

CHAPTER IV

RESULTS AND DISCUSSION

In this experimental study, the effect of precipitating conditions on the properties of Mg-HEDP precipitate were carried out. The precipitating conditions were varied to obtain different degrees of supersaturation, two levels of the solution pH, and two molar ratios of Mg^{2+} :HEDP in solution. The experimental data were shown in the Appendix A. Summary of the results is shown in Table 4.1.

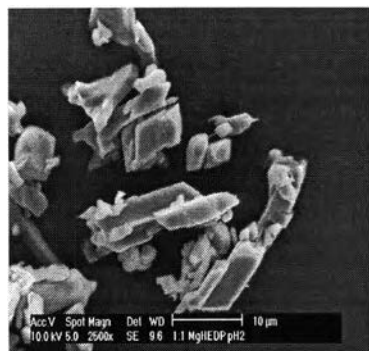
4.1 Effect of Degree of Supersaturation on Mg-HEDP Precipitate Properties

To study the effect of the degree of supersaturation on the properties of Mg-HEDP precipitate, four different solutions were prepared with high and low values of molar product, and two levels of Mg^{2+} :HEDP molar ratios and two pH values. For an initial Mg^{2+} :HEDP molar ratio in solution of 10:1, and a constant pH of 6, two values of molar product prepared were 0.03 and 0.005 M^2 which corresponded to HEDP concentrations of 0.0548 M and 0.0224 M, respectively. As shown in Table 4.1, the chemical compositions (Mg:HEDP ratio in precipitate) of these two precipitates are the same, 2:1. Moreover, by visual inspection with a Scanning Electron Microscope (SEM) of these two precipitates, the morphologies are similar, as shown in Figure 4.1. The results of the batch dissolution experiments, also confirmed the similarity between these two precipitates according to their same solubility values. Based on these results, a conclusion can be drawn that the degree of supersaturation had little effect on the resulting precipitate properties. In addition, two more precipitates were formed at an initial Mg^{2+} :HEDP molar ratio in solution of

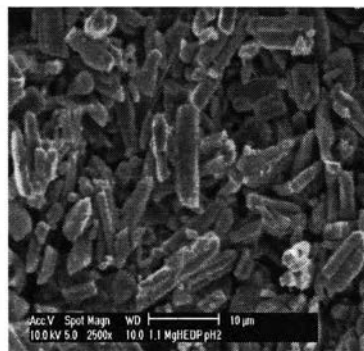
Table 4.1 Summary of experimental results of batch synthesis.

| Experimental conditions | | | | Precipitate characteristics | | |
|--|------------------------------|--|----|--|------------------------|--|
| Molar product: [HEDP][Mg ²⁺] (M ²) | HEDP concentration (M) | Mg ²⁺ :HEDP molar ratio in solution | pH | Mg:HEDP molar ratio in precipitate | Precipitate morphology | Equilibrium saturation level of HEDP (ppm) |
| 1 | 1 | 1 : 1 | 2 | 1 : 2 | Platelet | 12,410 |
| 0.16 | 0.4 | 1 : 1 | 2 | 1 : 2 | Platelet | * |
| 1 | 0.33 | 10 : 1 | 2 | 3 : 2 | Fibrous spindles | 10,620 |
| 0.005 | 0.0224 | 1 : 1 | 6 | 3 : 2 | Irregular flaky | * |
| 0.03 | 0.0548 | 10 : 1 | 6 | 2 : 1 | Granular | 1,330 |
| 0.005 | 0.0224 | 10 : 1 | 6 | 2 : 1 | Granular | 1,210 |

* No analysis at this condition

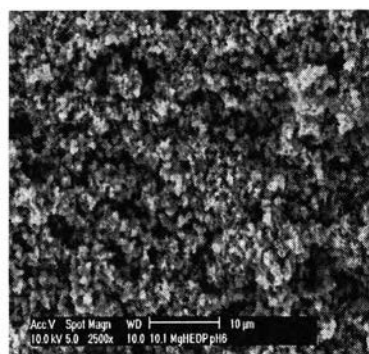


Molar product = 0.16 M²

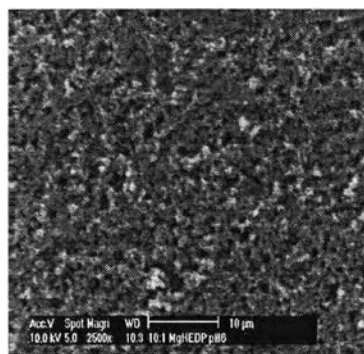


Molar product = 1 M²

Precipitate was formed at a 1:1 molar ratio and a pH of 2



Molar product = 0.005 M²



Molar product = 0.03 M²

Precipitate was formed at a 10:1 molar ratio and a pH of 6

Figure 4.1 Effect of the degree of supersaturation on the resulting precipitate morphologies.

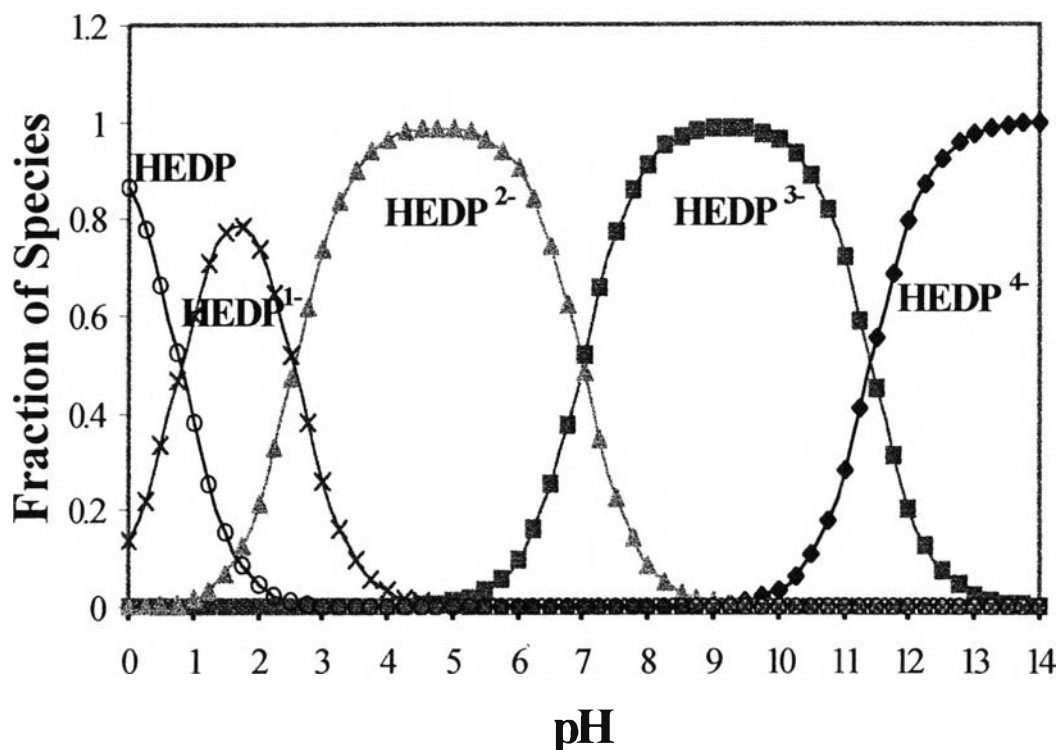
1:1, a constant pH of 2, and two values of molar product of 1 and 0.16 M² which corresponded to HEDP concentrations of 1M and 0.4M, respectively. As shown in Table 4.1, both precipitates have the same Mg:HEDP molar ratio of 3:2. The morphologies of these two precipitates were also the same. Again, the similarity of these two precipitate demonstrated that the degree of supersaturation had little effect on the resulting precipitate properties.

4.2 Coupled Effect of pH and Mg²⁺:HEDP Molar Ratio of Precipitating Solution on Mg-HEDP Precipitate Properties

The results shown in Table 4.1 clearly indicate that both the pH and Mg²⁺:HEDP molar ratio in solution affect the precipitates properties of the chemical composition in precipitate, the morphology and the solubility.

4.2.1 Coupled Effect of pH and Mg²⁺:HEDP Molar Ratio of Precipitating Solution on Mg:HEDP Molar Ratio in Precipitate

At a given initial Mg²⁺:HEDP molar ratio (i.e., 1:1), the molar ratio of Mg:HEDP in the precipitates increased from 1:2 to 3:2 when the solution pH increased from 2 to 6. Moreover, at a higher initial Mg²⁺:HEDP molar ratio of 10:1 in solution, the molar ratio of Mg:HEDP in the precipitates further increased from 3:2 to 2:1 when the solution pH increased from 2 to 6. These phenomena occurred because when the pH increases, the number of hydrogens deprotonated from each HEDP molecule increases due to the solution equilibrium shifting (See pK_a values in Figure 4.2). As a result, each HEDP molecule will have more reacting sites to react with the magnesium atoms which, in turn, increases the higher Mg:HEDP molar ratio in the precipitates.



Acidity constants in 0.05 M tetramethylammonium chloride at 298 K

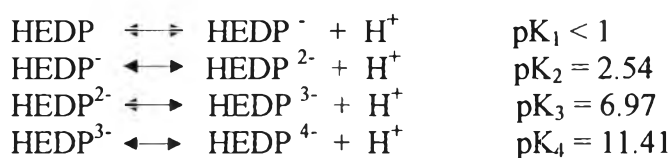


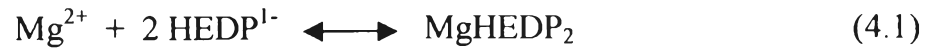
Figure 4.2 Effect of pH on the deprotonation of HEDP and the resulting species composition.

At a given initial pH (i.e., pH of 2) the molar ratio of Mg:HEDP in the precipitates increased from 1:2 to 3:2 when Mg^{2+} :HEDP molar ratio of precipitating solution increased from 1:1 to 10:1 as shown in Table 4.1. In addition, at a constant pH of 6, the molar ratio of Mg:HEDP in the precipitates also increased from 3:2 to 2:1 when molar ratio of Mg^{2+} :HEDP in the solution

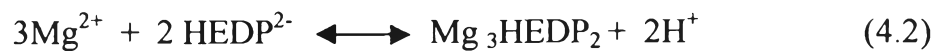
increased from 1:1 to 10:1. These results can be explained that the excess magnesium alters the chelation chemistry of the system to shift the solution equilibrium, resulting in a reduction of the pK_a value. The reduction in the pK_a values causes an increase in the amount of hydrogen deprotonation on each HEDP molecule and an increase in the precipitate's magnesium/HEDP molar ratio.

It reveals that to increase the magnesium:HEDP molar ratio in precipitate, the precipitating solution's pH and the Mg^{2+} :HEDP molar ratio need to be increased. This trend is similar to the results obtained from the previous study on the calcium-HEDP precipitate (Browning and Fogler, 1995 and 1996). One additional point worth noting is that the chemical compositions of the resulting Mg-HEDP precipitates cannot be predicted solely from the calculated values obtained from the HEDP pK_a data as shown in Figure 4.2. The calculation of the each species of HEDP is shown in Appendix B. This point can be clarified with the aid of Figure 4.2 where the fraction of each deprotonated HEDP species is shown as function of the solution pH. The pH where the fractions of two different deprotonated species are equal defined a pK_a value. It is apparent from Figure 4.2 that at a pH of 2, the HEDP molecules have deprotonated one to two hydrogens. However when HEDP solution was mixed with magnesium with the Mg^{2+} :HEDP molar ratio of 10:1 in solution and at the same pH, the 3:2 precipitate formed, indicating that three hydrogens had been deprotonated. This phenomenon is a direct result of the effect that magnesium cations have a potential to enhance the bonding of magnesium onto HEDP.

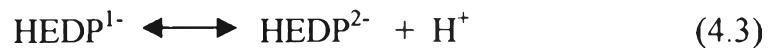
At a constant pH of 2, the composition of the precipitates changed from 1:2 to 3:2 when the precipitating solution's Mg^{2+} :HEDP molar ratio changed from 1:1 to 10:1. To provide a clearer understanding of this phenomenon, the reactions that govern the formation of these precipitates must be examined. The reaction to form a 1:2 precipitate can be written as



In a similar manner, assuming that HEDP species has to deprotonate at least two hydrogens to form a 3:2 precipitate, the precipitation reaction for the 3:2 precipitate can be written as



In addition to the precipitation reactions, the following deprotonation reaction also occurs at these conditions:



By coupling these equations together, a simple equilibrium expression relating to the 1:2 and 3:2 precipitates can be written as

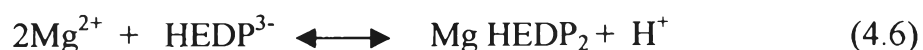


It is apparent from Equation 4.4 that an increase in the magnesium concentration or a decrease in the hydrogen concentration (an increase in the pH) will drive the equilibrium reaction to form a 3:2 precipitate.

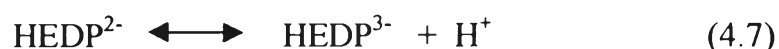
This phenomenon can be seen at a pH of 6 as well. The composition of the precipitates changed from 3:2 to 2:1 when the precipitating solution's Mg^{2+} :HEDP molar ratio changed from 1:1 to 10:1. The reaction to form a 3:2 precipitate can be written as



Assuming that HEDP species has to deprotonate at least three hydrogens to form a 2:1 precipitate, the precipitation reaction for a 2:1 precipitate can be written as



The following deprotonation reaction also occurs at these conditions



By coupling these equations together, a simple equilibrium expression relating the 1:2 and 3:2 precipitates can be written as

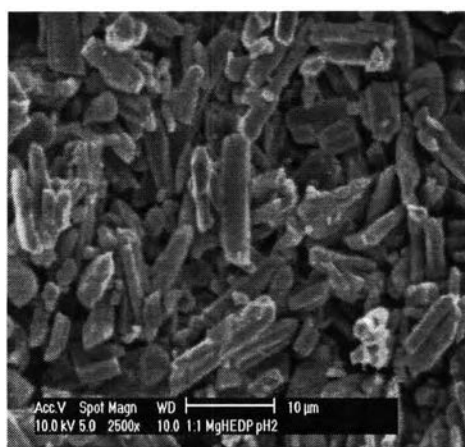


Equation 4.8 indicates that an increase in the magnesium concentration or a decrease in the hydrogen concentration (increase in the pH) will also drive the equilibrium reaction to form a 2:1 precipitate.

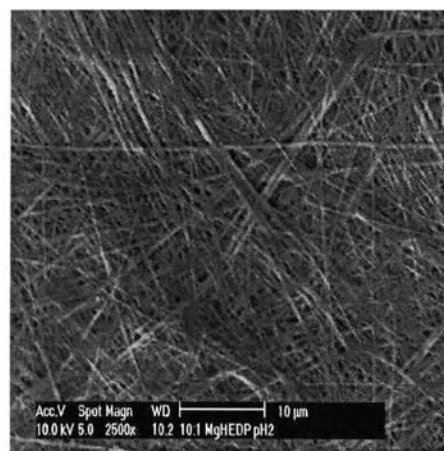
From the results shown in Table 4.2, 4.6 M magnesium chloride solution was added into 1M HEDP solution, the 1:2 precipitate was formed when the molar ratio of Mg^{2+} :HEDP in solution equal 1:35.27. Then, the magnesium chloride solution was kept adding more until the molar ratio of Mg^{2+} :HEDP in solution equal about 8.2:1, all of the 1:2 precipitate disappeared and the solution become clear. After this solution was left for five days, the 3:2 precipitate occurred. The morphologies of precipitate that formed before and after solution becomes clear are shown in Figure 4.3. This experiment confirmed that the Mg^{2+} :HEDP molar ratio in solution affected the resulting precipitate.

Table 4.2 Experimental results of precipitate transformation as a function of molar ratio of Mg^{2+} :HEDP in solution (at a constant pH of 2).

| Concentrations of Mg^{2+} and HEDP in solution (mol/l) | | Molar ratio of Mg^{2+} :HEDP in solution | Molar ratio of Mg:HEDP in precipitate | Note |
|--|-------|--|---------------------------------------|--|
| Mg^{2+} | HEDP | | | |
| 0.013 | 0.446 | 1:35.27 | 1:2.05 | First precipitate |
| 3.146 | 0.384 | 8.20:1 | - | Precipitate gone (clear solution) |
| 3.146 | 0.384 | 8.20:1 | 3:2.00 | Appearance of precipitate after 5 days |



Precipitate that formed before solution clear (1:2 precipitate)



Precipitate that formed after solution clear (3:2 precipitate)

Figure 4.3 Morphological structures of precipitates formed before and after the solution clear under the studied conditions described in Table 4.2.

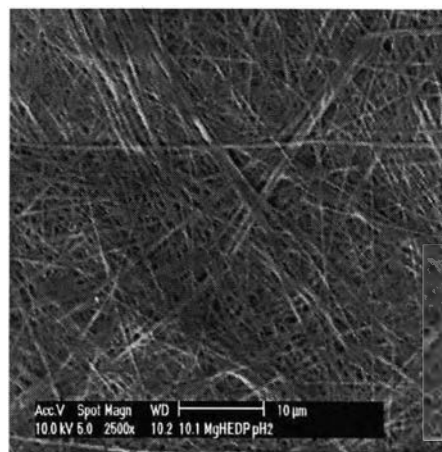
Each HEDP molecule has four ionizable protons that means four distinct Mg-HEDP molar ratios of precipitates can be formed. Three Mg:HEDP molar ratios in precipitates of 1:2, 3:2 and 2:1 were formed in these studied conditions. As shown in Table 4.1, at the Mg^{2+} :HEDP molar ratio of 1:1 and the pH of 2 in solution, the 1:2 precipitate was formed while at the pH of 6, the 3:2 precipitate was formed. Therefore, it can be concluded that the 1:1 Mg-HEDP precipitate is possibly formed at the 1:1 molar ratio in the solution and a pH value between 2 and 6. On the other hand, as can be seen from Table 4.2, at the pH of 2 and the Mg^{2+} :HEDP molar ratio of 1:35 in the solution, the 1:2 precipitate was formed while at the Mg^{2+} :HEDP molar ratio of the 8.2:1 in the solution, the 3:2 precipitate was formed. Therefore at a pH of 2, the 1:1 Mg-HEDP precipitate is possibly formed at a initial Mg^{2+} :HEDP molar ratio in solution between 1:35 and 8.2:1.

4.2.2 Coupled Effect of pH and Mg^{2+} :HEDP Molar Ratio in Precipitating Solution on Morphologies of Mg-HEDP Precipitates

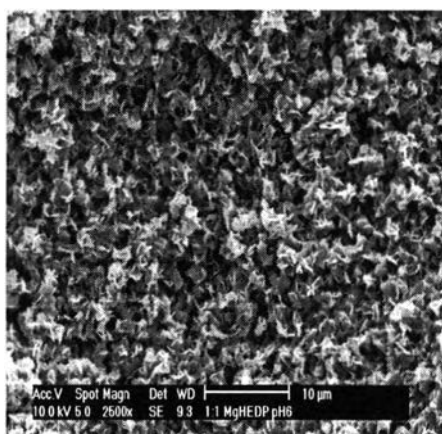
The morphologies of the four precipitates synthesized were studied by using a Scanning Electron Microscope (SEM). The micrographs of the resulting precipitates are shown in Figure 4.4. At a pH of 2 and an initial precipitating Mg^{2+} :HEDP molar ratio of 1:1, the 1:2 precipitate obtained had platelet structure while at a pH of 2 and an initial Mg^{2+} :HEDP molar ratio of 10:1, the 3:2 precipitate consisted of polydispersed, fibrous spindles. At a high pH of 6 and a low precipitating Mg^{2+} :HEDP molar ratio of 1:1, the 3:2 precipitate had irregularly flaky structure. In contrast at a high pH of 6 and a high initial Mg^{2+} :HEDP molar ratio of 10:1, the 2:1 precipitate had a granular or amorphous surface structure. Therefore, the pH and Mg^{2+} :HEDP molar ratio of precipitating solution strongly affected the morphologies of precipitates.



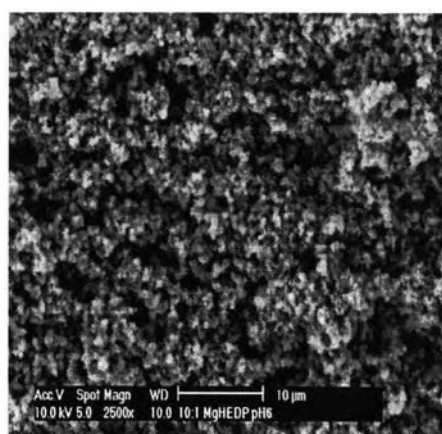
Magnesium:HEDP = 1:2



Magnesium:HEDP = 3:2



Magnesium:HEDP = 3:2



Magnesium:HEDP = 2:1

Figure 4.4 Morphological structures of distinct Mg-HEDP precipitates.

The difference of precipitate morphologies was reconfirmed by using X-ray Diffraction (XRD). From the XRD patterns shown in Figure 4.5, sharp intensity peaks were observed with the 1:2 and 3:2 precipitates which their morphologies were platelet structure and spindle, respectively. It clearly indicated that these precipitates are crystalline in nature. In contrast, the curve of the 2:1 precipitate that the precipitate morphology was granular particles had no distinct peaks, signifying an amorphous precipitate. This result can be interpreted that the lower molar ratio in precipitate results in the higher crystallinity.

4.2.3 Coupled Effect of pH and Mg²⁺:HEDP Molar Ratio of

Precipitating Solution on Solubility of Mg-HEDP Precipitate

From the results shown in Table 4.1, the 1:2 precipitate had the highest values of equilibrium solubility while the 2:1 precipitate had the lowest equilibrium solubility. This difference in the solubility values may be due to the fact that the higher molar ratio in precipitate had fewer sites that could hydrate due to the strong magnesium attachment, resulting in a more hydrophobic and insoluble precipitate.

The possible structures of precipitates are shown in Figure 4.6. The 1:2 Mg-HEDP precipitate has one magnesium atom bonding with two HEDP molecules while the 3:2 Mg-HEDP precipitate has three magnesium atoms bonding with two HEDP molecules. This precipitate has two possible different structures because it has two different morphologies. For the 2:1 Mg-HEDP precipitate, each HEDP molecule has two magnesium atoms. In order to confirm that these structures are the actual structures, the surface and functional group analyses of the precipitates need to be performed.

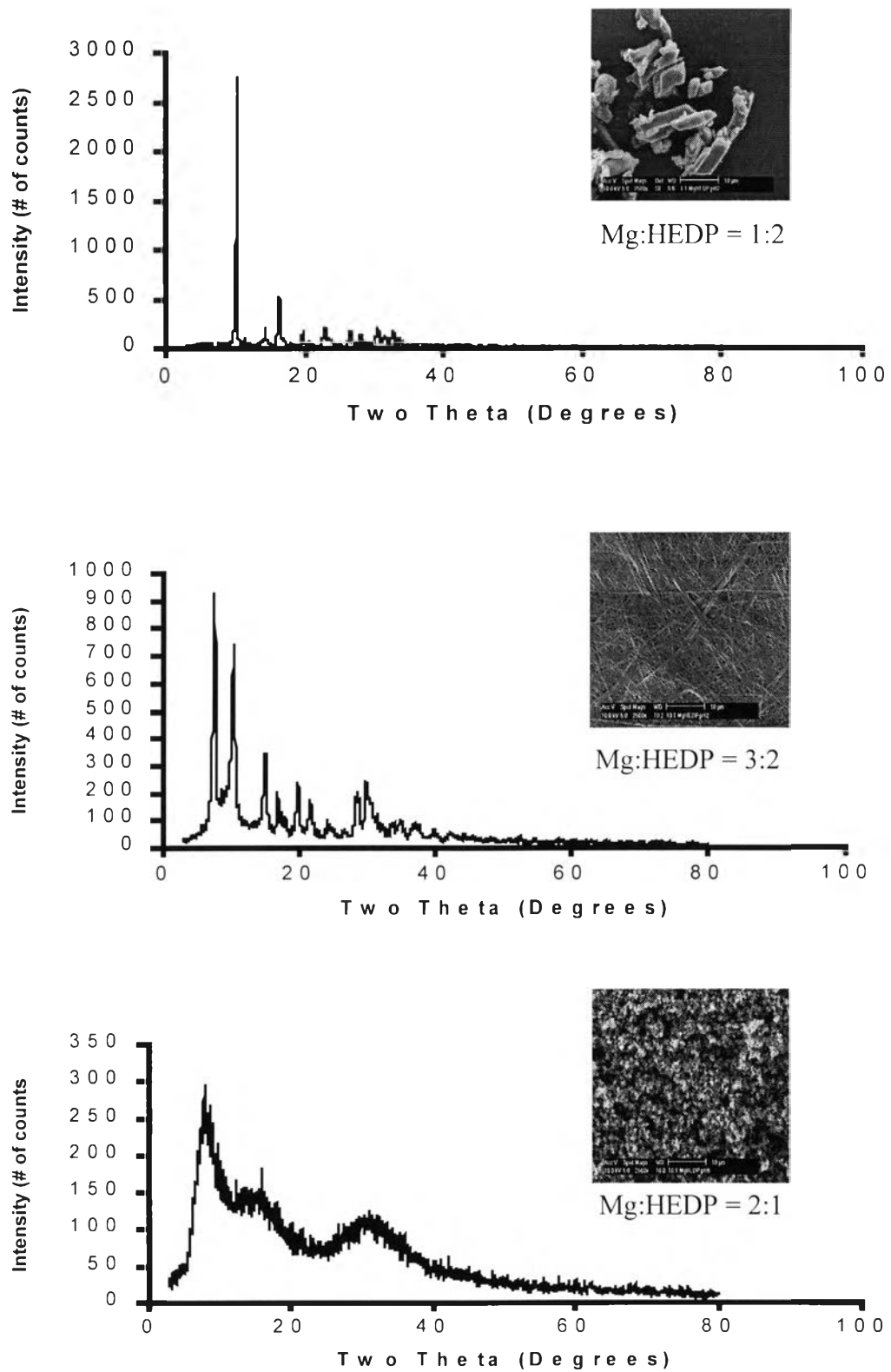
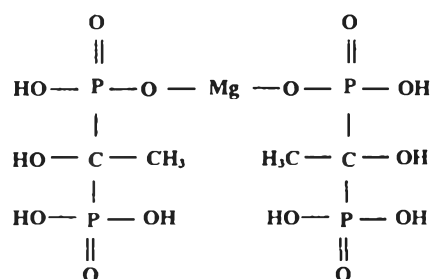
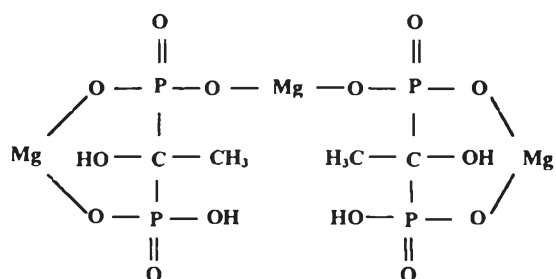


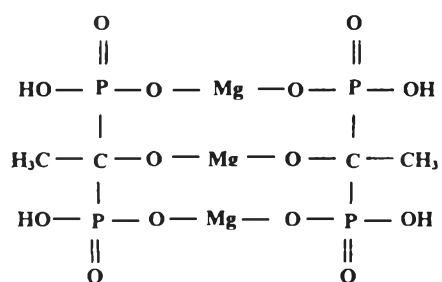
Figure 4.5 XRD patterns of three distinct precipitates obtained from this study.



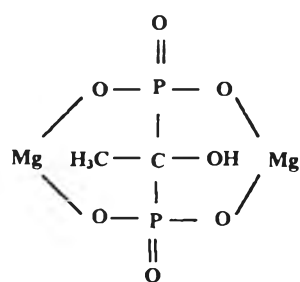
1 : 2 Magnesium-HEDP Precipitate



3 : 2 Magnesium-HEDP Precipitate



3 : 2 Magnesium-HEDP Precipitate



2 : 1 Magnesium-HEDP Precipitate

Figure 4.6 The possible structures of precipitates.