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Extraction of Copper, Lead and Nickel from Hydrochloric Acid Solutions by N-Methyl-N,N,N-Trioctyloctan-1-Ammonium Chloride 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 copper, lead and nickel with N-methyl-N,N,N-trioctyloctan-1-ammonium chloride from the mixture of elements prepared in artificial manner. We investigated the influence of HCl concentration and salts (NaCl, NaI and CH₃COONa) concentration in extraction of three elements (copper, lead and nickel) from water solutions. All extractions were done from HCl water solutions with $c = 2, 4$ and 6 mol dm^{-3} and in presence of NaCl, NaI and CH₃COONa salts, which we prepared in different concentrations. Extraction of copper from NaCl solution move from 12.5-76.8%, from NaI solution 100% and from CH₃COONa solution 5.1-88.2%. Extraction of lead from NaCl solution move from 0-48.5%, from NaI solution 100% and from CH₃COONa solution 32.6-82.1%. In solutions of NaCl, NaI and CH₃COONa we cannot extraction the nickel.

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1. Introduction

Solvent extraction of metals is an important technology in hydrometallurgical industry, analytical separations, and liquid waste treatment [1]. Metal ions, cations, and anions are extracted from an aqueous phase into an organic phase through reversible chemical reactions, forming organic-soluble neutral complexes. Extractant usually has very low solubility in an aqueous phase, but interacts with metal ions and obtains high solubility in an organic phase complex. So, extraction is described by a heterogeneous chemical reaction on either side of the aqueous organic interface to the final equilibrium concentrations of the reaction product. In addition, the chemical reaction of solutes with organic compounds (termed as extractants, or reagents), dissolved in the organic solvent (diluent), is accompanied by the distribution of product complexes between two immiscible phases. The extent of complexation for any solute–ligand system is defined by equilibrium constant, which is termed stability or formation constant for metal–ligand interaction [2].

Kimura has done the extraction of some metals including copper, lead and nickel, from HCl solution with concentration 0.01 mol dm^{-3} , 0.1 mol dm^{-3} and 1 mol dm^{-3} with di-(2-Ethylhexyl) phosphoric acid (50% in toluene). He found that copper was extracted 50% from solution of HCl with concentration 0.01 mol dm^{-3} , lead was extracted 97% from HCl solution with concentration 0.01 mol dm^{-3} , while nickel was extracted 2% from HCl solution with concentration 0.1 mol dm^{-3} [3].

Organic are able to form complexes with metals ions and for that we can use them to extract metals ions from hydrometallurgical solutions [4-24]. Based on that we have investigated the extraction of copper, lead and nickel with N-methyl-N,N,N-trioctyl-octan-1-ammonium chloride from mixture of elements prepared in artificial way.

2. Materials and Methods

Chemically pure substances have been used in all solutions. As organic phase we used 10% solution of N-methyl-N,N,N-trioctyl-octan-1-ammonium chloride in methyl isobutyl ketone. Methyl isobutyl ketone was used as carrier solvent for organic bases. This solvent was mixed totally with N-methyl-N,N,N-trioctyl-octan-1-ammonium chloride. The structural formula of N-methyl-N,N,N-trioctyl-octan-1-ammonium chloride is shown in Figure 1.

N-methyl-N,N,N-trioctyl-octan-1-ammonium chloride 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 copper, lead and nickel quantities in water solutions, we used atomic absorption spectrophotometer Perkin Elmer AAnalyst 800. For extraction, we used 10% of N-methyl-N,N,N-trioctyl-octan-1-ammonium chloride in methyl isobutyl ketone. All extraction were done from HCl water solutions with concentrations 2, 4 and 6 mol dm^{-3} and in presence of NaCl, NaI and CH_3COONa salts. Also the water solutions of NaCl, NaI and CH_3COONa salts, we have prepared in different concentrations. Extraction of copper, lead and nickel was done with separator funnel of 150 cm^3 . 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 cm³ of water model and 10 cm³ of organic solution were mixed in separator.

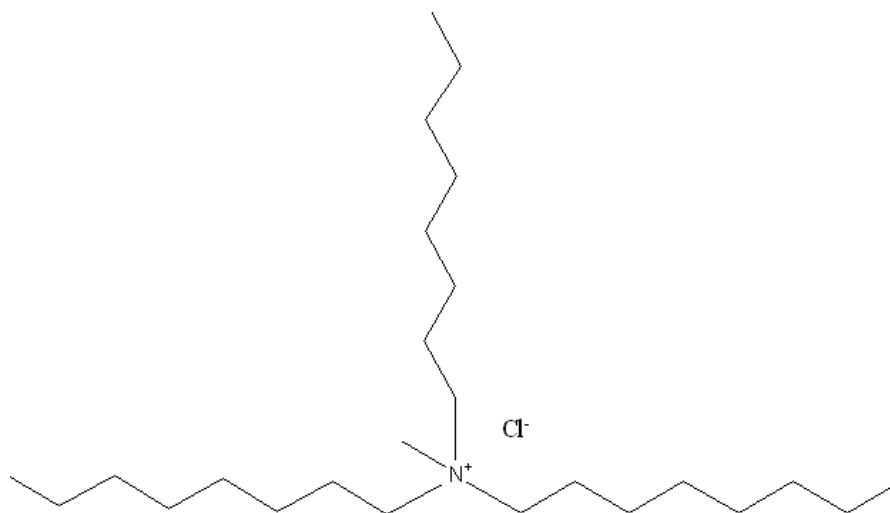


Figure 1: Structure of N-methyl-N,N,N-trioctylammonium chloride

2.1. Preparation of standard solutions

Preparation of standard solution of copper: Dissolve 1.000 g of copper metal in 50 cm³ of 5 mol dm⁻³ nitric acid. Dilute to 1 dm³ in a volumetric flask with deionized water. Or dissolve 3.7980 g of copper nitrate (Cu(NO₃)₂ x3H₂O) in 250 cm³ of deionized water. Dilute to 1 dm³ in a volumetric flask with deionised water.

Preparation of standard solution of lead: Dissolve 1.000 g of lead metal in 50 cm³ of 2 mol dm⁻³ nitric acid. Dilute to 1 dm³ in a volumetric flask with deionized water. Or dissolve 1.5980 g of lead nitrate (Pb(NO₃)₂) in 100 cm³ of deionized water. Dilute to 1 dm³ in a volumetric flask with deionised water.

Preparation of standard solution of nickel: Dissolve 1.000 g of nickel in 20 cm³ of 5 concentration nitric acid. Dilute to 1 dm³ in a volumetric flask with deionized water. Or dissolve 4.9530 g of nickel nitrate (Ni(NO₃)₂ x6H₂O) in 1 dm³ of deionized water.

3. 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, D_c, 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:

$$E = \left\{ \frac{Dc \cdot v_{aq}/v_{org}}{1 + (Dc \cdot v_{aq}/v_{org})} \right\} \times 100$$

where v_{aq} and v_{org} are the volumes of the aqueous and organic phases of the extraction process, respectively. For

equal volumes of immiscible phases, E becomes:

$$E = \left\{ \frac{Dc}{1 + Dc} \right\} \times 100$$

The concentration measurements related to organic phase's samples showed significant irreproducibility. So, back calculation 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 copper, lead and nickel with N-methyl-N,N,N-trioctyl-octan-1-ammonium chloride in presence of NaCl

c(HCl)/ mol dm ⁻³	γ(NaCl)/ g dm ⁻³	Percentage (%)		
		Copper	Lead	Nickel
2	20	12.5	48.5	-
4	20	41.6	32.6	-
6	20	75.2	10.8	-
2	40	13.4	32.9	-
4	40	45.4	18.4	-
6	40	76.8	-	-
2	60	15.8	10.1	-
4	60	46.2	4.3	-
6	60	74.1	-	-

Table 2: Extraction of copper, lead and nickel with N-methyl-N,N,N-trioctyl-octan-1-ammonium chloride in presence of NaI

c(HCl)/ mol dm ⁻³	γ(NaI)/ g dm ⁻³	Percentage (%)		
		Copper	Lead	Nickel
2	20	100	100	-
4	20	100	100	-
6	20	100	100	-
2	40	100	100	-
4	40	100	100	-
6	40	100	100	-
2	60	100	100	-
4	60	100	100	-
6	60	100	100	-

Table 3: Extraction of copper, lead and nickel with N-methyl-N,N,N-trioctyl-octan-1-ammonium chloride in presence of CH₃COONa

c(HCl)/ mol dm ⁻³	γ(CH ₃ COONa)/ g dm ⁻³	Percentage (%)		
		Copper	Lead	Nickel
2	20	10.2	82.1	-
4	20	30.5	66.8	-
6	20	58.2	34.1	-
2	40	6.1	80.2	-
4	40	26.7	65.2	-
6	40	54.8	32.6	-
2	60	5.1	75.2	-
4	60	25.3	62.9	-
6	60	54.9	40.2	-

Extraction of copper, lead and nickel from acidic solution containing sodium chloride is shown in Figure 2a-c. Extraction curve of copper obtained from sodium chloride solution are almost same. Extraction percentage of copper from sodium chloride solutions will increase with increasing of HCl concentration. The influence of sodium chloride concentration in extraction of copper is lower. The joint characteristic during the copper extraction from the solutions sodium chloride is that the extracted percentage of copper increases by increasing the concentration of HCl. In all cases the extraction percentage of nickel is zero. Extraction percentage of lead from sodium chloride solutions is decrease with increasing of HCl concentration. The influence of sodium

chloride concentration in extraction of lead is big. From Figure 3b we can see that in HCl solution with concentration of 6 mol dm⁻³, extraction of lead is zero and with decrease of acidities extraction of lead will increase continually till 32.9% (in solution of 2 mol dm⁻³ HCl).

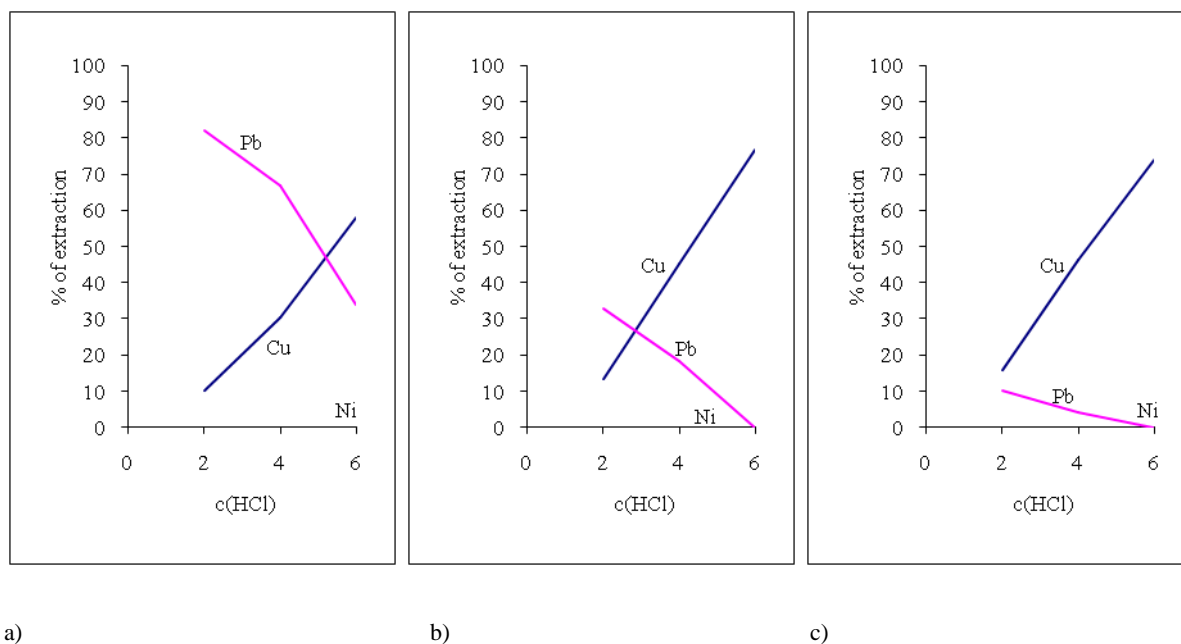


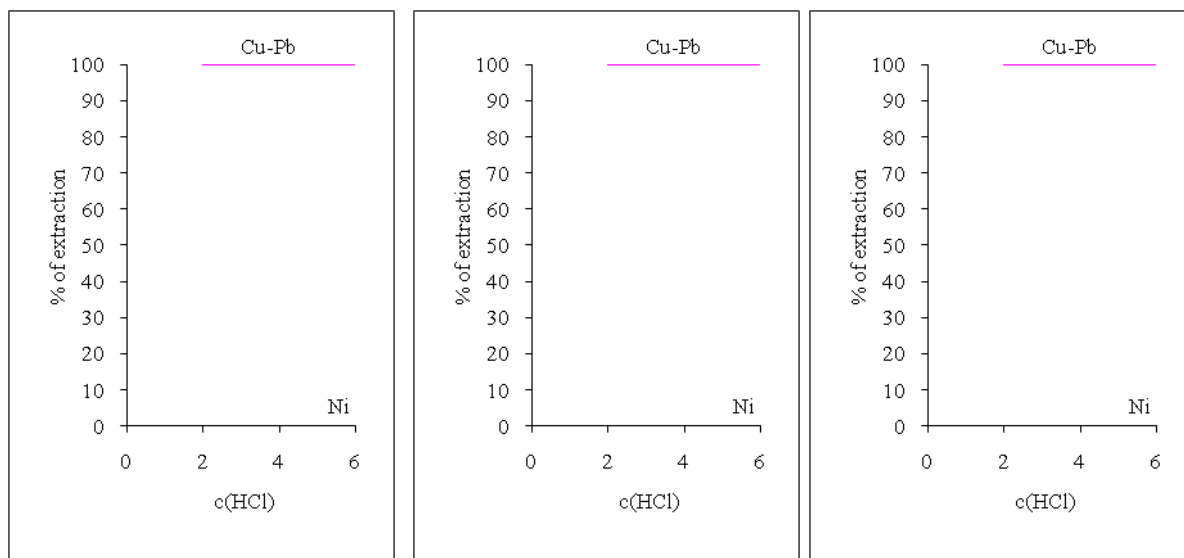
Figure 2: Extraction curves, of elements with N-methyl-N,N,N-trioctylctan-1-ammonium chloride shown, as function of HCl and NaCl concentrations:

- a) $\gamma(\text{NaCl})=20 \text{ g dm}^{-3}$; b) $\gamma(\text{NaCl})=40 \text{ g dm}^{-3}$; c) $\gamma(\text{NaCl})=60 \text{ g dm}^{-3}$

Extraction of copper, lead and nickel from acidic solution containing sodium iodide is shown in Figure 3a-c. Copper and lead in all cases are extracted 100%. In all cases the extraction percentage of nickel is zero.

Extraction of copper, lead and nickel from acidic solution containing sodium acetate is shown in Figure 4a-c.

From Figure 4a-c we can see that in HCl solution with concentration of 2 mol dm⁻³, extraction of copper is small and with increasing of acidities extraction of copper will increase continually till 58.2%, 54.8% and 54.9% (in solution of 6 mol dm⁻³HCl). So, HCl concentrations have higher influence in extraction of copper. Extraction curve of copper obtained from sodium acetate solution are almost same. The influence of sodium acetate concentration in extraction of copper is lower. In all cases the extraction percentage of nickel is zero. Extraction percentage of lead from sodium acetate solutions is decrease with increasing of HCl concentration. The influence of sodium acetate concentration in extraction of lead is lower. From Figure 4a-c we can see that in HCl solution with concentration of 6 mol dm⁻³, extraction of lead is 34.1%, 32.6% and 40.2% and with decrease of acidities extraction of lead will increase continually till 82.1%, 80.2% and 75.2% (in solution of 2 mol dm⁻³ HCl). Extraction curve of lead obtained from sodium acetate solution are almost same.



a)

b)

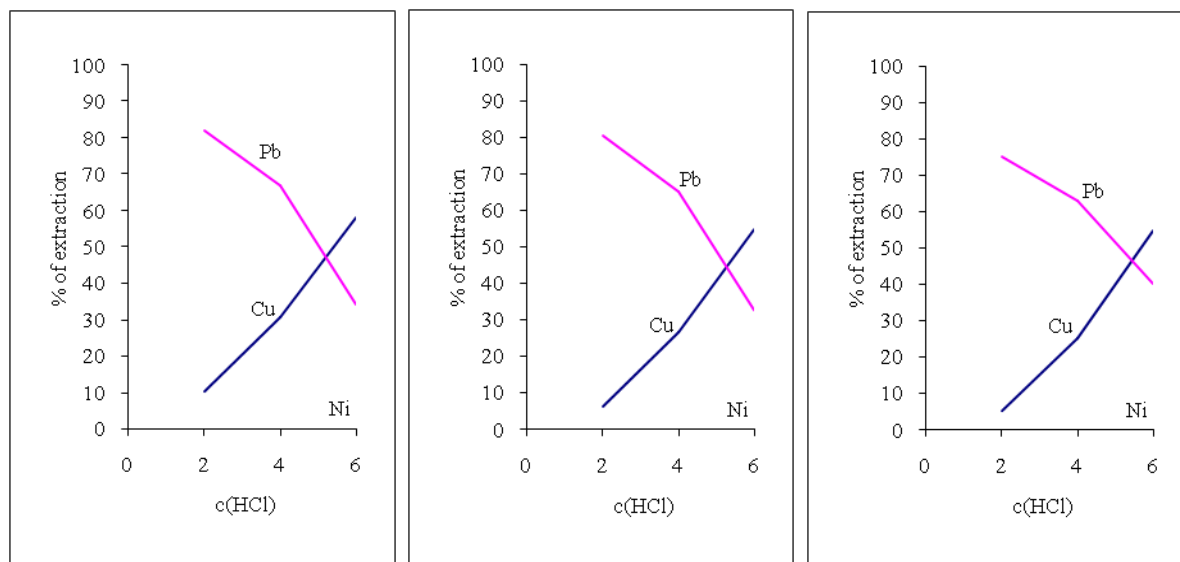
c)

Figure 3: Extraction curves, of elements with N-methyl-N,N,N-trioctyloctan-1-ammonium chloride shown, as function of HCl and NaCl concentrations:

a) $\gamma(\text{NaI})=20 \text{ g dm}^{-3}$;

b) $\gamma(\text{NaI})=40 \text{ g dm}^{-3}$;

c) $\gamma(\text{NaI})=60 \text{ g dm}^{-3}$



a)

b)

c)

Figure 4: Extraction curves, of elements with N-methyl-N,N,N-trioctyloctan-1-ammonium chloride shown, as function of HCl and CH_3COONa concentrations:

a) $\gamma(\text{CH}_3\text{COONa})=20 \text{ g dm}^{-3}$;

b) $\gamma(\text{CH}_3\text{COONa})=40 \text{ g dm}^{-3}$;

c) $\gamma(\text{CH}_3\text{COONa})=60 \text{ g dm}^{-3}$

As optimal condition to separate copper and lead from nickel is the extraction of copper and lead from HCl solutions with concentration 2, 4 and 6 mol dm⁻³ in presence of sodium iodide with concentration 20, 40 and 60 g dm⁻³. Using these condition 100% of copper and lead was in organic phase and all of nickel remains in water phase.

As optimal condition to separate copper from lead is the extraction of copper from HCl solution with concentration 6 mol dm⁻³ in presence of sodium chloride with concentration of 40 g dm⁻³. Using these condition 76.8% of copper was in organic phase and all of lead remains in water phase.

4. Conclusion

From our results we can conclude:

- Extraction of copper from sodium chloride solution move from 12.5-76.8%, from sodium iodide solution 100% and from sodium acetate solution 5.1-88.2%.
- Extraction of lead from natrium chloride solution move from 0-48.5%, from sodium iodide solution 100% and from sodium acetate solution 32.6-82.1%.
- Extraction of nickel from sodium chloride, sodium iodide and sodium acetate is 0%.

The influence of sodium chloride, sodium iodide and sodium acetate concentration in extraction of copper is lower. The influence of sodium iodide and sodium acetate concentration in extraction of copper is lower. The influence of sodium chloride concentration in extraction of lead is big.

- As optimal condition to separate copper and lead from nickel is the extraction of copper and lead from HCl solutions with concentration 2, 4 and 6 mol dm⁻³ in presence of sodium iodide with concentration 20, 40 and 60 g dm⁻³. Using these condition 100% of copper and lead was in organic phase and all of nickel remains in water phase.
- As optimal condition to separate copper from lead is the extraction of copper from HCl solution with concentration 6 mol dm⁻³ in presence of sodium chloride with concentration of 40 g dm⁻³. Using these condition 76.8% of copper was in organic phase and all of lead remains in water phase.

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