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Extraction of Sb (III) and Co (II) from Hydrochloric Acid Solutions by N,N-Dioctyl-1-Octanamine in Methyl Isobutyl Ketone

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ABSTRACT

Amines as organic molecules are able to form complexes with metals ions and this is the reason why we can use them to extract metals ions from hydrometallurgical solutions. Based on that, we have investigated the extraction of antimony and cobalt with N,N-dioctyl-1-octanamine from the mixture of elements prepared in artificial manner. We investigated the influence of HCl concentration and concentration of the salts (NaCl, NaI and CH₃COONa) in extraction of two elements (antimony and cobalt) from water solutions. All extractions were done from water solutions of HCl with concentrations 3, 6 and 9 mol L^{-1} and in presence of NaCl, NaI and CH₃COONa salts, Extraction of antimony from NaCl solution range from 80-100 %, from NaI solution 100 % and from CH₃COONa solution 8.0 -100 %. Extraction of cobalt from NaCl solution move from 4.0-50.0 %, from NaI solution 0-25.0 % and from CH₃COONa solution 0-40.0 %. As optimal condition to separate antimony from cobalt is the extraction of antimony from HCl solution with concentration 3 mol L^{-1} in presence of NaI. Using these condition 100 % of antimony was in organic phase and all of cobalt remains in water phase.

Keywords: Extraction, antimony, cobalt, N,N-dioctyl-1-octanamine, organic phase, aqueous phase.

INTRODUCTION

The use of solvent extraction as a unit operation in hydrometallurgy now extends to a wide range of metals from a variety of feed materials including low-grade ores, scrap and waste, and dilute aqueous solutions. Extraction of metals with organic bases with large molecular masse is forced in the last years [1]. The importance of metals extraction, with organic bases, is in the selectivity of organic compounds for anionic metal complexes, obtained in reversible way in water solution, which are more stable than simple anions [2].

Systems that we will discuss here, are some extracted species formed as result of interactions between a neutral species or anionic metallic species in water solution and salts of any organic bases or their cation in organic or in water phase. This kind of extraction is known as associated ionic extraction, where a cationic part is alkyl ammonium, arsenium or phosphonium cation [3, 4, 5, 6].

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Faiku et al., [7, 8] have investigated the extraction of antimony and cobalt with mixture of N,N-dioctyl-1octanamine and N,N-dioctyl-1-octan ammonium chloride and only with N,N-dioctyl-1-octan ammonium chloride. They have found that all changing factors have influence in extraction percentage of Antimony and Cobalt in organic phase.

Kimura [9] has done the extraction of some metals including antimony and cobalt, from HCl solution with concentration 1 mol L^{-1} , 4 mol L^{-1} , 6 mol L^{-1} and 9 mol L^{-1} with bis (2-Ethylhexyl)- orthophosphoric acid and hydrochloric acid. He found that antimony extracted 99.9% from solution of HCl with concentration 9 mol L^{-1} , while cobalt was extracted 56% from HCl solution with concentration 9 mol L^{-1} .

Organic molecules as alamine 336 [10, 11, 12], aliquat 336 [13, 14, 15], N,N-dioctyl-1-octanamine [16] are able to form complexes with metals ions and for that we can use them to extract metals ions from hydrometallurgical solutions. Based on that we have investigated the extraction of antimony and Cobalt with Mixture of N,N-Dioctyl-1-Octanamine from mixture of elements prepared in artificial way.

MATERIALS AND METHODS

In this study we used reagents with p.a. purities from which we have prepared solutions with dissolving the appropriate amount of cobalt chloride (CoCl2 × 6H2O) and antimony potassium tartarate hemi hydrate (K(SbO)C₄H₄O₆ x ¹/₂ H₂O) in distillate water. Water solutions of antimony and cobalt with metal concentration of 1g L⁻¹ were prepared using CoCl2 × 6H2O and K(SbO)C₄H₄O₆ x ¹/₂ H₂O. As organic phase we used 10% solution of N,N-dioctyl-1-octanamine in methyl isobutyl ketone. Methyl isobutyl ketone was used as carrier solvent for organic bases. This solvent was mixed totally with N,N-Dioctyl-1-Octanamine. The structural formula of N,N-Dioctyl-1-octanamine is shown in Fig. 1.



Figure 1: Structure of N,N-dioctyl-1-octanammine

N,N-Dioctyl-1-octanamine can form complex salts, with a large number of metals, which are not soluble in water, but are soluble in organic phases. To determine the antimony and cobalt quantities in water solutions, we used atomic absorption spectrophotometer Perkin Elmer AAnalyst 800.

For extraction, we used 10% of N,N-Dioctyl-1-octanamine in methyl isobutyl ketone. All extraction were done from HCl water solutions with concentrations 3, 6 and 9 mol L^{-1} and in presence of NaCl, NaI and CH₃COONa salts. Also the water solutions of NaCl, NaI and CH₃COONa salts, we have prepared in different concentrations. Extraction of antimony and cobalt was done with separator funnel of 150 mL. We used a series of nine separator funnels with standard mixture solutions and series of nine separator funnels without standard, where are present just water solution of acid and salt. About 10 mL of water model and 10 mL of organic solution were mixed in separator

funnel twice for one minute. Mixture was left to stay during nights and then we have separated organic phase from water phase. Water phase was used to determine elements (antimony and cobalt) that were present (remain) in it.

RESULTS AND DISCUSSION

The ratio of concentration of M in the extract to its concentration in the aqueous phase for this system is called the concentration distribution ratio, Dc, thus

 $D_c = [M]_{org} / [M]_{aq}$

[M]org was determined through back-calculation using measured [M]initial and [M]aq values as

 $[M]_{org} = [M]_{initial} - [M]_{aq}$

Dc, as an index of metal extractability, is used to calculate the percentage of the extracted metal, E:

 $E = \{(D_c. v_{aq}/v_{org}) / (1 + (D_c. v_{aq}/v_{org}))\}x \ 100$

where vaq and vorg are the volumes of the aqueous and organic phases of the extraction process, respectively. For equal volumes of immiscible phases, E becomes:

 $E = \{D_c / (1+D_c)\} \ge 100$

The concentration measurements related to organic phase's samples showed significant irreproducibility. So, backcalculation method was preferred to obtain more robust and reliable data. The diluent by itself does not extract the M species, but may modify the interfacial parameters to improve extraction properties and to reduce settling periods. In Table 1-3 are results obtained experimentally for extraction of elements as function of acid and salts concentrations. For extraction of elements in organic phase we took three experiments with three different salts concentrations which all of them are nine systems. From these systems we have done extraction.

Table 1: Extraction of antimony and cobalt with N,N-Dioctyl-1-octanamine in presence of NaCl

c(HCl)/ mol dm ⁻³	γ(NaCl)/ g L ⁻¹	Antimony	Cobalt
3	20	80.0	12.2
6	20	100	39.5
9	20	100	50.0
3	40	80.5	7.2
6	40	100	38.4
9	40	100	48.1
3	60	84.4	4.0
6	60	100	35.6
9	60	100	45.1

Table 2: Extraction of antimony and cobalt with N,N-Dioctyl-1-octanamine in presence of NaI

c(HCl)/ mol dm ⁻³	γ (NaI)/ g L ⁻¹	Antimony	Cobalt
3	20	100	-
6	20	100	8.2
9	20	100	25.9
3	40	100	-
6	40	100	5.3
9	40	100	12.7
3	60	100	-
6	60	98.0	2.7
9	60	100	10.1

Extraction of antimony and cobalt from acidic solution containing NaCl, is shown in Fig. 2a-c. Extraction curve of antimony obtained from sodium chloride solution are almost same. Extraction percentage of antimony from sodium chloride solutions will increase with increasing of HCl concentration. The influence of sodium chloride concentration in extraction of antimony is lower. The joint characteristic during the cobalt extraction from the

solutions sodium chloride is that the extracted percentage of cobalt increases by increasing the concentration of HCl. The influence of sodium chloride concentration in extraction of cobalt is lower.

c(HCl)/ mol dm ⁻³	γ(CH ₃ COONa)/ g L ⁻¹	Antimony	Cobalt
3	20	22.1	-
6	20	100	23.4
9	20	100	40.0
3	40	10.4	-
6	40	100	12.2
9	40	100	25.0
3	60	8.6	-
6	60	100	5.0
9	60	100	27.0

Table 3: Extraction of antimony and cobalt with N,N-Dioctyl-1-octanamine in presence of CH₃COONa



Figure 2: Exraction curves, of elements with N,N-Dioctyl-1-octanamine shown, as function of HCl and NaCl concentrations:

a) γ (NaCl)=20 g L⁻¹ ; b) γ (NaCl)=40 g L⁻¹ ; c) γ (NaCl)=60 g L⁻¹

Extraction of antimony and cobalt from acidic solution containing NaI, is shown in Fig. 3a-c. Antimony in all cases is extracted 100%. From Fig. 3a-c we can see that in HCl solution with concentration of 3 mol L^{-1} , extraction of cobalt is zero and with increasing of acidities extraction of cobalt will increase continually till 25.9% (in solution of 9 mol L^{-1} HCl and in presence of NaI with concentration 20 g L^{-1}). So, NaI concentrations have small influence in extraction of cobalt.

Extraction of antimony and cobalt from acidic solution containing CH₃COONa, is shown in Fig. 4a-c. From Fig. 4a-c we can see that in HCl solution with concentration of 3 mol L⁻¹, extraction of antimony is small and with increasing of acidities extraction of antimony will increase continually till 100% (in solution of 6 mol L⁻¹ and 9 mol L⁻¹ HCl). So, HCl concentrations have higher influence in extraction of antimony. Extraction curve of antimony obtained from sodium acetate solution are almost same. From Fig. 4a-c we can see that in HCl solution with concentration of 3 mol L⁻¹, extraction of cobalt is zero. The joint characteristic during the cobalt extraction from the solutions sodium acetate is that the extracted percentage of cobalt increases by increasing the concentration of HCl. Is found that extraction of cobalt is 40.0% when extraction was done in HCl solution with concentration 9 mol L⁻¹ and in presence of sodium acetate with concentration 20 g L⁻¹ (Fig. 4a).



Figure 3: Exraction curves, of elements with N,N-Dioctyl-1-octanamine shown, as function of HCl and NaI concentrations:



a) γ (NaI)=20 g L⁻¹; b) γ (NaI)=40 g L⁻¹; c) γ (NaI)=60 g L⁻¹

a) b) c) Figure 4: Exraction curves, of elements with N,N-Dioctyl-1-octanamine shown, as function of HCl and CH₃COONa concentrations:

CONCLUSION

From our results we can conclude:

• Extraction of antimony from NaCl move from 80.0- 100%, from NaI solution 100% and from CH_3COONa solution 8.0-100%.

• Extraction of cobalt from NaCl solution move from 4-50.0 %, from NaI solution 0-25.0 % and from CH_3COONa solution 0-40.0 %.

- Extraction percentage of antimony and cobalt increase with increasing of HCl concentration.
- Influence of salts concentration (NaCl, NaI and CH₃COONa) is small.

a) γ (CH₃COONa)=20 g L⁻¹; b) γ (CH₃COONa)=40 g L⁻¹; c) γ (CH₃COONa)=60 g

• As optimal condition to separate antimony from cobalt is the extraction of antimony from HCl solution with concentration 3 mol L^{-1} in presence of NaI. Using these condition 100 % of antimony was in organic phase and all of cobalt remains in water phase.

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