

## Extraction of Ca(II) and Mg(II) from Hydrochloric Acid Solutions by N,N-Dioctyl-1-Octanamine in Methyl Isobutyl Ketone

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**Abstract: Problem statement:** 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. **Approach:** Based on that, we have investigated the extraction of Calcium and Magnesium with N,N-dioctyl-1-octanamine from the mixture of elements prepared in artificial manner. We investigated the influence of HCl concentration and salts (NaCl, NaI and CH<sub>3</sub>COONa) concentration in extraction of two elements (Calcium and Magnesium) from water solutions. All extractions were done from HCl water solutions with  $c = 3, 6$  and  $9 \text{ mol L}^{-1}$  and in presence of NaCl, NaI and CH<sub>3</sub>COONa salts, which we prepared in different concentrations. **Results:** Extraction of Calcium from NaCl solution move from 50-75%, from NaI solution 0-90% and from CH<sub>3</sub>COONa solution 37-81%. Extraction of Magnesium from NaCl solution move from 0-10%. In solution of NaI we can not extract the Magnesium and from CH<sub>3</sub>COONa solution the extraction of magnesium moves from 0-30%. **Conclusion:** As optimal condition to separate Calcium from Magnesium is the extraction of Calcium from HCl solution with concentration  $9 \text{ mol L}^{-1}$  in presence of NaI with concentration of  $60 \text{ g L}^{-1}$ . Using these condition 90% of Calcium was in organic phase and all of magnesium remains in water phase.

**Key words:** Extraction, calcium, magnesium, N,N-dioctyl-1-octanamine, organic phase, aqueous phase

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### INTRODUCTION

Extraction of metals with organic bases with large molecular masse is forced in the last years (Cox *et al.*, 2004). 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 (Sengupra and Yizhak, 2001).

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 (McClellan *et al.*, 1974).

Faiku *et al.* (2009) have investigated the extraction of Calcium and Magnesium with mixture of N,N-

dioctyl-1-octanamine 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 calcium and magnesium in organic phase.

Kimura (1960) has done the extraction of some metals including Calcium and Magnesium, from HCl solution with concentration  $0.01 \text{ mol L}^{-1}$ ,  $0.1 \text{ mol L}^{-1}$  and  $1 \text{ mol L}^{-1}$  with di-(2-Ethylhexyl) phosphoric acid (50% in toluene). He found that Calcium was extracted 11% from solution of HCl with concentration  $0.1 \text{ mol L}^{-1}$ , while Magnesium was extracted 36% from HCl solution with concentration  $0.01 \text{ mol L}^{-1}$ .

Organic molecules as alamine 336 (Filiz, 2007; Sayar and Filz, 2007; 2009), aliquat 336 (Atanassova *et al.*, 2002; El-Nadi *et al.*, 2009), are able to form complexes with metals ions and for that we can use them to extract metals ions from hydrometallurgical solutions.

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Based on that we have investigated the extraction of Calcium and Magnesium with 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  $\text{CaCl}_2 \times 6\text{H}_2\text{O}$  and  $\text{MgCl}_2$  in distillate water. Water solutions of Calcium and Magnesium with metal concentration of  $1\text{g L}^{-1}$  were prepared using  $\text{CaCl}_2 \times 6\text{H}_2\text{O}$  and  $\text{MgCl}_2$ . 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.

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 Ca and Mg quantities in water solutions, we used absorber spectrophotometer Buck Scientific Model 200A.

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  $\text{L}^{-1}$  and in presence of NaCl, NaI and  $\text{CH}_3\text{COONa}$  salts. Also the water solutions of NaCl, NaI and  $\text{CH}_3\text{COONa}$  salts, we have prepared in different concentrations. Extraction of Calcium and Magnesium was done with separator funnel of 150 mL.

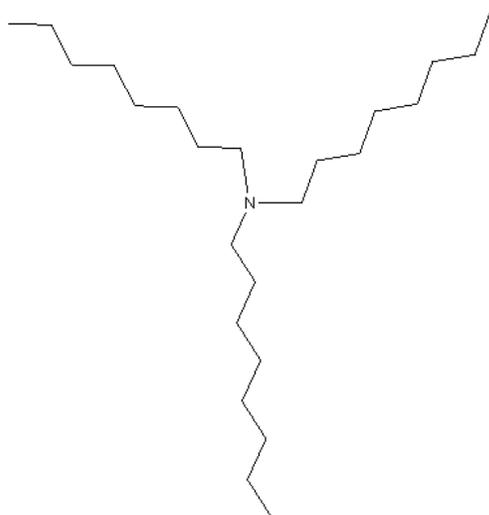


Fig. 1: Structure of N,N-dioctyl-1-octanamine

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 Calcium and Magnesium) that were present (remain) in it.

### RESULTS

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 calcium and magnesium with N,N-dioctyl-1-octanamine in presence of NaCl

c(HCl) mol <sup>-1</sup> L <sup>-1</sup>	γ(NaCl) g <sup>-1</sup> L <sup>-1</sup>	Ca	Mg
3	20	50.0	5.2
6	20	65.2	7.1
9	20	70.1	10.0
3	40	60.6	3.3
6	40	63.2	5.1
9	40	68.4	8.0
3	60	66.1	-
6	60	69.2	-
9	60	75.0	2.1

Table 2: Extraction of calcium and magnesium with N,N-dioctyl-1-octanamine in presence of NaI

c(HCl) mol <sup>-1</sup> L <sup>-1</sup>	γ(NaI) g <sup>-1</sup> L <sup>-1</sup>	Ca	Mg
3	20	-	-
6	20	22.4	-
9	20	88.4	-
3	40	32.5	-
6	40	71.6	-
9	40	82.0	-
3	60	40.2	-
6	60	84.1	-
9	60	90.0	-

Table 3: Extraction of calcium and magnesium with N,N-dioctyl-1-octanamine in presence of NaAc

c(HCl) mol <sup>-1</sup> L <sup>-1</sup>	γ(NaAc) g <sup>-1</sup> L <sup>-1</sup>	Ca	Mg
3	20	37.0	-
6	20	63.5	5.5
9	20	81.0	30.0
3	40	41.7	-
6	40	62.5	-
9	40	68.0	6.0
3	60	43.4	-
6	60	62.6	-
9	60	71.1	12.2

**DISCUSSION**

Extraction of Calcium from acidic solution containing NaCl, is shown in Fig. 2a-c. NaCl and HCl concentrations have a little influence in extraction percentage of Calcium.

Extraction of Calcium from acidic solution that contains NaI, is presented in Fig. 3a-c. The presence of NaI has high influence in extraction percentage of Calcium. From Fig. 3a we can see that in HCl solution with concentration of 3 mol L<sup>-1</sup>, extraction of Calcium is zero and with increasing of acidities extraction of Calcium will increase continually till 88.4% (in solution of 9 mol L<sup>-1</sup> HCl). So, HCl and NaI

concentrations have higher influence in extraction of Calcium.

Extraction curve of Calcium obtained from sodium acetate solution are almost same. Extraction percentage of Calcium from sodium acetate solutions will increase with increasing of HCl concentration. The influence of sodium acetate concentration in extraction of Calcium is lower (Fig. 4-c).

In all cases the extraction percentage of Magnesium is lower or is zero (Fig. 2a-c; 3a-c; 4a-c). One exception we found that extraction of Magnesium is 30% when extraction was done in HCl solution with concentration 9 mol L<sup>-1</sup> and in presence of sodium acetate with concentration 20 g L<sup>-1</sup> (Fig. 4a).

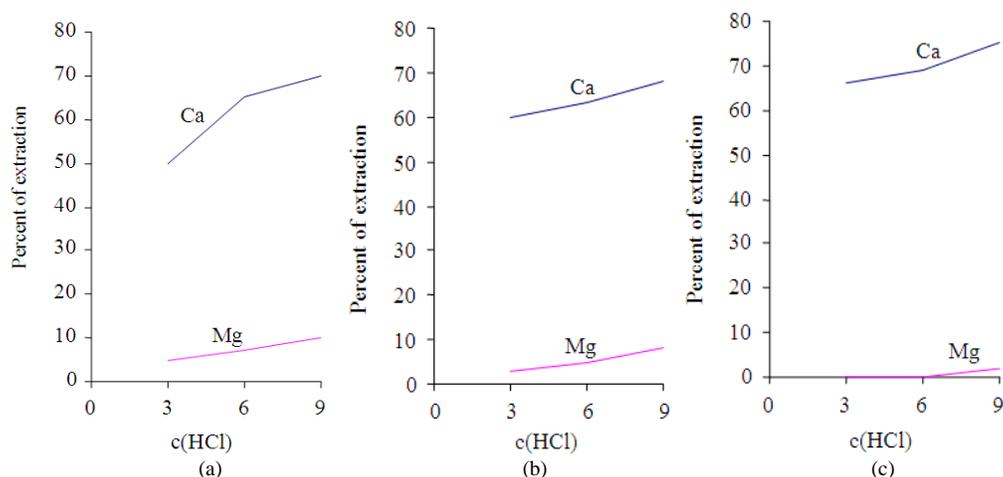


Fig. 2: Extraction curves, of elements with N,N-dioctyl-1-octanamine shown, as function of HCl and NaCl concentrations: (a)  $\gamma(\text{NaCl}) = 20 \text{ g L}^{-1}$ ; (b)  $\gamma(\text{NaCl}) = 40 \text{ g L}^{-1}$ ; (c)  $\gamma(\text{NaCl}) = 60 \text{ g L}^{-1}$

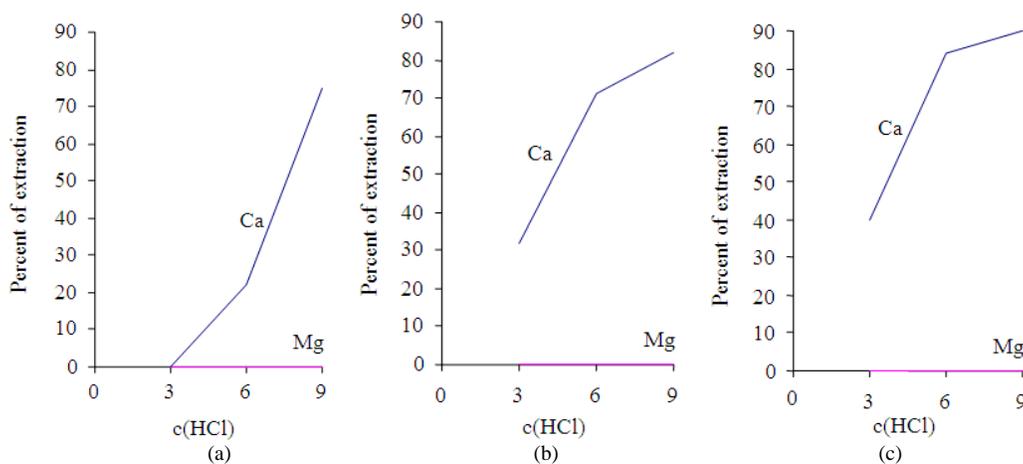


Fig. 3: Extraction curves, of elements with N,N-dioctyl-1-octanamine shown, as function of HCl and NaI concentrations: (a)  $\gamma(\text{NaI}) = 20 \text{ g L}^{-1}$ ; (b)  $\gamma(\text{NaI}) = 40 \text{ g L}^{-1}$ ; (c)  $\gamma(\text{NaI}) = 60 \text{ g L}^{-1}$

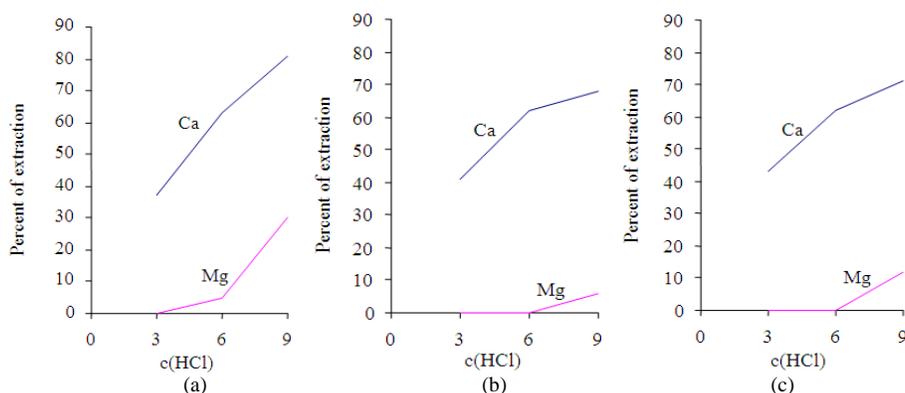


Fig. 4: Extraction curves of elements with *N,N*-dioctyl-1-octanamine shown, as function of HCl and NaAc concentrations: (a)  $\gamma(\text{NaAc}) = 20 \text{ g L}^{-1}$ ; (b)  $\gamma(\text{NaAc}) = 40 \text{ g L}^{-1}$ ; (c)  $\gamma(\text{NaAc}) = 60 \text{ g L}^{-1}$

### CONCLUSION

From our results we can conclude:

- Extraction of Calcium from NaCl move from 50-75%, from NaI solution 0-90% and from  $\text{CH}_3\text{COONa}$  solution 37-81%
- Extraction of Mangesium from NaCl solution move from 0-10%. In solution of NaI we can not extract the magnesium and from  $\text{CH}_3\text{COONa}$  solution the percentage extraction of magnesium moves from 0-30%
- Extraction percentage of Calcium and Magnesium increase with increasing of HCl concentration
- As optimal condition to separate Calcium from Magnesium is the extraction of Calcium from HCl solution with concentration  $9 \text{ mol L}^{-1}$  in presence of NaI with concentration of  $60 \text{ g L}^{-1}$ . Using these condition 90% of Calcium was in organic phase and all of magnesium remains in water phase

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