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Study on Flotation Separation of Cobalt(II) by NaCl-NH₄SCN-DDBAC System

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Abstract. The flotation separation behaviors of Co²⁺ using NaCl-NH₄SCN-dodecyl dimethyl benzyl ammonium chloride(DDBAC) system and the conditions for the separation of Co²⁺ were studied. The results showed that in the presence of 1.5 g NaCl, when the dosage of 0.10 mol/L NH₄SCN solution was 0.30 mL and 0.0010 mol/L DDBAC solution was 1.00 mL respectively, the ternary association complex settlement of (DDBAC)₂[Co(SCN)₄] which formed by DDBAC⁺, SCN⁻ and Co²⁺ floated above water phase and liquid-solid phases was formed with clear interface. While Ni²⁺, Fe³⁺, Al³⁺ and Mn²⁺ could not be floated. Therefore, the quantitative separation of Co²⁺ from Ni²⁺, Fe³⁺, Al³⁺ and Mn²⁺ could be achieved. The quantitative flotation separation of Co²⁺ in the sample of synthetic water was performed, and the recoveries were 92.3%~98.6%.

1. Introduction

Cobalt is one of the essential microelements for humans, animals and plants. The deficiency of cobalt in human and animals results in retarding growth rate, anaemia and so on, while ingesting excessive cobalt leads to toxic effects, such as vasodilatation, flushing and cardiomyopathy. So, it is very important and necessary to develop new method for the separation/enrichment and determination of trace cobalt. Some different methods have been reported for the separation/enrichment of Co(II), including solvent extraction[1-2], liquid-liquid extraction[3], solid phase extraction[4-5], cloud point extraction[6-7], flotation separation[8], HPLC[9].

This study showed that in the presence of 1.5 g NaCl, ternary association complex settlement of NH₄SCN-DDBAC-Co was formed by Co²⁺, SCN⁻ and DDBAC cation (DDBAC⁺), which floated above the water phase and liquid-solid phases was formed. So, Co²⁺ was floated quantitatively, while Ni²⁺, Fe³⁺, Al³⁺ and Mn²⁺ stayed in water phase. The quantitative separation of Co²⁺ from Ni²⁺, Fe³⁺, Al³⁺ and Mn²⁺ could be achieved. This proposed was applied to the separation of Co²⁺ in the sample of synthetic water with satisfactory results.

2. Experimental

2.1 Equipment and reagents

722S spectrophotometer (Shanghai No.3 Analysis Equipment Plant) was used for photometric measurements.

DDBAC solution: 0.001 mol·L⁻¹. NH₄SCN solution: 0.1 mol·L⁻¹. Borax solution: 0.1 mol·L⁻¹. 4-(2-pyridylazo) resorcinol (PAR) ethanol solution: 1.0×10⁻³ mol·L⁻¹. A stock of standard solution of



Co^{2+} :1.000 $\text{g}\cdot\text{L}^{-1}$, a working standard solution was prepared by appropriately diluting the stock standard solution.

2.2 Method

Condition experimental: 50 μg of Co^{2+} , a given amounts of 0.1 $\text{mol}\cdot\text{L}^{-1}$ NH_4SCN solution and 0.001 $\text{mol}\cdot\text{L}^{-1}$ DDBAC solution were added into a comparison tube(25mL). Then the mixture was diluted to 10 mL. 1.5 g NaCl was added to the solution and shaken for 1 min before allowing it to stand for 2 min.

1.00 mL of aqueous solution in the lower layer was transferred into another comparison tube(25mL), and 1.5 mL PAR ethanol solution and 3.0 mL borax solution was added. The solution was diluted to the mark. The content of Co^{2+} was determined at 510 nm with reagent as blank. The flotation yield of Co^{2+} (E/%) was calculated.

Separation experimental: The settlement was dissolved in ethanol, and the content of Co^{2+} was determined in the same method. The flotation yield of Co^{2+} (E/%) was calculated.

Photometric analysis of other metal ions was referring the reference10.

3. Results and discussion

3.1. Effect of NH_4SCN dosage

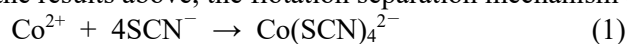
Co^{2+} (50 μg) and 0.001 $\text{mol}\cdot\text{L}^{-1}$ DDBAC solution(1.00 mL) are applied to the proposed method, the effect of NH_4SCN dosage on the E/%(Co^{2+}) was studied(Figure 1). Figure 1 show that the E/%(Co^{2+}) increased with the increase of NH_4SCN dosage. When the NH_4SCN dosage was zero, the flotation yield of Co^{2+} was zero. When the NH_4SCN solution was 0.20 mL or more, the E/%(Co^{2+}) was 100%. Hence, 0.30 mL NH_4SCN solution was chosen.

3.2. Effect of DDBAC dosage

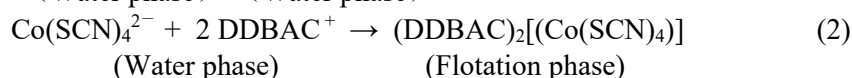
Co^{2+} (50 μg) and 0.1 $\text{mol}\cdot\text{L}^{-1}$ NH_4SCN solution (0.30 mL) are applied to the proposed method, the effect of DDBA dosage on the E/%(Co^{2+}) was studied(shown in Figure 2). The E/%(Co^{2+}) was zero without DDBAC. With the increase of DDBAC dosage, the E/%(Co^{2+}) increased. When the dosage of DDBAC was reached 0.75 mL, the E/%(Co^{2+}) was 100%. Furthermore, the E/%(Co^{2+}) does not change with a further increase of DDBAC dosage. Hence, 1.00 mL DDBAC solution was selected.

3.3. Flotation separation mechanism of Co^{2+}

Based on the results above, the flotation separation mechanism of Co^{2+} was presumed:



(Water phase) (Water phase)



(Water phase)

(Flotation phase)

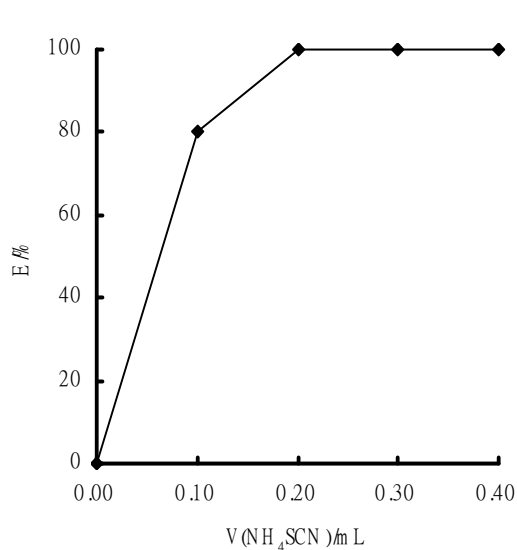


Figure1. Effect of NH_4SCN dosage on the flotation yield of Co^{2+}
 Co^{2+} : $50\mu\text{g}$; DDBAC($0.001\text{ mol}\cdot\text{L}^{-1}$): 1.00 mL ; NH_4SCN : $0.1\text{ mol}\cdot\text{L}^{-1}$

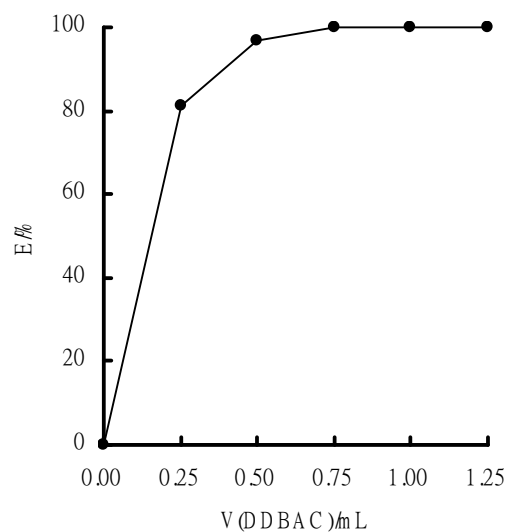


Figure 2. Effect of DDBAC dosage on the flotation yield of Co^{2+}
 Co^{2+} : $50\mu\text{g}$; NH_4SCN ($0.1\text{ mol}\cdot\text{L}^{-1}$): 0.30 mL ; DDBAC: $0.001\text{ mol}\cdot\text{L}^{-1}$

3.4. Effect of different salts

Under selected conditions, the effects of different salts (NaCl , NaNO_3 , $(\text{NH}_4)_2\text{SO}_4$ and KBr) on liquid-solid divarication and the $E/(\text{Co}^{2+})$ were investigated. The results showed that liquid-solid divarication could be realized when the presence of each of NaCl , NaNO_3 , $(\text{NH}_4)_2\text{SO}_4$ and KBr . However, the presence of $(\text{NH}_4)_2\text{SO}_4$, NaNO_3 and KBr decreased the $E/(\text{Co}^{2+})$ in a certain extent. The existence of NaCl speeded up liquid-solid divarication and made the interface clearer, and consequently Co^{2+} was floated faster. When NaCl dosage was $0.50, 1.00, 1.50\text{ g}$, the flotation yield of Co^{2+} was $88.8\%, 91.0\%$ and 100% . Therefore, 1.50 g NaCl was chosen.

3.5. The flotation yield of different metal ions

Co^{2+} ($50\mu\text{g}$), $0.1\text{ mol}\cdot\text{L}^{-1}\text{NH}_4\text{SCN}$ (0.30 mL) and $0.001\text{ mol}\cdot\text{L}^{-1}$ DDBAC (1.00 mL) are applied to the proposed method, the $E/(\text{Co}^{2+})$ was 100% . Under the same conditions, the flotation yield of Ni^{2+} , Fe^{3+} , Mn^{2+} and Al^{3+} were all less. Therefore, Co^{2+} can be separated from Ni^{2+} , Fe^{3+} , Mn^{2+} and Al^{3+} in the solution.

3.6. Separation experiments

The flotation separations of Co^{2+} from Ni^{2+} , Fe^{3+} , Mn^{2+} and Al^{3+} in synthesized samples of binary and polybasic system were researched. The results were shown in Table 1 and Table 2.

Table 1. The flotation separation results of binary-mixed ions

Mixed ions	Dosage of metal ions(μg)		Content of metal ions in water phase (μg)		Flotation yield($E/\%$)	
	Co	Me	Co	Me	Co	Me
$\text{Co}^{2+}\text{-Ni}^{2+}$	50	100	0.1	97.3	99.8	2.7
	50	200	0.2	187.4	99.6	6.3

	50	400	0	384.9	100	3.8
Co ²⁺ -Fe ³⁺	50	100	0.2	97.6	99.6	2.4
	50	200	0.3	189.3	99.4	5.4
	50	400	0.1	390.4	99.8	2.4
Co ²⁺ - Mn ²⁺	50	100	0.1	92.2	99.8	7.8
	50	200	0.2	183.5	99.6	8.3
	50	400	0.1	373.4	99.8	6.7
Ni ²⁺ - Al ³⁺	50	100	0.1	98.3	99.8	1.7
	50	200	0.2	198.8	99.6	0.6
	50	400	0.1	390.7	99.8	2.3

Me indicates Ni²⁺, Fe³⁺, Mn²⁺ and Al³⁺.

Table 2. Flotation separation results of Co²⁺ from polybasic-mixed ions

Number of the synthesized samples	1	2	3	4	5
Dosage of Co ²⁺ (μg)	100.0	200	300	40.0	50.0
Dosage of Ni ²⁺ , Fe ³⁺ , Mn ²⁺ and Al ³⁺ (μg)	100.0	100	15.0	200.0	20.0
Co ²⁺ found in solid phase (μg)	93.0	188.3	295.9	369.0	467.8
Flotation yield of Co ²⁺ (E/%)	93.0	94.2	98.6	92.3	93.6

4. Conclusion

In this paper, the flotation separation of Co²⁺ from Ni²⁺, Fe³⁺, Mn²⁺ and Al³⁺ was reported. In NaCl-NH₄SCN-DDBAC-H₂O system, Co²⁺ could be quantitatively floated. In the same conditions, Ni²⁺, Fe³⁺, Mn²⁺ and Al³⁺ could not be floated or minor floatation. So, the flotation separation of Co²⁺ from Ni²⁺, Fe³⁺, Mn²⁺ and Al³⁺ could be achieved. The proposed method has been successfully used for the separation of Co²⁺ in the sample of synthetic water with satisfactory results.

Acknowledgement

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