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Supplementary Materials

Mechanistic Study and Application of Anionic/Cationic Combination Collector ST-8 for the Flotation of Spodumene

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Both dodecylamine and sodium oleate are weak electrolytes and undergo hydrolysis reactions when dissolved in water with the following acid-base equilibrium, dissociation equilibrium, conjugation equilibrium reactions and equilibrium constants:

Acidolytic dissociation equilibrium:

$$RNH_3^+ \rightleftharpoons RNH_{2(\mathrm{aq})} + H^+ \quad K_a = \frac{[H^+][RNH_{2(aq)}]}{[RNH_3^+]} = 10^{-10.63} \tag{S1}$$

Dissolution equilibrium:

$$RNH_{2(S)} \rightleftharpoons RNH_{2(\mathrm{aq})} \quad S = 2.0 \times 10^{-5}\mathrm{mol/l} \tag{S2}$$

From Equation S2, it can be seen that when $[RNH_{2(\mathrm{aq})}] = S$, an amine precipitate is formed.

Ion-conjugation equilibrium:

$$2RNH_3^+ \rightleftharpoons (RNH_3^+)_2^{2+} \quad K_d = \frac{(RNH_3^+)_2^{2+}}{[RNH_3^+]^2} = 10^{2.08} \tag{S3}$$

Ion-molecule association equilibrium: $RNH_3^+ + RNH_{2(\mathrm{aq})} \rightleftharpoons (RNH_3^+ \cdot RNH_{2(\mathrm{aq})})$

$$K_{1m} = \frac{[RNH_3^+ \cdot RNH_{2(\mathrm{aq})}]}{[RNH_3^+][RNH_{2(\mathrm{aq})}]} = 10^{3.12} \tag{S4}$$

Then MBE is $C_T = [RNH_{2(\mathrm{aq})}] + [RNH_3^+] + [(RNH_3^+)_2^{2+}] + [RNH_3^+ \cdot RNH_{2(\mathrm{aq})}]$

Substituting equations S1, 2, 3 and 4 into the MBE equation and making $K_B = \frac{[H^+]}{K_a}$, we get

$$(K_d K_B^2 + \mathrm{K}_{1m} K_B)[RNH_{2(\mathrm{aq})}]^2 + (1 + K_B)[RNH_{2(\mathrm{aq})}] - C_T = 0 \tag{S5}$$

From the mixed collector concentration of 6×10-4mol/l and the molar ratio of sodium oleate to dodecylamine of 6:1, it can be obtained that the concentration of dodecylamine is $C_T = 6 \times 10^{-4} \times \frac{1}{7} = 8.6 \times 10^{-5}\mathrm{mol/l}$, By checking the table of pHs of dodecylamine precipitation at different concentrations, it can be obtained that pHs=10.5.

Therefore, when $\mathrm{p}H < \mathrm{p}H_S$ from Equation S5, we have

$$[RNH_{2(\mathrm{aq})}] = \frac{-(1+K_B) + \sqrt{(1+K_B)^2 + 4(K_d {K_B}^2 + K_{1m} K_B) C_T}}{2(K_d {K_B}^2 + K_{1m} K_B)}$$

Let: $X = K_d {K_B}^2 + K_{1m} K_B \quad Y = -(1 + K_B + \sqrt{(1+K_B)^2 + 4XC^T}$

Then: $[RNH_{2(\mathrm{aq})}] = \frac{Y}{2X}$, namely:

$$\begin{aligned} log[RNH_{2(\mathrm{aq})}] &= log\,Y - log\,X - log\,2 \\ &= log(-1 - K_B \\ &+ \sqrt{(1+K_B)^2 + 4(K_d {K_B}^2 + K_{1m} K_B) C_T}) - \log(K_d {K_B}^2 \\ &+ K_{1m} K_B) - \log 2 \end{aligned} \tag{S6}$$

$$=\log\left(-1-10^{10.63-pH}+\sqrt{(1+10^{10.63-pH})^2+4(10^{23.34-2pH}+10^{13.75\text{-pH}})\times 8.6\times 10^{-5}}\right)$$

$$-\,log(10^{23.34-2pH}+10^{13.75\text{-pH}})-log\,2$$

The same reasoning leads to:

$$log[RNH_3^+]=logK_B+log\,Y-log\,X-log\,2 \quad \text{(S7)}$$

$$log[(RNH_3^+)_2^{2+}]=logK_d+2\,logK_B+2\,log\,Y-2\,log\,X-2\,log\,2 \quad \text{(S8)}$$

$$log[RNH_3^+\cdot RNH_{2(\text{aq})}]=\text{logK}_{1m}+logK_B+2\,log\,Y-2\,log\,X-2\,log\,2 \quad \text{(S9)}$$

When $pH\geq pH_S$, $[RNH_{2\,(\text{aq})}]=S=2\times 10^{-5}\text{mol/l}$

From Eqs. S1, 3, and 4, we have:

$$[RNH_3^+]=K_B\cdot S\big[\big(RNH_3^+\cdot RNH_{2(\text{aq})}\big)\big]=K_{1m}\cdot K_B\cdot S^2$$

$$[(RNH_3^+)_2^{2+}]=K_d\cdot K_B^2\cdot S^2 \quad K_B=\frac{[H^+]}{K_a}=\frac{10^{-pH}}{K_a}=10^{10.63\text{-p}H}$$

$$[RNH_{2(S)}]=C_T-S-K_B\cdot S-K_{1m}\cdot K_B\cdot S^2-K_d\cdot {K_B}^2\cdot S^2$$

Then:

$$log[RNH_{2(\text{aq})}]=log\,S \quad \text{(S10)}$$

$$log[RNH_3^+]=pK_a-pH+log\,S \quad \text{(S11)}$$

$$log[(RNH_3^+\cdot RNH_{2(\text{aq})})]=\text{log}K_{1m}+\text{p}K_a-pH+2\,log\,S \quad \text{(S12)}$$

$$log[(RNH_3^+)_2^{2+}]=logK_d+2\text{p}\,K_a-2pH+2\,log\,S \quad \text{(S13)}$$

$$log[RNH_{2(S)}]=log(C_T-S-10^{10.63-pH}\cdot S-K_{1m}\cdot 10^{10.63-pH}\cdot S^2-K_d\cdot 10^{21.23-2pH}\cdot S^2 \quad \text{(S14)}$$

Sodium oleate and oleic acid in water dissolution equilibrium is similar, that is, oleic acid instead of sodium oleate to carry out the calculation of the concentration of its components in relation to pH. The solubility of oleic acid is $S=10^{-7.6}$mol/l, and usually the concentration of oleic acid in the pulp is greater than the solubility at the flotation dosage, at which time dissolved oleic acid $HOl_{(aq)}$ in aqueous solution and the insoluble liquid oleic acid $HOl_{(s)}$ become a saturated solution between, and the equilibrium is as follows:

$$\begin{aligned} &HOl_{(l)}\rightleftharpoons HOl_{(\text{aq})} && S=10^{-7.6}\\ &HOl_{(\text{aq})}\rightleftharpoons H^++Ol^- && K_a=\frac{[H^+][Ol^-]}{[HOl_{(\text{aq})}]}=10^{-4.95}\\ &2Ol^-\rightleftharpoons (Ol)_2^{2-} && K_d=\frac{[(Ol)_2^{2-}]}{[Ol^-]^2}=10^{4.0}\\ &HOl_{(\text{aq})}+Ol^-\rightleftharpoons H(Ol)_2^- && K_{1m}=\frac{[H(Ol)_2^-]}{[HOl_{(\text{aq})}][Ol^-]}=10^{4.7} \end{aligned} \quad \text{(S15)}$$

MBE:

$$C_T=[HOl_{(\text{aq})}]+[Ol^-]+[(Ol)_2^{2-}]+[H(Ol)_2^-] \quad \text{(S16)}$$

Substituting Eq. S15 into Eq. S16 and making $K_H=\frac{K_a}{[H^+]}$, then:

$$(K_{1m}K_H + K_dK_H^2)[HOl_{(aq)}]^2 + (1 + K_H)[HOl_{(aq)}] - C_T = 0 \quad (17)$$

From the mixed trap concentration of 6×10-4mol/l and the molar ratio of sodium oleate to dodecylamine of 6:1, it can be obtained that the concentration of sodium oleate is $C_T = 6 \times 10^{-4} \times \frac{6}{7} = 5.1 \times 10^{-4}$mol/l, and by checking the table of pH1 of oleic acid precipitation at different concentrations, it can be obtained that pH_1=8.7。

Therefore, when $pH > pH_1$ Equation 17 yields:

$$[HOl_{(aq)}] = \frac{-(1+K_H) + \sqrt{(1+K_H)^2 + 4(K_dK_H{}^2 + K_{1m}K_H)C_T}}{2(K_dK_H{}^2 + K_{1m}K_H)}$$

Let $Z = K_dK_H{}^2 + K_{1m}K_H$; $W = -(1+K_H) + \sqrt{(1+K_H)^2 + 4ZC^T}$

Similar to the calculation of dodecylamine, then:

$$log[HOl_{(aq)}] = log\,W - log\,Z - \log 2 \quad (S18)$$

$$log[Ol^-] = logK_H + log\,W - log\,Z - log\,2 \quad (S19)$$

$$log[(Ol)_2^{2-}] = logK_d + 2\,logK_H + 2\,log\,W - 2\,log\,Z - 2\,log\,2 \quad (S20)$$

$$log[H(Ol)_2^-] = \log K_{1m} + logK_H + 2\,log\,W - 2\,log\,Z - 2\,log\,2 \quad (S21)$$

When $pH \leq pH_1$, then

$$log[HOl_{(aq)}] = log\,S \quad (S22)$$

$$log[Ol^-] = logK_a + log\,S + pH \quad (S23)$$

$$log[(Ol)_2^{2-}] = logK_d + 2\,(\log K_a + log\,S + pH) \quad (S24)$$

$$log[H(Ol)_2^-] = \log K_{1m} + logK_a + 2\,log\,S + pH \quad (S25)$$

$$log[HOl_{(S)}] = log\,(C_T - S - 10^{pH-4.95} \cdot S - K_{1m} \cdot 10^{pH-4.95} \cdot S^2 - K_d \cdot 10^{2pH-9.9} \cdot S^2 \quad (S26)$$

The relationship between the concentration of each component of dodecylamine and sodium oleate and pH was calculated from the above and plotted as a logC-pH diagram.