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APPENDICES

APPENDIX A

Batch Synthesis Procedure

Precipitating condition

pH	Molar ratio in solution Mg ²⁺ :HEDP	Molar product [HEDP][Mg] (M ²)	Conditions of HEDP and Mg before mixing			
			Conc. of HEDP (M)	Volume of HEDP solution (ml)	Conc. of Mg (M)	Volume of Mg solution (ml)
2	1:1	1.000	1.2771	78.2	4.6	21.8
2	1:1	0.160	0.4380	91.3	4.6	8.7
2	10:1	1.000	1.0000	31.3	4.6	68.7
6	1:1	0.005	0.0730	96.8	2.235	3.7
6	10:1	0.005	0.0249	90.0	2.235	10.0
6	10:1	0.030	0.0725	75.5	2.235	24.5

Note Total volume after mixing equal 100 ml.

APPENDIX B

Calculation of the Fraction of HDEP Species

1-Hydroxyethylidene-1,1diphosphonic acid is a polyprotic acid which dissociates in several steps, each of which is defined by an equilibrium constant as follows:

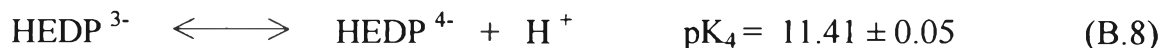
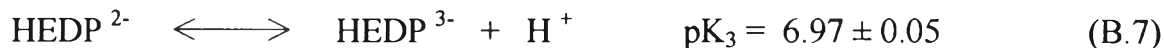
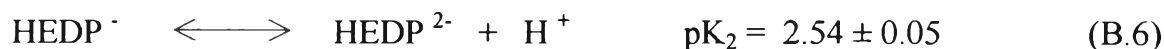
$$K_1 = \frac{[HEDP^-][H^+]}{[HEDP]} \quad (B.1)$$

$$K_2 = \frac{[HEDP^{2-}][H^+]}{[HEDP^-]} \quad (B.2)$$

$$K_3 = \frac{[HEDP^{3-}][H^+]}{[HEDP^{2-}]} \quad (B.3)$$

$$K_4 = \frac{[HEDP^{4-}][H^+]}{[HEDP^{3-}]} \quad (B.4)$$

When concentrations are specified in mol/l. The equilibrium constant at 25°C has the following values:



The total HEDP concentration is the sum of above species

$$H_T = [HEDP^{4-}] + [HEDP^{3-}] + [HEDP^{2-}] + [HEDP^-] + [HEDP] \quad (B.9)$$

From the above equilibrium equations the concentration of each ionic species can be defined as follow:

$$[HEDP] = \frac{[HEDP^-][H^+]}{K_1} \quad (B.10)$$

$$[HEDP^-] = \frac{[HEDP^{2-}][H^+]}{K_2} \quad (B.11)$$

$$[HEDP^{2-}] = \frac{[HEDP^{3-}][H^+]}{K_3} \quad (B.12)$$

$$[HEDP^{3-}] = \frac{[HEDP^{4-}][H^+]}{K_4} \quad (B.13)$$

To take log Equation (B.10), we obtain

$$\log[HEDP] = \log[HEDP^-] + \log[H^+] - \log[K_1] \quad (B.14)$$

$$\text{where } \text{pH} = -\log[H^+] \quad \text{and} \quad \text{p}K_1 = -\log K_1 \quad (B.15)$$

Substituting and rearranging, it becomes

$$\log \frac{[HEDP]}{[HEDP^-]} = \text{p}K_1 - \text{pH} \quad (B.16)$$

$$[HEDP] = [HEDP^-] \times 10^{\text{p}K_1 - \text{pH}} \quad (B.17)$$

In the same manner, we can obtain

$$[HEDP^-] = [HEDP^{2-}] \times 10^{\text{p}K_2 - \text{pH}} \quad (B.18)$$

$$[HEDP^{2-}] = [HEDP^{3-}] \times 10^{\text{p}K_3 - \text{pH}} \quad (B.19)$$

$$[HEDP^{3-}] = [HEDP^{4-}] \times 10^{\text{p}K_4 - \text{pH}} \quad (B.20)$$

The total HEDP concentration can then be expressed as:

$$H_T = [HEDP^{4-}] \times (1 + 10^{\text{p}K_4 - \text{pH}} + 10^{\text{p}K_3 + \text{p}K_4 - 2\text{pH}} + 10^{\text{p}K_2 + \text{p}K_3 + \text{p}K_4 - 3\text{pH}} + 10^{\text{p}K_1 + \text{p}K_2 + \text{p}K_3 + \text{p}K_4 - 4\text{pH}}) \quad (B.21)$$

Define

$$A = (1 + 10^{\text{p}K_4 - \text{pH}} + 10^{\text{p}K_3 + \text{p}K_4 - 2\text{pH}} + 10^{\text{p}K_2 + \text{p}K_3 + \text{p}K_4 - 3\text{pH}} + 10^{\text{p}K_1 + \text{p}K_2 + \text{p}K_3 + \text{p}K_4 - 4\text{pH}}) \quad (B.22)$$

Hence, Equation (B.21) becomes

$$\therefore [HEDP^{4-}] = H_T / A \quad (B.23)$$

and

$$\begin{aligned} \text{Fraction of } HEDP^{4-} \text{ species} &= [HEDP^{4-}] / H_T & (B.24) \\ &= 1/A \end{aligned}$$

Similarity, we can obtain

$$\text{Fraction of } HEDP^{3-} \text{ species} = 10^{pK_4 - pH} / A \quad (B.25)$$

$$\text{Fraction of } HEDP^{2-} \text{ species} = 10^{pK_4 + pK_3 - 2pH} / A \quad (B.26)$$

$$\text{Fraction of } HEDP^- \text{ species} = 10^{pK_4 + pK_3 + pK_2 - 3pH} / A \quad (B.27)$$

$$\text{Fraction of } HEDP \text{ species} = 10^{pK_4 + pK_3 + pK_2 + pK_1 - 4pH} / A \quad (B.28)$$

Substituting the values of pK_1 , pK_2 , pK_3 and pK_4 , the fraction of HEDP species is obtained.

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