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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:

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

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

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

$$K_4 = \frac{[HEDP4^-][H^+]}{[HEDP^{3-}]} \quad (B.4)$$

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

HEDP	$\longleftrightarrow$	$HEDP^-$ + H^+	$pK_1 < 1$	(B.5)
$HEDP^-$	$\longleftrightarrow$	$HEDP^{2-}$ + H^+	$pK_2 = 2.54 \pm 0.05$	(B.6)
$HEDP^{2-}$	$\longleftrightarrow$	$HEDP^{3-}$ + H^+	$pK_3 = 6.97 \pm 0.05$	(B.7)
$HEDP^{3-}$	$\longleftrightarrow$	$HEDP^{4-}$ + H^+	$pK_4 = 11.41 \pm 0.05$	(B.8)

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

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

where $pH = - \log [H^+]$ and $pK_1 = - \log K_1$ (B.15)

Substituting and rearranging, it becomes

$$\log \frac{[HEDP]}{[HEDP^-]} = pK_1 - pH \quad (B.16)$$

$$[HEDP] = [HEDP^-] \times 10^{pK_1 - pH} \quad (B.17)$$

In the same manner, we can obtain

$$[HEDP^-] = [HEDP^{2-}] \times 10^{pK_2 - pH} \quad (B.18)$$

$$[HEDP^{2-}] = [HEDP^{3-}] \times 10^{pK_3 - pH} \quad (B.19)$$

$$[HEDP^{-3}] = [HEDP^{4-}] \times 10^{pK_4 - pH} \quad (B.20)$$

The total HEDP concentration can then be expressed as:

$$H_T = [HEDP^{4-}] \times$$

$$(1 + 10^{pK_4 - pH} + 10^{pK_3 + pK_4 - 2pH} + 10^{pK_2 + pK_3 + pK_4 - 3pH} + 10^{pK_1 + pK_2 + pK + pK_{43} - 4pH}) \quad (B.21)$$

Define

$$A = (1 + 10^{pK_4 - pH} + 10^{pK_3 + pK_4 - 2pH} + 10^{pK_2 + pK_3 + pK_4 - 3pH} + 10^{pK_1 + pK_2 + pK + pK_{43} - 4pH}) \quad (B.22)$$

Hence, Equation (B.21) becomes

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

and Fraction of $HEDP^{4-}$ species = $[HEDP^{4-}]/H_T$ (B.24)

$= 1/A$

Similarity, we can obtain

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

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

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

Fraction of $HEDP$ species = $10^{pK_4+pK_3+pK_2+pK_1-4pH}/A$ (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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