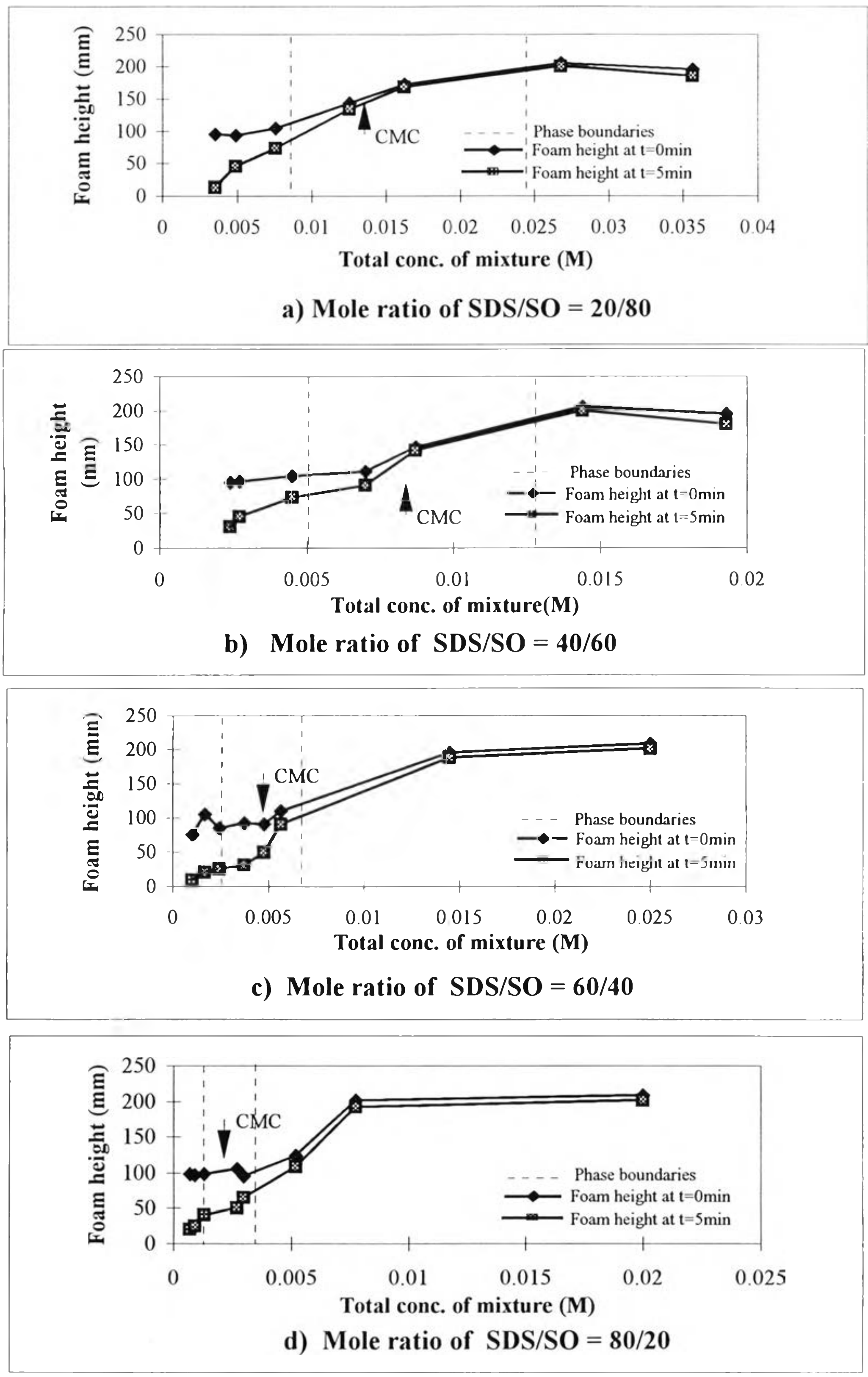
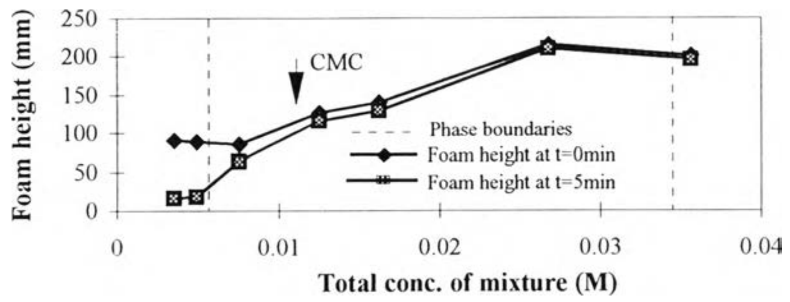
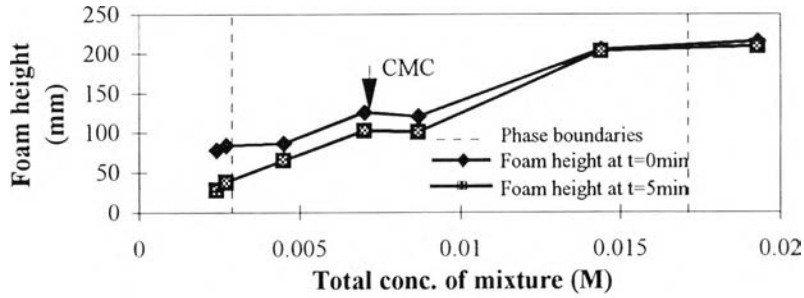


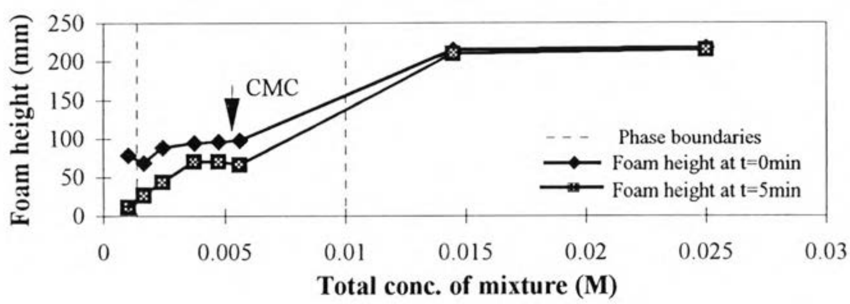
Figure 4.27 Relationship between foam height and mixture concentration in the presence of 0.0005 M calcium by the Ross-Miles method.



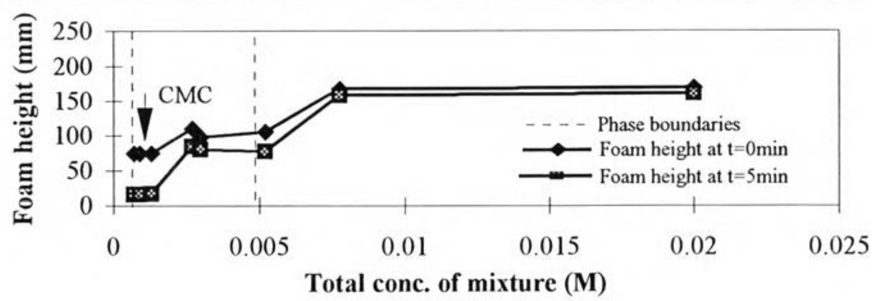
a) Mole ratio of SDS/SO = 20/80



b) Mole ratio of SDS/SO = 40/60

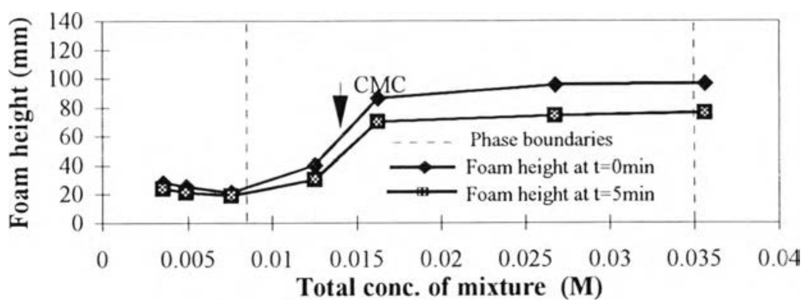


c) Mole ratio of SDS/SO = 60/40

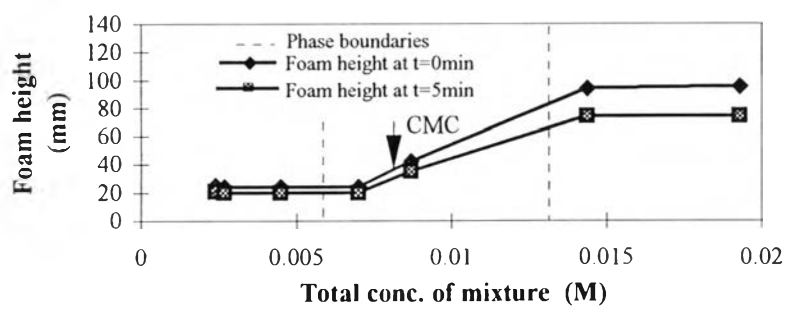


d) Mole ratio of SDS/SO = 80/20

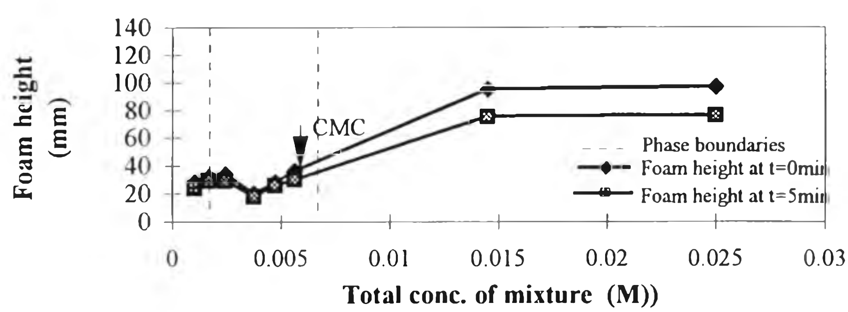
Figure 4.28 Relationship between foam height and mixture concentration in the presence of 0.001 M calcium by the Ross-Miles method.



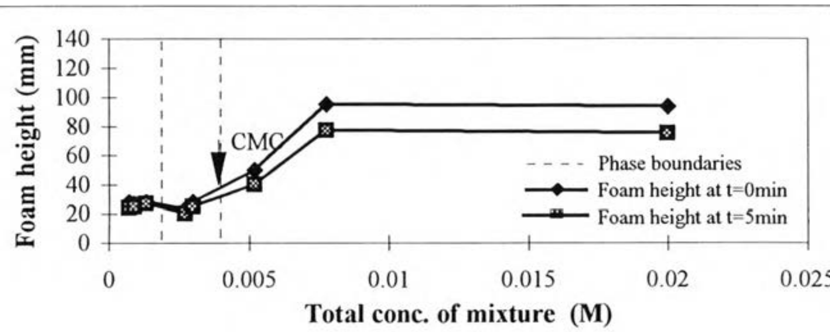
a) Mole ratio of SDS/SO = 20/80



b) Mole ratio of SDS/SO = 40/60

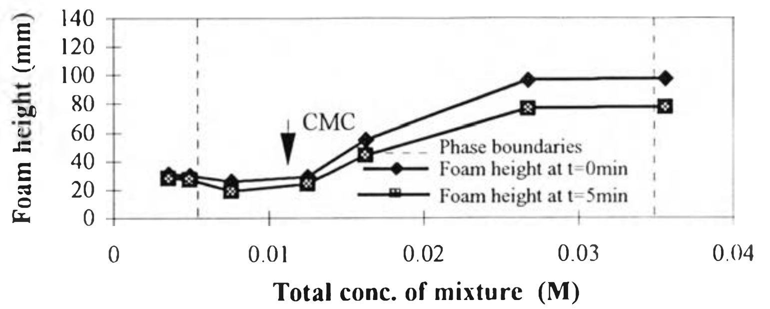


c) Mole ratio of SDS/SO = 60/40

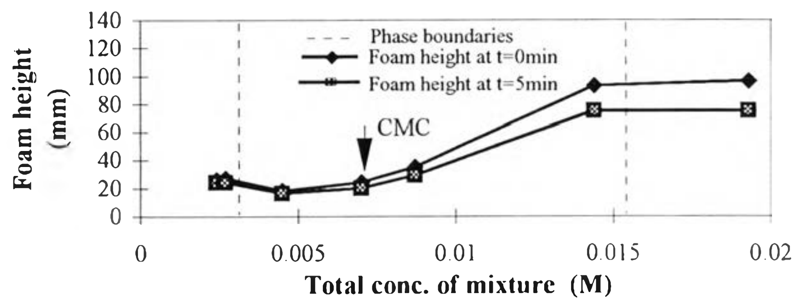


d) Mole ratio of SDS/SO = 80/20

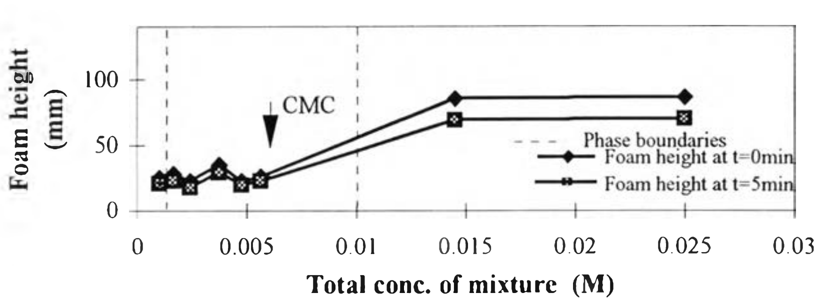
Figure 4.29 Relationship between foam height and mixture concentration in the presence of 0.0005 M calcium by the Mixing method.



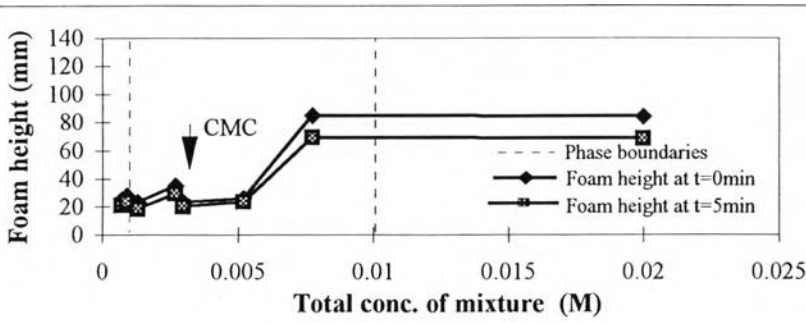
a) Mole ratio of SDS/SO = 20/80



b) Mole ratio of SDS/SO = 40/60



c) Mole ratio of SDS/SO = 60/40



d) Mole ratio of SDS/SO = 80/20

Figure 4.30 Relationship between foam height and mixture concentration in the presence of 0.001 M calcium by the Mixing method.

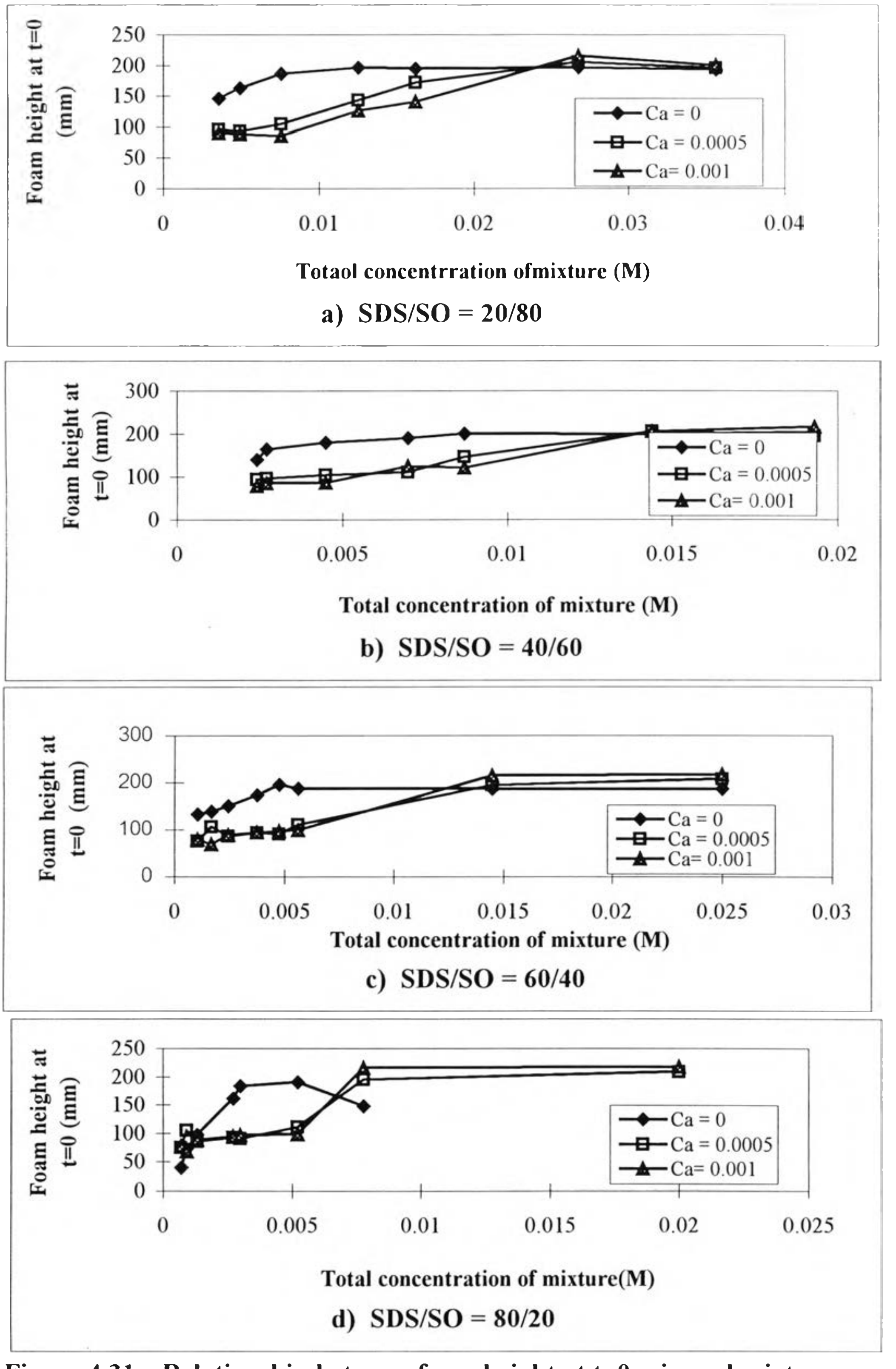


Figure 4.31 **Relationship between foam height at t=0 min and mixture concentration at different calcium concentrations by the Ross-Mile method.**

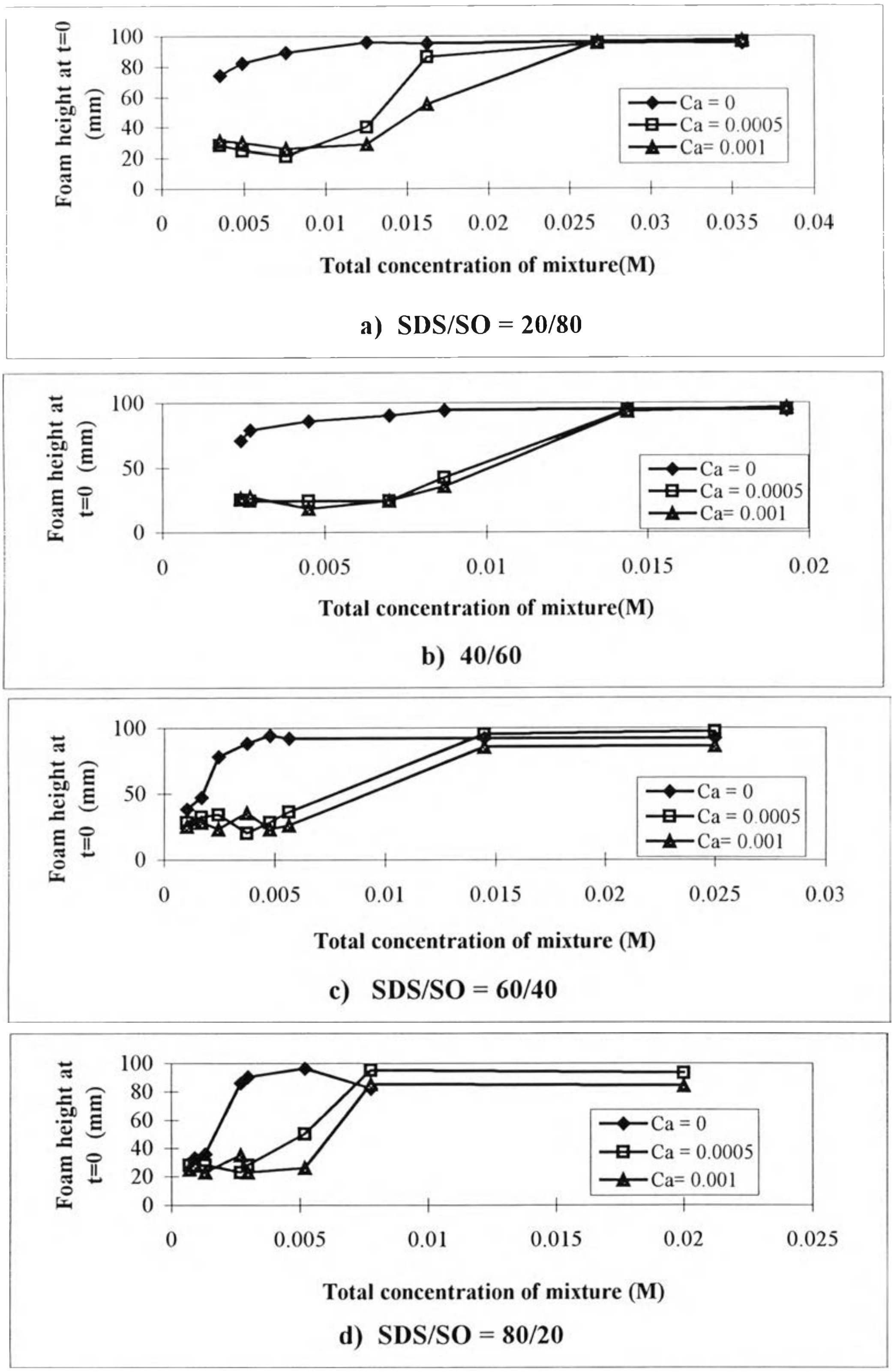


Figure 4.32 **Relationship between foam height at t=0 min and mixture concentration at different calcium concentrations by the Mixing method.**

Foam stability

Fig. 4.33 compares the stability index of SDS/SO mixtures at different calcium levels by the Ross-Miles method. It can be seen that the stability index was greatly reduced by the presence of calcium at concentration below the CMC at all mixture ratios. However, above the CMC, calcium had little or no effect on foam stability.

In the Mixing method (Fig. 4.34), the presence of calcium was found to have no significant effect on foam stability in all mixture ratios.

The results from both the Ross-Miles and Mixing methods show that CMC plays a decisive in the foaming surfactants and their mixtures, the existence of the phase boundary in the mixtures did not seem to have any effect on the foaming behavior of the mixtures.

4.3.4 Effect of Calcium on the Different Mole Ratios of SDS/SO Mixtures

Foamability

Fig 4.35 and 4.36 compare the effect of calcium on the foamability of different mole ratios of SDS/SO by Ross-Miles amd Mixing method. In Fig. 4.35a, it can be seen that, when there was no calcium in the system, all the curves fitted very close to each other indicating that the different mixture ratios had little effect on the foamability of the mixture and the foam height depended mainly on the total mixture concentration.

However, when calcium was added to the system (Fig. 4.35b and 4.35c), the curves diverged from each other with a reduction in the initial foam height, a slower increase to maximum foam height, and an increase in concentration required to reached the maximum. The effect was found to be greater with higher mole ratios of soap.

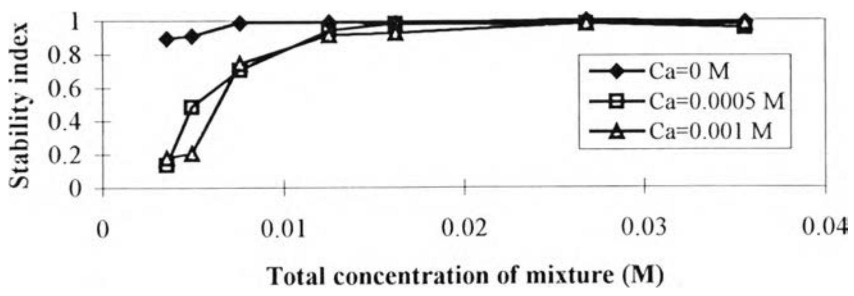
The results show that calcium depressed the foamability of the mixture solution at low surfactant concentration and the effect was more pronounced with mixture containing higher mole ratio of soap in the mixture in both the Ross-Miles and the Mixing methods.

Foam stability

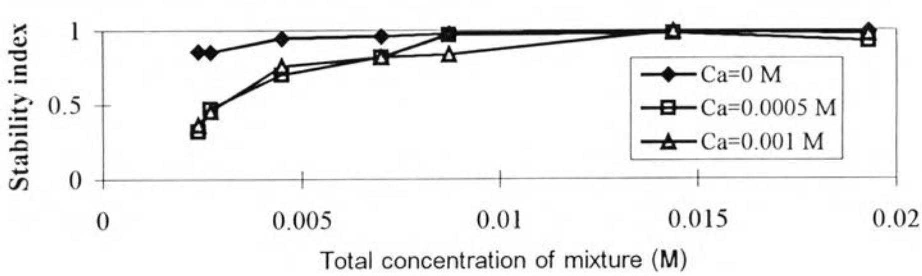
Fig. 4.37 and 4.38 compare the effect of calcium on the foam stability of different mole ratios of SDS/SO by the Ross-Miles and Mixing method. In the Ross-Miles method, it can be seen that when there was no calcium in the system (Fig. 4.37a), all the curves fitted closely to each other indicating that foam stability did not depend on the mole ratio of each component but depended mainly on the total concentration of the mixture. However, when calcium was added (Fig. 4.37b and 4.37c), the curves diverged from each other with reduction in foam stability at low concentration and the effect was greater with higher mole ratio of soap in the mixture.

In the Mixing method (Fig.4.38), it was found that foam stability was almost constant with the stability index at 0.8 throughout all the mixture ratios and at all calcium levels.

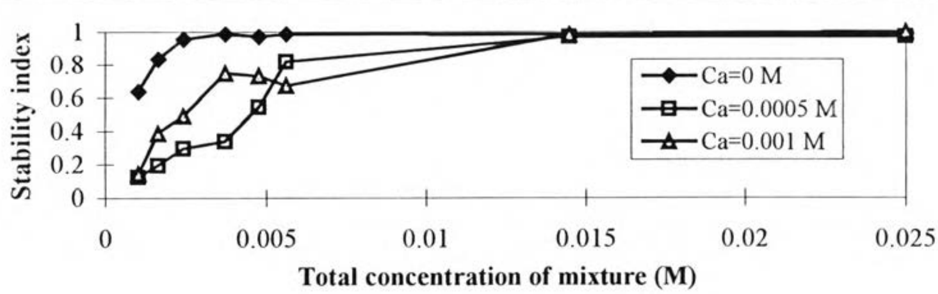
The results show that calcium had an effect on foam stability at low mixture concentration in the Ross-Miles method but it did not effect foam stability in the Mixing method.



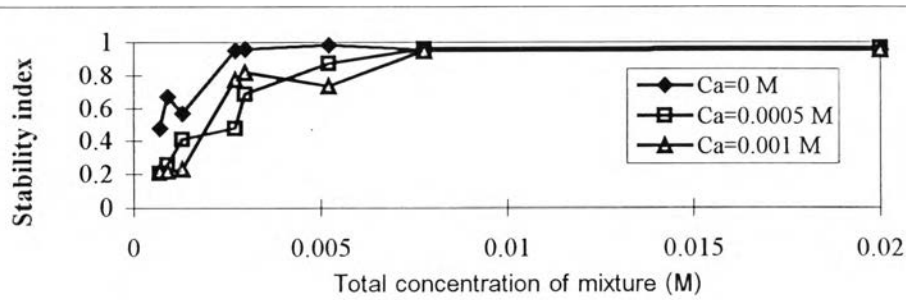
a) SDS/SO = 20/80



b) SDS/SO = 40/60



c) SDS/SO = 60/40



d) SDS/SO = 80/20

Figure 4.33 Relationship between stability index and mixture concentration at different calcium concentrations by the Ross-Miles method.

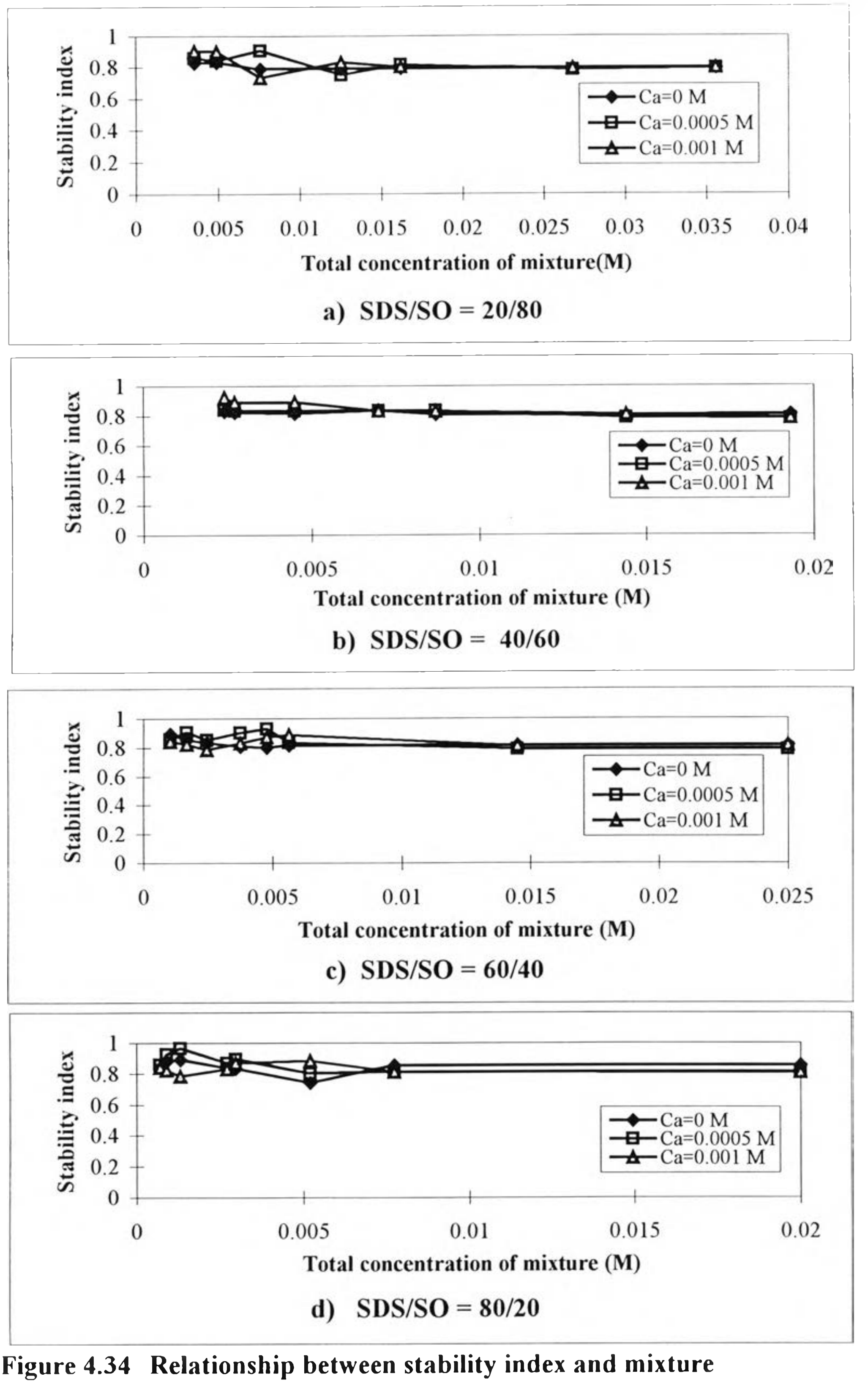


Figure 4.34 Relationship between stability index and mixture concentration at different calcium concentrations by the Mixing method.

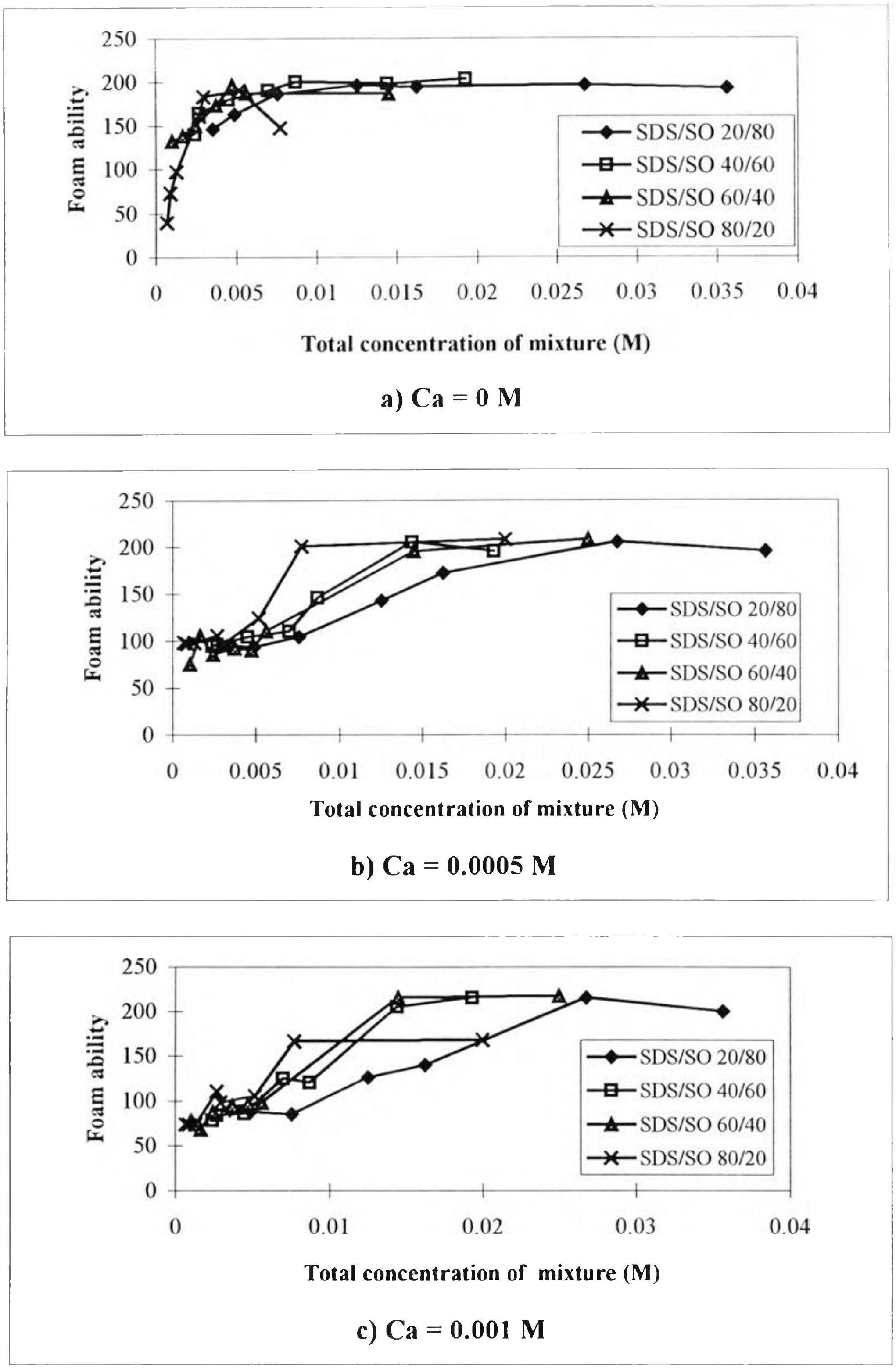


Figure 4.35 Comparison of the effect of calcium levels on the foamability of SDS/SO mixtures at different ratios by the Ross-Miles method.

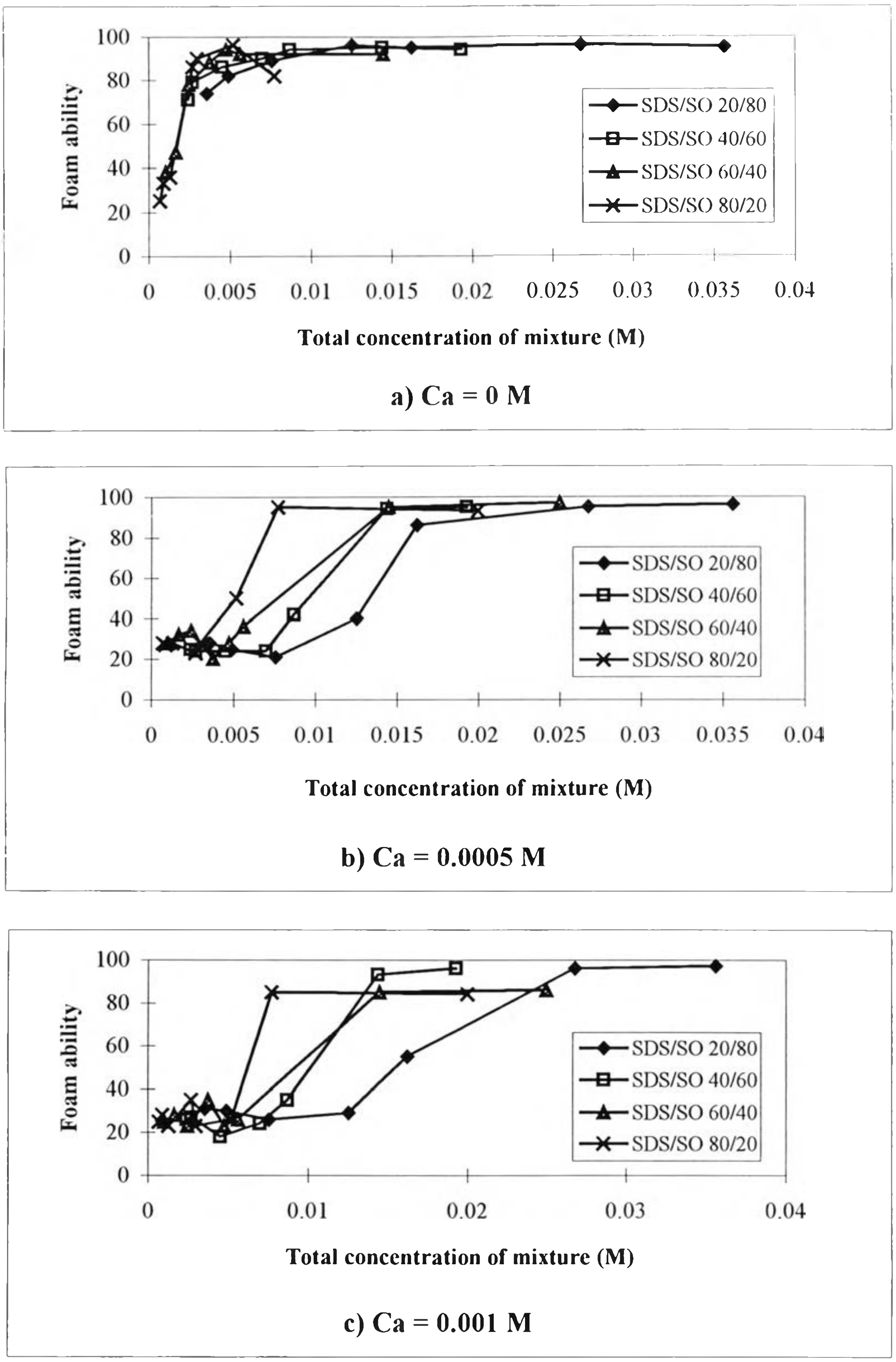


Figure 4.36 Comparison of the effect of calcium levels on the foamability of SDS/SO mixtures at different ratios by the Mixing method.

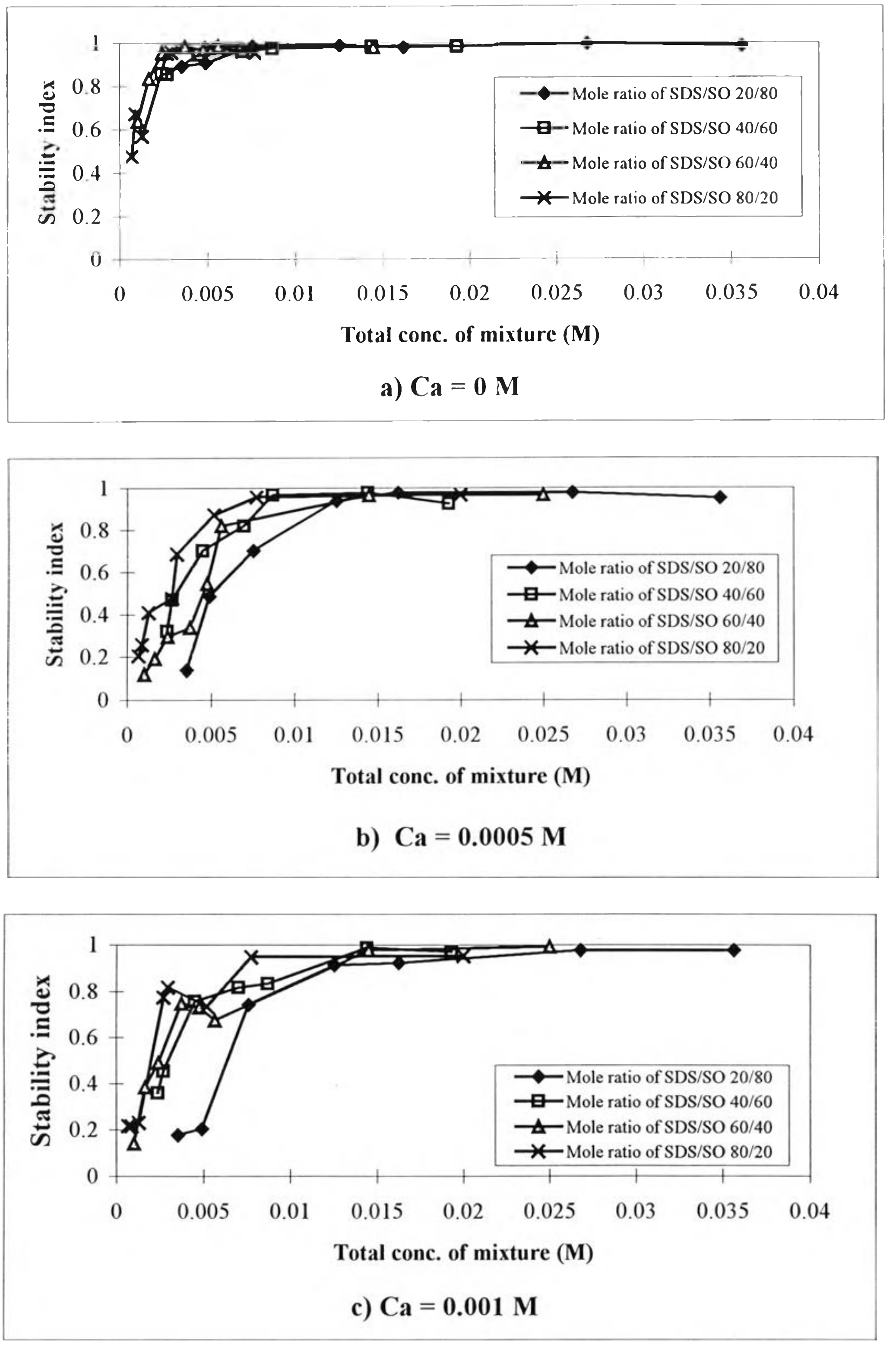


Figure 4.37 Comparison of the effect of calcium levels on stability index of SDS/SO mixtures at different ratios by the Ross-Miles method.

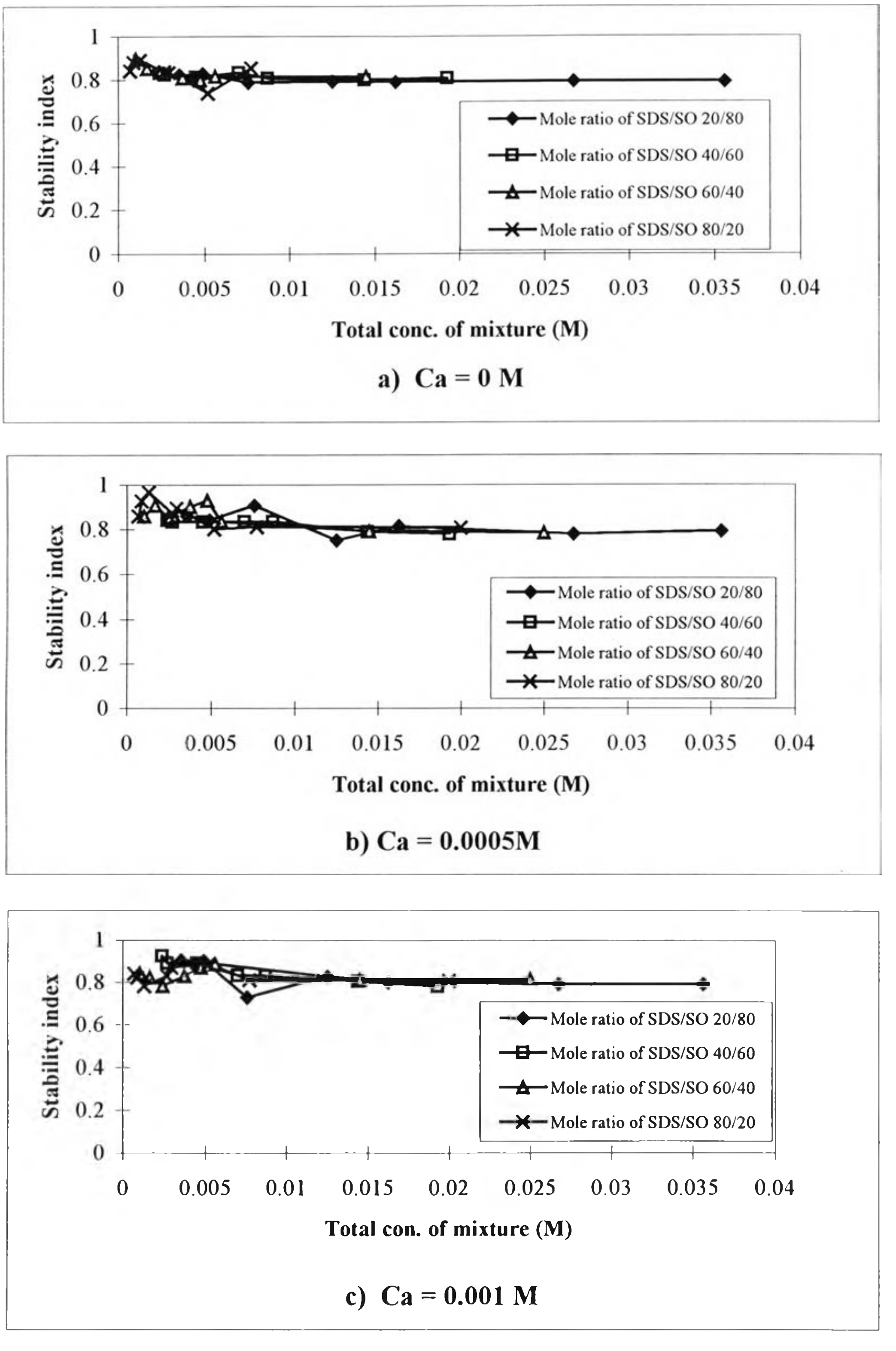


Figure 4.38 Comparison of the effect of calcium levels on stability index of SDS/SO mixtures at different ratios by the Mixing method.