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APPENDICES

Appendix A Solubility of BaSO₄ Precipitates in EDTA

The solubility of $BaSO_4$ precipitates in 0.25 M EDTA solution was first investigated. The effect of pH of EDTA solution on $BaSO_4$ solubility was studied by adjusting the originally prepared EDTA solution pH of 4.6 to 13 by adding potassium hydroxide. Figure 4.1 shows the solubility of $BaSO_4$ in these two different solution pHs. The results demonstrated that when pH of EDTA solution was increased from 4.6 to 13, the remarkable increase in the solubility of $BaSO_4$ from 334 mg/l to 1324 mg/l was observed. This can be explained by using the equilibrium acid constants (pK_a) of EDTA. The deprotonation curve of EDTA presenting the fraction of deprotonated species at different pH values is shown in Figure 4.2. It was indicated that EDTA can be completely deprotonated at pH 13, thus it can basically dissolve much more amount of $BaSO_4$ than at original condition of pH 4.6. The value of $BaSO_4$ solubility at pH 13 was adequate to be used as the condition for completely dissolving the $BaSO_4$ precipitates in order to establish the correlation between the turbidity and the amount of $BaSO_4$ precipitates.
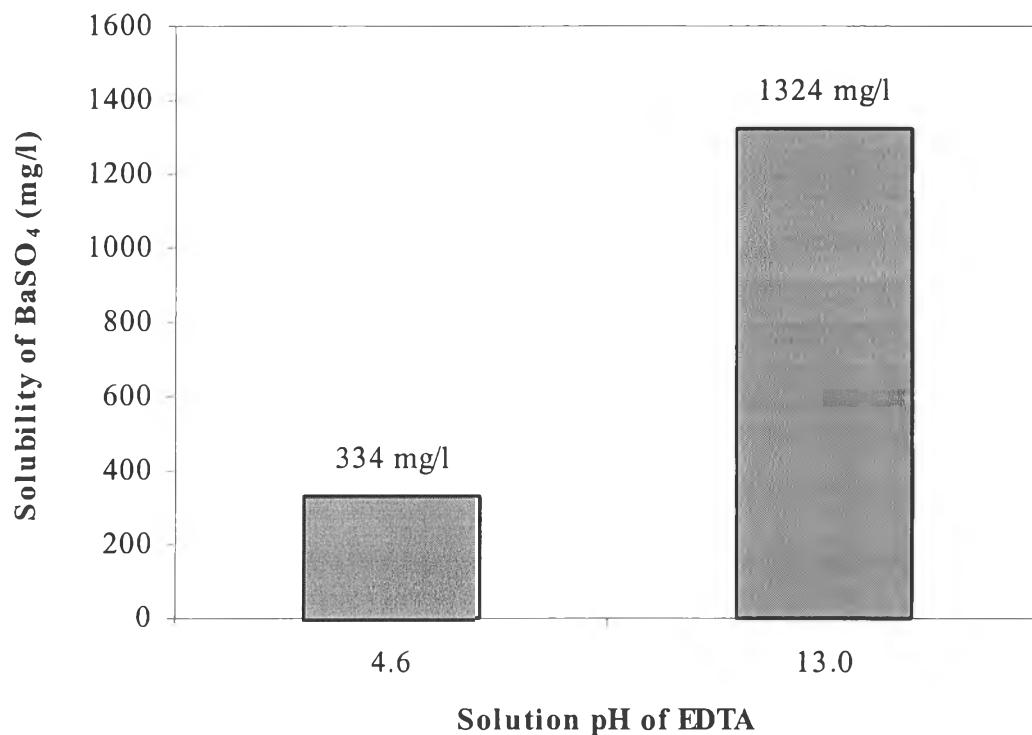
**Figure A.1** The solubility of $BaSO_4$ in EDTA solution at pH 4.6 and 13.0.
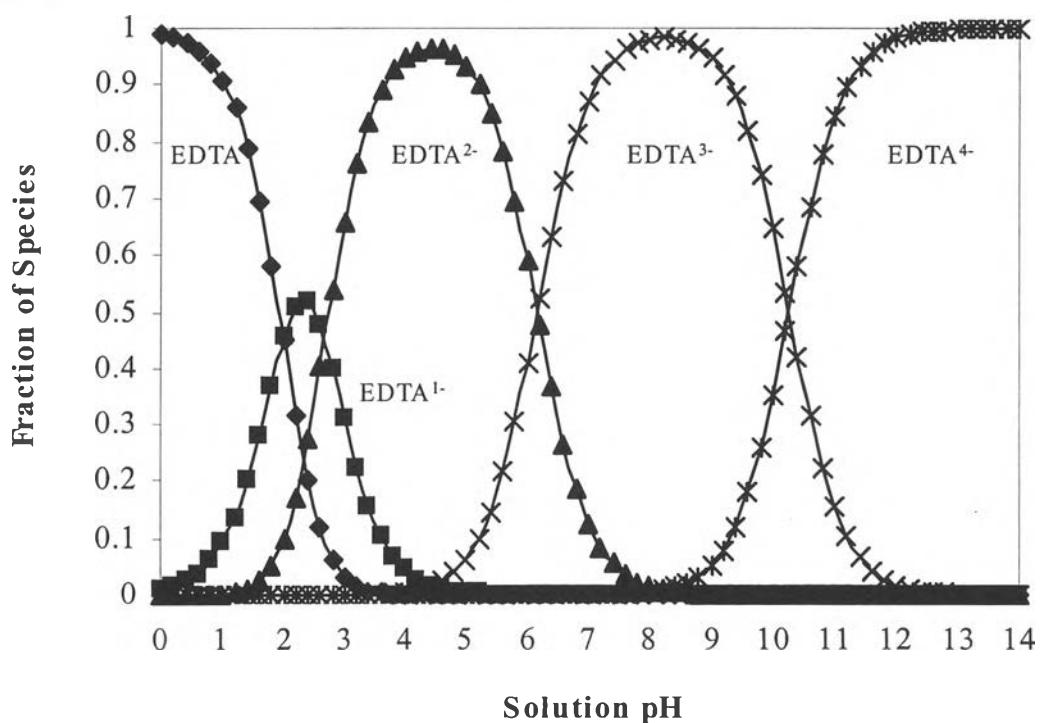
Figure A.2 The deprotonation curve of EDTA and the resulting species composition as a function of solution pH.

Appendix B Experimental Data

1. Experimental Data of the Critical Supersaturation Ratio

Table B.1 The critical supersaturation ratio data for the absence of scale inhibitors.

Testing time (h)	Critical supersaturation ratio						Average
	pH 4		pH 6		pH 8		
	Batch 1	Batch 2	Batch 1	Batch 2	Batch 1	Batch 2	
2	1.55E+02	1.68E+02	1.68E+02	1.41E+02	1.38E+02	1.62E+02	1.55E+02
24	1.43E+02	1.30E+02	1.40E+02	1.34E+02	1.30E+02	1.24E+02	1.34E+02
48	1.19E+02	1.26E+02	1.24E+02	1.26E+02	1.25E+02	1.24E+02	1.24E+02
72	1.17E+02	1.18E+02	1.12E+02	1.00E+02	1.06E+02	1.14E+02	1.11E+02
96	9.70E+01	1.07E+02	8.99E+01	9.85E+01	9.69E+01	1.15E+02	1.01E+02
192	9.50E+01	9.78E+01	8.81E+01	8.96E+01	8.66E+01	9.52E+01	9.21E+01
360	8.30E+01	7.71E+01	7.38E+01	7.31E+01	6.99E+01	7.71E+01	7.57E+01
720	6.59E+01	6.08E+01	6.69E+01	6.01E+01	5.65E+01	5.45E+01	6.08E+01
2250	5.54E+01	4.68E+01	5.05E+01	5.13E+01	4.89E+01	3.77E+01	4.84E+01

Table B.2 The critical supersaturation ratio data for ATMP 2.5 x 10^{-5} M and initial solution pH of 6.

Testing time (h)	Critical supersaturation ratio		
	Batch 1	Batch 2	Average
2	2.48E+03	1.62E+03	2.05E+03
24	1.73E+03	1.27E+03	1.50E+03
48	3.81E+02	8.03E+02	5.92E+02
72	5.75E+02	3.20E+02	4.48E+02
96	2.63E+02	4.83E+02	3.73E+02
192	2.86E+02	2.92E+02	2.89E+02
360	2.54E+02	3.43E+02	2.98E+02
720	2.18E+02	2.97E+02	2.57E+02
2250	2.10E+02	3.04E+02	2.57E+02

Table B.3 The critical supersaturation ratio data for ATMP 5.0 x 10^{-5} M and initial solution pH of 6.

Testing time (h)	Critical supersaturation ratio		
	Batch 1	Batch 2	Average
2	3.29E+03	2.90E+03	3.09E+03
24	2.32E+03	2.02E+03	2.17E+03
48	1.96E+03	1.70E+03	1.83E+03
72	1.17E+03	1.58E+03	1.37E+03
96	9.10E+02	1.12E+03	1.02E+03
192	8.44E+02	1.11E+03	9.77E+02
360	7.75E+02	1.05E+03	9.12E+02
720	7.39E+02	1.03E+03	8.86E+02
2250	7.93E+02	1.00E+03	8.97E+02

Table B.4 The critical supersaturation ratio data for ATMP 7.5 x 10^{-5} M and initial solution pH of 6.

Testing time (h)	Critical supersaturation ratio		
	Batch 1	Batch 2	Average
2	3.89E+03	3.31E+03	3.60E+03
24	3.49E+03	3.16E+03	3.33E+03
48	3.29E+03	2.78E+03	3.03E+03
72	3.24E+03	2.85E+03	3.05E+03
96	2.97E+03	2.58E+03	2.78E+03
192	2.44E+03	2.06E+03	2.25E+03
360	2.23E+03	1.97E+03	2.10E+03
720	2.44E+03	1.84E+03	2.14E+03
2250	2.33E+03	1.84E+03	2.08E+03

Table B.5 The critical supersaturation ratio data for ATMP 1.0 x 10^{-4} M and initial solution pH of 6.

Testing time (h)	Critical supersaturation ratio		
	Batch 1	Batch 2	Average
2	4.59E+03	5.38E+03	4.99E+03
24	4.75E+03	4.26E+03	4.50E+03
48	4.29E+03	3.88E+03	4.08E+03
72	4.04E+03	3.73E+03	3.89E+03
96	3.92E+03	3.48E+03	3.70E+03
192	3.52E+03	3.12E+03	3.32E+03
360	2.95E+03	2.88E+03	2.91E+03
720	2.70E+03	2.86E+03	2.78E+03
2250	2.82E+03	2.64E+03	2.73E+03

Table B.6 The critical supersaturation ratio data for ATMP 7.5 x 10^{-3} M and initial solution pH of 6.

Testing time	Critical supersaturation ratio		
(h)	Batch 1	Batch 2	Average
2	1.35E+04	1.31E+04	1.33E+04
24	1.15E+04	1.10E+04	1.12E+04
48	1.14E+04	1.09E+04	1.11E+04
72	1.09E+04	1.13E+04	1.11E+04
96	1.00E+04	9.66E+03	9.85E+03
192	8.22E+03	7.93E+03	8.07E+03
360	8.14E+03	7.53E+03	7.83E+03
720	7.86E+03	7.50E+03	7.68E+03
2250	7.79E+03	7.61E+03	7.70E+03

Table B.7 The critical supersaturation ratio data for ATMP 7.5 x 10^{-5} M and initial solution pH of 4.

Testing time	Critical supersaturation ratio		
(h)	Batch 1	Batch 2	Average
2	1.79E+03	1.60E+03	1.70E+03
24	7.89E+02	1.20E+03	9.97E+02
48	7.92E+02	4.45E+02	6.18E+02
72	7.50E+02	3.41E+02	5.45E+02
96	4.74E+02	2.91E+02	3.83E+02
192	4.13E+02	2.56E+02	3.34E+02
360	4.06E+02	2.37E+02	3.21E+02
720	4.35E+02	2.21E+02	3.28E+02
2250	4.20E+02	2.13E+02	3.17E+02

Table B.8 The critical supersaturation ratio data for ATMP 7.5 x 10^{-5} M and initial solution pH of 8.

Testing time	Critical supersaturation ratio		
(h)	Batch 1	Batch 2	Average
2	6.63E+03	5.81E+03	6.22E+03
24	5.67E+03	5.14E+03	5.41E+03
48	4.73E+03	4.50E+03	4.61E+03
72	4.68E+03	4.13E+03	4.40E+03
96	4.57E+03	3.89E+03	4.23E+03
192	4.21E+03	3.71E+03	3.96E+03
360	4.15E+03	3.74E+03	3.95E+03
720	4.07E+03	3.71E+03	3.89E+03
2250	4.03E+03	3.79E+03	3.91E+03

Table B.9 The critical supersaturation ratio data for DTPMP 2.5 x 10^{-5} M and initial solution pH of 6.

Testing time (h)	Critical supersaturation ratio		
	Batch 1	**Batch 2**	**Average**
2	8.21E+03	8.78E+03	8.50E+03
24	6.95E+03	7.50E+03	7.23E+03
48	6.41E+03	6.92E+03	6.66E+03
72	6.34E+03	7.36E+03	6.85E+03
96	5.97E+03	6.83E+03	6.40E+03
192	5.53E+03	6.38E+03	5.95E+03
360	5.13E+03	5.63E+03	5.38E+03
720	4.85E+03	5.54E+03	5.20E+03
2250	4.69E+03	5.61E+03	5.15E+03

Table B.10 The critical supersaturation ratio data for DTPMP 5.0 x 10^{-5} M and initial solution pH of 6.

Testing time (h)	Critical supersaturation ratio		
	Batch 1	**Batch 2**	**Average**
2	9.84E+03	1.09E+04	1.04E+04
24	8.58E+03	9.38E+03	8.98E+03
48	7.86E+03	9.00E+03	8.43E+03
72	7.66E+03	8.27E+03	7.96E+03
96	7.54E+03	7.72E+03	7.63E+03
192	6.94E+03	7.33E+03	7.14E+03
360	6.65E+03	6.21E+03	6.43E+03
720	6.55E+03	6.92E+03	6.74E+03
2250	6.36E+03	6.73E+03	6.54E+03

Table B.11 The critical supersaturation ratio data for DTPMP 7.5 x 10^{-5} M and initial solution pH of 6.

Testing time (h)	Critical supersaturation ratio		
	Batch 1	**Batch 2**	**Average**
2	1.23E+04	1.33E+04	1.28E+04
24	1.17E+04	1.28E+04	1.23E+04
48	1.05E+04	1.17E+04	1.11E+04
72	9.90E+03	1.06E+04	1.02E+04
96	9.41E+03	1.02E+04	9.81E+03
192	8.52E+03	9.48E+03	9.00E+03
360	8.21E+03	9.17E+03	8.69E+03
720	8.46E+03	8.66E+03	8.56E+03
2250	8.10E+03	9.18E+03	8.64E+03

Table B.12 The critical supersaturation ratio data for DTPMP 1.0×10^{-4} M and initial solution pH of 6.

Testing time	Critical supersaturation ratio		
(h)	Batch 1	Batch 2	Average
2	1.44E+04	1.56E+04	1.50E+04
24	1.38E+04	1.43E+04	1.41E+04
48	1.36E+04	1.42E+04	1.39E+04
72	1.31E+04	1.34E+04	1.33E+04
96	1.23E+04	1.29E+04	1.26E+04
192	1.15E+04	1.24E+04	1.20E+04
360	1.09E+04	1.18E+04	1.14E+04
720	1.01E+04	1.07E+04	1.04E+04
2250	9.91E+03	1.02E+04	1.01E+04

Table B.13 The critical supersaturation ratio data for DTPMP 7.5×10^{-3} M and initial solution pH of 6.

Testing time	Critical supersaturation ratio		
(h)	Batch 1	Batch 2	Average
2	3.10E+04	3.34E+04	3.22E+04
24	3.03E+04	3.20E+04	3.11E+04
48	2.85E+04	3.11E+04	2.98E+04
72	2.80E+04	3.00E+04	2.90E+04
96	2.67E+04	2.86E+04	2.76E+04
192	2.43E+04	2.78E+04	2.60E+04
360	2.33E+04	2.60E+04	2.46E+04
720	2.39E+04	2.46E+04	2.42E+04
2250	2.27E+04	2.40E+04	2.34E+04

Table B.14 The critical supersaturation ratio data for DTPMP 7.5×10^{-5} M and initial solution pH of 4.

Testing time	Critical supersaturation ratio		
(h)	Batch 1	Batch 2	Average
2	1.04E+04	1.10E+04	1.07E+04
24	9.66E+03	1.05E+04	1.01E+04
48	9.08E+03	9.91E+03	9.49E+03
72	8.65E+03	9.40E+03	9.03E+03
96	7.66E+03	8.42E+03	8.04E+03
192	7.04E+03	7.54E+03	7.29E+03
360	6.50E+03	7.14E+03	6.82E+03
720	6.49E+03	7.01E+03	6.75E+03
2250	6.39E+03	7.30E+03	6.84E+03

Table B.15 The critical supersaturation ratio data for DTPMP 7.5 x 10^{-5} M and initial solution pH of 8.

Testing time (h)	Critical supersaturation ratio		
	Batch 1	Batch 2	Average
2	1.45E+04	1.48E+04	1.47E+04
24	1.40E+04	1.46E+04	1.43E+04
48	1.30E+04	1.36E+04	1.33E+04
72	1.27E+04	1.32E+04	1.30E+04
96	1.22E+04	1.28E+04	1.25E+04
192	1.13E+04	1.23E+04	1.18E+04
360	1.01E+04	1.07E+04	1.04E+04
720	9.95E+03	1.09E+04	1.04E+04
2250	9.84E+03	1.07E+04	1.03E+04

Table B.16 The critical supersaturation ratio data for PPCA 2.5 x 10^{-5} M and initial solution pH of 6.

Testing time (h)	Critical supersaturation ratio		
	Batch 1	Batch 2	Average
2	1.66E+04	1.85E+04	1.76E+04
24	1.44E+04	1.64E+04	1.54E+04
48	1.38E+04	1.57E+04	1.47E+04
72	1.29E+04	1.50E+04	1.40E+04
96	1.20E+04	1.42E+04	1.31E+04
192	1.04E+04	1.36E+04	1.20E+04
360	1.06E+04	1.28E+04	1.17E+04
720	9.79E+03	1.26E+04	1.12E+04
2250	9.66E+03	1.20E+04	1.08E+04

Table B.17 The critical supersaturation ratio data for PPCA 5.0 x 10^{-5} M and initial solution pH of 6.

Testing time (h)	Critical supersaturation ratio		
	Batch 1	Batch 2	Average
2	2.28E+04	2.40E+04	2.34E+04
24	1.86E+04	2.09E+04	1.98E+04
48	1.80E+04	1.93E+04	1.86E+04
72	1.66E+04	1.81E+04	1.73E+04
96	1.57E+04	1.70E+04	1.63E+04
192	1.44E+04	1.59E+04	1.52E+04
360	1.28E+04	1.44E+04	1.36E+04
720	1.28E+04	1.39E+04	1.34E+04
2250	1.25E+04	1.43E+04	1.34E+04

Table B.18 The critical supersaturation ratio data for PPCA 7.5×10^{-5} M and initial solution pH of 6.

Testing time	Critical supersaturation ratio		
(h)	Batch 1	Batch 2	Average
2	2.74E+04	2.81E+04	2.77E+04
24	2.50E+04	2.51E+04	2.50E+04
48	2.26E+04	2.50E+04	2.38E+04
72	2.17E+04	2.35E+04	2.26E+04
96	2.20E+04	2.33E+04	2.27E+04
192	2.09E+04	2.13E+04	2.11E+04
360	1.90E+04	2.06E+04	1.98E+04
720	1.83E+04	1.93E+04	1.88E+04
2250	1.78E+04	1.95E+04	1.87E+04

Table B.19 The critical supersaturation ratio data for PPCA 1.0×10^{-4} M and initial solution pH of 6.

Testing time	Critical supersaturation ratio		
(h)	Batch 1	Batch 2	Average
2	3.17E+04	3.27E+04	3.22E+04
24	2.88E+04	3.10E+04	2.99E+04
48	2.81E+04	2.91E+04	2.86E+04
72	2.56E+04	2.84E+04	2.70E+04
96	2.44E+04	2.57E+04	2.51E+04
192	2.34E+04	2.51E+04	2.43E+04
360	2.29E+04	2.42E+04	2.35E+04
720	2.19E+04	2.41E+04	2.30E+04
2250	2.15E+04	2.34E+04	2.25E+04

Table B.20 The critical supersaturation ratio data for PPCA 7.5×10^{-3} M and initial solution pH of 6.

Testing time	Critical supersaturation ratio		
(h)	Batch 1	Batch 2	Average
2	8.09E+04	7.09E+04	7.59E+04
24	7.09E+04	6.32E+04	6.71E+04
48	6.26E+04	5.85E+04	6.05E+04
72	6.20E+04	5.57E+04	5.89E+04
96	6.00E+04	5.28E+04	5.64E+04
192	5.55E+04	4.79E+04	5.17E+04
360	4.96E+04	4.30E+04	4.63E+04
720	4.77E+04	4.23E+04	4.50E+04
2250	4.68E+04	4.43E+04	4.55E+04

Table B.21 The critical supersaturation ratio data for PPCA 7.5 x 10^{-5} M and initial solution pH of 4.

Testing time	Critical supersaturation ratio		
(h)	Batch 1	Batch 2	Average
2	2.16E+04	2.07E+04	2.11E+04
24	1.99E+04	1.78E+04	1.88E+04
48	1.95E+04	1.64E+04	1.80E+04
72	1.75E+04	1.57E+04	1.66E+04
96	1.65E+04	1.53E+04	1.59E+04
192	1.54E+04	1.41E+04	1.47E+04
360	1.35E+04	1.20E+04	1.28E+04
720	1.31E+04	1.16E+04	1.24E+04
2250	1.35E+04	9.70E+03	1.16E+04

Table B.22 The critical supersaturation ratio data for PPCA 7.5 x 10^{-5} M and initial solution pH of 8.

Testing time	Critical supersaturation ratio		
(h)	Batch 1	Batch 2	Average
2	3.44E+04	3.35E+04	3.39E+04
24	3.06E+04	3.18E+04	3.12E+04
48	2.95E+04	2.80E+04	2.87E+04
72	2.82E+04	2.77E+04	2.80E+04
96	2.83E+04	2.62E+04	2.72E+04
192	2.71E+04	2.51E+04	2.61E+04
360	2.55E+04	2.18E+04	2.37E+04
720	2.34E+04	2.26E+04	2.30E+04
2250	2.29E+04	2.28E+04	2.28E+04

2. Experimental Data of the Particle Size Distribution

Table B.23 The particle size distribution data for ATMP 2.5 x 10^{-5} M and initial solution pH of 6.

Particle size (µm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	0	0	0	0
1 - 2	0	0	0	0
2 - 3	0	0	0	0.5
3 - 4	0.2	0	0	0
4 - 5	71.4	2.7	10.6	1.2
5 - 6	28.4	47.9	8.9	18
6 - 7	0	54.8	65.2	56.8
7 - 8	0	0	15.3	23.5
Mean diameter (µm)	4.82	6.09	6.61	6.78

Table B.24 The particle size distribution data for ATMP 5.0 x 10^{-5} M and initial solution pH of 6.

Particle size (µm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	0	0	0	0
1 - 2	0	0.5	0	0
2 - 3	0.9	0	0	0.7
3 - 4	42.7	8.9	3.2	0.7
4 - 5	53.3	27.3	15.2	18.4
5 - 6	3.1	61.5	44.7	51.1
6 - 7	0	1.8	36.9	26.2
7 - 8	0	0	0	2.9
Mean diameter (µm)	4.58	5.44	5.80	5.88

Table B.25 The particle size distribution data for ATMP 7.5 x 10^{-5} M and initial solution pH of 6.

Particle size (µm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	0.3	0	0	0
1 - 2	0	0	0	0.9
2 - 3	2.3	0.9	1.8	1.8
3 - 4	60.6	20.7	8.3	4.2
4 - 5	36.8	54.9	63.1	47.5
5 - 6	0	23.5	25.1	35.2
6 - 7	0	0	1.7	10.4
7 - 8	0	0	0	0
Mean diameter (µm)	3.78	4.58	4.89	4.94

Table B.26 The particle size distribution data for ATMP 1.0 x 10^{-4} M and initial solution pH of 6.

Particle size (μm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	28.5	17.9	4.8	6.4
1 - 2	37.9	13.5	20.9	15.6
2 - 3	24.4	41.3	33.4	24.5
3 - 4	9.2	26.6	37	36.3
4 - 5	0	0.7	3.9	16.9
5 - 6	0	0	0	0.3
6 - 7	0	0	0	0
Mean diameter (μm)	1.86	2.57	2.87	2.90

Table B.27 The particle size distribution data for ATMP 7.5 x 10^{-5} M and initial solution pH of 4.

Particle size (μm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 – 1	0	0	0	0
1 – 2	0	0	0	0
2 – 3	0	0	0	0
3 – 4	0	0.5	0	0
4 – 5	46.4	0	0.9	0
5 – 6	53.6	20.3	9.2	5.3
6 – 7	0	64.4	46.2	28.5
7 – 8	0	14.8	43.7	63.5
8 – 9	0	0	0	2.7
Mean diameter (μm)	5.03	6.45	6.97	7.21

Table B.28 The particle size distribution data for ATMP 7.5 x 10^{-5} M and initial solution pH of 8.

Particle size (μm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	25.4	7.4	4.9	4.8
1 - 2	18.3	19.4	15	10.7
2 - 3	54.5	42.1	28.9	24.5
3 - 4	1.8	30.6	46.8	43.7
4 - 5	0	0.5	4.4	15.9
5 - 6	0	0	0	0.4
6 - 7	0	0	0	0
7 - 8	0	0	0	0
Mean diameter (μm)	2.32	2.86	3.09	3.13

Table B.29 The particle size distribution data for DTPMP 2.5 x 10^{-5} M and initial solution pH of 6.

Particle size (µm)	Percent by volume at different testing time			
	2 h	**24 h**	**48 h**	**72 h**
0 - 1	0	0.9	0	0
1 - 2	4.9	0	0.2	0.8
2 - 3	32.1	1.8	1.7	3.7
3 - 4	63	23.2	10.9	13.6
4 - 5	0	56.7	62.8	42
5 - 6	0	17.4	24.4	37.5
6 - 7	0	0	0	2.4
7 - 8	0	0	0	0
Mean diameter (µm)	3.21	4.34	4.76	4.89

Table B.30 The particle size distribution data for DTPMP 5.0 x 10^{-5} M and initial solution pH of 6.

Particle size (µm)	Percent by volume at different testing time			
	2 h	**24 h**	**48 h**	**72 h**
0 - 1	0	0	0	0.4
1 - 2	3.8	0.9	0.3	0
2 - 3	45.7	17.5	16.7	6.3
3 - 4	47.3	43.7	29.8	22.4
4 - 5	3.2	36.2	46.1	52.8
5 - 6	0	1.2	6.3	18
6 - 7	0	0.5	0.8	0
7 - 8	0	0	0	0.1
Mean diameter (µm)	3.07	3.88	4.22	4.27

Table B.31 The particle size distribution data for DTPMP 7.5 x 10^{-5} M and initial solution pH of 6.

Particle size (µm)	Percent by volume at different testing time			
	2 h	**24 h**	**48 h**	**72 h**
0 - 1	0.5	3.6	6.6	0.9
1 - 2	11.3	9.9	6.6	1.7
2 - 3	74.2	20.1	13.9	18.4
3 - 4	8.9	50.5	58.5	64.8
4 - 5	5.1	15.9	14.4	11.1
5 - 6	0	0	0	3.1
6 - 7	0	0	0	0
7 - 8	0	0	0	0
Mean diameter (µm)	2.48	3.17	3.45	3.46

Table B.32 The particle size distribution data for DTPMP 1.0×10^{-4} M and initial solution pH of 6.

Particle size (μm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	50.8	27.1	10.6	18.8
1 - 2	23.3	43.5	57.5	53.7
2 - 3	13.9	16.2	21.3	17.1
3 - 4	6.3	9.1	4.2	3.3
4 - 5	5.7	4.1	3.8	2.9
5 - 6	0	0	2.6	4.2
6 - 7	0	0	0	0
7 - 8	0	0	0	0
Mean diameter (μm)	1.01	1.62	1.89	1.87

Table B.33 The particle size distribution data for DTPMP 7.5×10^{-5} M and initial solution pH of 4.

Particle size (μm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	0	0	0	0
1 - 2	2.2	0	0	0
2 - 3	21.2	0.5	0	0
3 - 4	76.6	16.8	5.9	3.7
4 - 5	0	54.8	45.7	42.4
5 - 6	0	27.9	48.1	50.4
6 - 7	0	0	0.3	3.5
7 - 8	0	0	0	0
Mean diameter (μm)	3.36	4.58	4.92	5.09

Table B.34 The particle size distribution data for DTPMP 7.5×10^{-5} M and initial solution pH of 8.

Particle size (μm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	48.4	29.2	24.3	21.5
1 - 2	12.6	35.7	29.9	43.8
2 - 3	24.9	22.3	31.7	19
3 - 4	14.1	11.6	9.4	9.2
4 - 5	0	1.2	4.7	3.9
5 - 6	0	0	0	2.6
6 - 7	0	0	0	0
7 - 8	0	0	0	0
Mean diameter (μm)	1.13	1.57	1.71	1.74

Table B.35 The particle size distribution data for PPCA 2.5 x 10^{-5} M and initial solution pH of 6.

Particle size (μm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	12.3	2.7	4.2	1.1
1 - 2	58.7	12.4	5.9	9.3
2 - 3	24.5	53.1	34.3	28.6
3 - 4	4.5	27.9	42	48.2
4 - 5	0	3.9	12.9	9.1
5 - 6	0	0	0.7	3.7
6 - 7	0	0	0	0
7 - 8	0	0	0	0
Mean diameter (μm)	1.77	2.79	3.10	3.18

Table B.36 The particle size distribution data for PPCA 5.0 x 10^{-5} M and initial solution pH of 6.

Particle size (μm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	23.3	5.8	7.7	3.1
1 - 2	45.8	22.6	16.3	19.3
2 - 3	11.7	49.2	52.9	42.8
3 - 4	16.7	18.7	17.6	28.9
4 - 5	2.5	3.7	5.5	4.6
5 - 6	0	0	0	1.3
6 - 7	0	0	0	0
7 - 8	0	0	0	0
Mean diameter (μm)	1.65	2.37	2.59	2.63

Table B.37 The particle size distribution data for PPCA 7.5 x 10^{-5} M and initial solution pH of 6.

Particle size (μm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	42.7	20.1	9.8	14.2
1 - 2	37.5	44.6	42.8	40.5
2 - 3	10.3	23.4	30.7	24.3
3 - 4	7.5	5.7	9	15.4
4 - 5	0.7	4.5	7.3	3.3
5 - 6	1.3	1.7	0.4	2.3
6 - 7	0	0	0	0
7 - 8	0	0	0	0
Mean diameter (μm)	1.19	1.72	1.89	1.91

Table B.38 The particle size distribution data for PPCA 1.0×10^{-4} M and initial solution pH of 6.

Particle size (µm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	67.4	32.7	28.5	18.8
1 - 2	15.8	45.1	43.3	53.4
2 - 3	7.7	10.6	17	14.5
3 - 4	3.4	2.7	6.1	8.2
4 - 5	4.5	7.5	3	4.3
5 - 6	1.2	1.4	2.1	0.8
6 - 7	0	0	0	0
7 - 8	0	0	0	0
Mean diameter (µm)	0.49	1.04	1.28	1.30

Table B.39 The particle size distribution data for PPCA 7.5×10^{-5} M and initial solution pH of 4.

Particle size (µm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	13.5	3.9	5.1	4.3
1 - 2	41.5	21.5	14.8	2.1
2 - 3	18.7	14.3	23.6	18.5
3 - 4	25.2	45.8	39.3	47
4 - 5	1.1	14.2	15.8	24.6
5 - 6	0	0.3	1.4	2.9
6 - 7	0	0	0	0.6
7 - 8	0	0	0	0
Mean diameter (µm)	1.98	3.08	3.26	3.35

Table B.40 The particle size distribution data for PPCA 7.5×10^{-5} M and initial solution pH of 8.

Particle size (µm)	Percent by volume at different testing time			
	2 h	24 h	48 h	72 h
0 - 1	45.8	29.1	16	22.9
1 - 2	25.5	39.7	47.3	39.5
2 - 3	10.8	15.4	28.5	18.9
3 - 4	14.2	8.5	4.2	12.7
4 - 5	1.1	6.2	3.6	5.2
5 - 6	2.6	0.9	0	0.8
6 - 7	0	0.2	0.4	0
7 - 8	0	0	0	0
Mean diameter (µm)	0.92	1.21	1.35	1.32

Appendix C Calculation Method for Deprotonation Curve of Scale Inhibitors

1. Equilibrium Acid Constant

The equilibrium acid constant is defined in terms of the activity of product species divided by reactant species as shown below:

Consider the following reaction:

$$HA + H_2O \leftrightarrow A^- + H_3O^+$$

The equilibrium acid constant is expressed as:

$$Ka = \frac{a_{H3O+} \, a_{A-}}{a_{HA}} \tag{C.1}$$

where 'a' denotes the activities of the hydrated species

Rearranging Eq. (C.1):

$$a_{H3O+} = \frac{(Ka)(a_{HA})}{a_{A-}} \tag{C.2}$$

Taking the logarithms both sides of Eq. (C.2):

$$-\log a_{H3O+} = -\log \left[\frac{(Ka)(a_{HA})}{a_{A-}} \right] \tag{C.3}$$

Rearranging Eq. (C.3):

$$-\log a_{H3O+} = -\left[\log Ka - \log \frac{a_{A-}}{a_{HA}}\right] \qquad (C.4)$$

where $pH = -\log a_{H3O+}$ and $pKa = -\log Ka$

Therefore, Eq. (C.4) becomes:

$$pH = pKa + \log\left[\frac{a_{A-}}{a_{HA}}\right] \qquad (C.5)$$

or

$$pH = pKa + \log\left[\frac{a_{basic\,species}}{a_{acidic\,species}}\right] \qquad (C.6)$$

2. Activity

The activity is defined as:

$$a_i = C_i f_i \qquad (C.7)$$

where C_i = Molar concentration (M)

f_i = Activity coefficient

Substituting Eq. (C.7) into Eq. (C.1):

$$Ka = \frac{(C_{H3O+} f_{H3O+})(C_{A-} f_{A-})}{(C_{HA} f_{HA})} \qquad (C.8)$$

Rearranging Eq. (C.8):

$$Ka = \frac{C_{H3O+} \, C_{A-}}{C_{HA}} \cdot \frac{f_{H3O+} \, f_{A-}}{f_{HA}} \tag{C.9}$$

$$Ka = Ka' \frac{f_{H3O+} \, f_{A-}}{f_{HA}} \tag{C.10}$$

where $\quad Ka' = \dfrac{C_{H3O+} \, C_{A-}}{C_{HA}}$

Rearranging Eq. (C.10):

$$Ka' = Ka \frac{f_{HA}}{f_{H3O+} \, f_{A-}} = f(T, f_i) \tag{C.11}$$

The Eq. (C.6) is normally used in terms of molar concentration unit (M), therefore the Eq. (C.6) is expressed as:

$$pH = pKa' + \log\left[\frac{C_{basic\ species}}{C_{acidic\ species}}\right] \tag{C.12}$$

In general, the equilibrium reaction of acid is shown as:

$$H_nA^{x-} \leftrightarrow H_{n-1}A^{(x+1)-} + H^+ \tag{C.13}$$

From Eq. (C.13), Eq. (C.12) becomes:

$$pH = pKa' + \log\left[\frac{C_{Hn-1A(x+1)-}}{C_{HnAx-}}\right] \tag{C.14}$$

From Eq. (C.11), it is illustrated that Ka' is a function of temperature (T) and activity coefficient (f$_i$), nevertheless the activity coefficient is also depended upon the ionic strength (I) as shown by the Debye-Huckel equation. The Debye-Huckel equation for dilute solution can be expressed as:

$$\log f_i = -\frac{A Z^2 I^{0.5}}{1+I^{0.5}} + 0.1 Z^2 I \qquad \text{(C.15)}$$

where f$_i$ = Activity coefficient

    I = Ionic strength (M)

    Z = Charge

    A = a temperature-dependent constant

       (at 25°C: A = 0.512)

Coupling Eq. (C.15) with Eq. (C.14), Eq. (C.14) becomes:

$$pH = pKa - \frac{(2x+1)A I^{0.5}}{(1+I^{0.5})} + 0.1(2x+1)I + \log\left[\frac{C_{Hn-1A(x+1)-}}{C_{HnAx-}}\right] \qquad \text{(C.16)}$$

where $pKa' = pKa - \frac{(2x+1)A I^{0.5}}{(1+I^{0.5})} + 0.1(2x+1)I$ \qquad (C.17)

3. Calculation Method for Deprotonation Curves

For example, the Aminotri(methylene phosphonic acid) (ATMP) is a polyprotic acid which dissociates in several steps depended upon the number ionizable protons contained in the molecule as shown below:

$$\text{ATMP} \leftrightarrow \text{ATMP}^- + \text{H}^+ \qquad\qquad pKa_1 < 2$$
$$\text{ATMP}^- \leftrightarrow \text{ATMP}^{2-} + \text{H}^+ \qquad\qquad pKa_2 < 2$$

$$\text{ATMP}^{2\text{-}} \leftrightarrow \text{ATMP}^{3\text{-}} + \text{H}^+ \qquad\qquad \text{pKa}_3 = 4.30$$

$$\text{ATMP}^{3\text{-}} \leftrightarrow \text{ATMP}^{4\text{-}} + \text{H}^+ \qquad\qquad \text{pKa}_4 = 5.46$$

$$\text{ATMP}^{4\text{-}} \leftrightarrow \text{ATMP}^{5\text{-}} + \text{H}^+ \qquad\qquad \text{pKa}_5 = 6.66$$

$$\text{ATMP}^{5\text{-}} \leftrightarrow \text{ATMP}^- + \text{H}^+ \qquad\qquad \text{pKa}_6 = 12.30$$
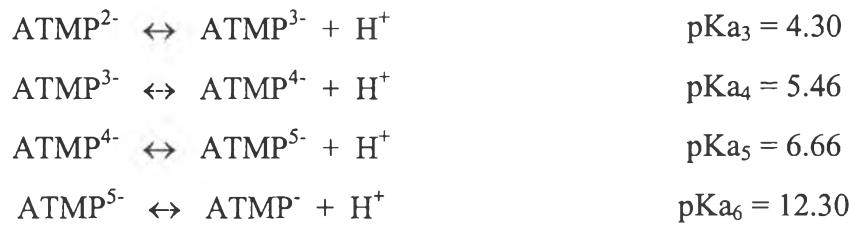
The dissociation of ATMP can be expressed in terms of six equilibrium acid constants as shown by the following equations:

$$Ka_1 = \frac{[\text{ATMP}^-][\text{H}^+]}{[\text{ATMP}]} \tag{C.18}$$

$$Ka_2 = \frac{[\text{ATMP}^{2-}][\text{H}^+]}{[\text{ATMP}^-]} \tag{C.19}$$

$$Ka_3 = \frac{[\text{ATMP}^{3-}][\text{H}^+]}{[\text{ATMP}^{2-}]} \tag{C.20}$$

$$Ka_4 = \frac{[\text{ATMP}^{4-}][\text{H}^+]}{[\text{ATMP}^{3-}]} \tag{C.21}$$

$$Ka_5 = \frac{[\text{ATMP}^{5-}][\text{H}^+]}{[\text{ATMP}^{4-}]} \tag{C.22}$$

$$Ka_6 = \frac{[\text{ATMP}^{6-}][\text{H}^+]}{[\text{ATMP}^{5-}]} \tag{C.23}$$

The total ATMP concentration is the summation of all ATMP species:

$$\text{ATMP}_{\text{Total}} = [\text{ATMP}^{6\text{-}}] + [\text{ATMP}^{5\text{-}}] + [\text{ATMP}^{4\text{-}}] + \ldots + [\text{ATMP}^-] + [\text{ATMP}] \tag{C.24}$$

From the equilibrium reaction indicating the several deprotonation steps of ATMP, the concentration of each deprotonated species can be expressed as:

$$[ATMP] = \frac{[ATMP^-][H^+]}{Ka_1} \qquad (C.25)$$

$$[ATMP^-] = \frac{[ATMP^{2-}][H^+]}{Ka_2} \qquad (C.26)$$

$$[ATMP^{2-}] = \frac{[ATMP^{3-}][H^+]}{Ka_3} \qquad (C.27)$$

$$[ATMP^{3-}] = \frac{[ATMP^{4-}][H^+]}{Ka_4} \qquad (C.28)$$

$$[ATMP^{4-}] = \frac{[ATMP^{5-}][H^+]}{Ka_5} \qquad (C.29)$$

$$[ATMP^{5-}] = \frac{[ATMP^{6-}][H^+]}{Ka_6} \qquad (C.30)$$

From Eq. (C.16) and (C.17), all deprotonated species can be rewritten in terms of pH and pKa' as shown below:

$$[ATMP] = [ATMP^-]10^{pKa1'-pH} \qquad (C.31)$$

$$[ATMP^-] = [ATMP^{2-}]10^{pKa2'-pH} \qquad (C.32)$$

$$[ATMP^{2-}] = [ATMP^{3-}]10^{pKa3'-pH} \qquad (C.33)$$

$$[ATMP^{3-}] = [ATMP^{4-}]10^{pKa4'-pH} \qquad (C.34)$$

$$[ATMP^{4-}] = [ATMP^{5-}]10^{pKa5'-pH} \qquad (C.35)$$

$$[ATMP^{5-}] = [ATMP^{6-}]10^{pKa6'-pH} \qquad (C.36)$$

where

$$pKa_1' = pKa_1 - \frac{A I^{0.5}}{(1+I^{0.5})} + 0.1I \qquad (C.37)$$

$$pKa_2' = pKa_2 - \frac{3A I^{0.5}}{(1+I^{0.5})} + 0.3I \qquad (C.38)$$

$$pKa_3' = pKa_3 - \frac{5AI^{0.5}}{(1+I^{0.5})} + 0.5I \qquad (C.39)$$

$$pKa_4' = pKa_4 - \frac{7AI^{0.5}}{(1+I^{0.5})} + 0.7I \qquad (C.40)$$

$$pKa_5' = pKa_5 - \frac{9AI^{0.5}}{(1+I^{0.5})} + 0.9I \qquad (C.41)$$

$$pKa_6' = pKa_6 - \frac{11AI^{0.5}}{(1+I^{0.5})} + 1.1I \qquad (C.42)$$

Substituting Eq. (C.31) – (C.36) in Eq. (C.24) and rearranging:

$$ATMP_{Total} = [ATMP^{6-}](1 + 10^{pKa6'-pH} + 10^{pKa6'+pKa5'-2pH} + 10^{pKa6'+pKa5'+pKa4'-3pH}$$

$$+ .... + 10^{pKa6'+pKa5'+pKa4'+pKa3'+pKa2'+pKa1'-6pH}) \qquad (C.43)$$

Defining:

$$A = (1 + 10^{pKa6'-pH} + 10^{pKa6'+pKa5'-2pH} + ... + 10^{pKa6'+pKa5'+pKa4'+pKa3'+pKa2'+pKa1'-6pH})$$

$$(C.44)$$

Substituting Eq. (C.44) in Eq. (C.43), Eq. (C.43) becomes:

$$[ATMP^{6-}] = \frac{ATMP_{Total}}{A} \qquad (C.45)$$

Therefore, the fraction of all deprotonated species can be calculated from the following equations:

$$\text{Fraction of } [ATMP^{6-}] \text{ species} = \frac{[ATMP^{6-}]}{ATMP_{Total}} = \frac{1}{A} \qquad (C.46)$$

$$\text{Fraction of } [ATMP^{5-}] \text{ species} = \frac{10^{pKa6'-pH}}{A} \qquad (C.47)$$

$$\text{Fraction of } [ATMP^{4-}] \text{ species} = \frac{10^{pKa6'+pKa5'-2pH}}{A} \qquad (C.48)$$

$$\text{Fraction of } [ATMP^{3-}] \text{ species} = \frac{10^{pKa6'+pKa5'+pKa4'-3pH}}{A} \qquad (C.49)$$

$$\text{Fraction of } [ATMP^{2-}] \text{ species} = \frac{10^{pKa6'+pKa5'+pKa4'+pKa3'-4pH}}{A} \qquad (C.50)$$

$$\text{Fraction of } [ATMP^{-}] \text{ species} = \frac{10^{pKa6'+pKa5'+pKa4'+pKa3'+pKa2'-5pH}}{A} \qquad (C.51)$$

$$\text{Fraction of } [ATMP] \text{ species} = \frac{10^{pKa6'+pKa5'+pKa4'+pKa3'+pKa2'+pKa1'-6pH}}{A} \qquad (C.52)$$

Substituting the values of pKa_1' to pKa_6' from Eq. (C.37) – (C.42) in Eq. (C.46) – (C.52), the fraction of all deprotonated species of ATMP is subsequently attained.

The deprotonation curves for DTPMP and EDTA can be obtained in the same manner as ATMP.

CURRICULUM VITAE

Name: Thammanoon Sreethawong

Date of Birth: December 10, 1979

Nationality: Thai

University Education:

1996 – 2000   Bachelor Degree of Engineering in Chemical Engineering (First Class Honors), Faculty of Engineering, Thammasat University, Thailand

Working Experience:

1999   Position: Student Internship in Technical Analysis Department

Company name: The Energy Conservation Center of Thailand (ECCT), Thailand