Extraction of Ca (II) and Mg (II) from Hydrochloric Acid Solutions by N, N-Dioctyl-1-Octan Ammonium Chloride 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-octan ammonium chloride from the mixture of elements (Ca and Mg) prepared in artificial manner. We have investigated the influence of HCl concentration and salts (NaCl, NaI and CH_3COONa) concentration in extraction of two elements (Ca and Mg) from water solutions. All extractions were done from HCl water solutions with c = 3, 6 and 9 mol L^{-1} and in presence of NaCl, NaI and CH_3COONa salts, which we prepared in different concentrations. **Results:** Extraction of Calcium from NaCl solution move from 18-30%, from NaI solution 55-77% and from CH_3COONa solution 50-71%. Extraction of Magnesium from NaCl solution move from 3-12%, from NaI solution 0-11% and from CH_3COONa solution 0-8%. **Conclusion:** As optimal condition to separate Calcium from Magnesium is the extraction of Calcium from HCl solution with concentration 9 mol L^{-1} in presence of NaI with concentration of 60 g L^{-1}. Using these condition 77% of Calcium was in organic phase and all of magnesium remains in water phase.

Key words: Magnesium remains, elements prepared, organic phase, artificial manner, ammonium chloride, large molecular masse, changing factors

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 *et al.*, 2004).

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 camion (McClellan *et al.*, 1974).

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-octanamine. They have found that all changing factors can influence in extraction percentage of calcium and magnesium in organic phase. As optimal condition to separate Calcium from Magnesium is the extraction of Calcium from HCl solution with concentration 9 mol L^{-1} in presence of NaI with concentration of 60 g L^{-1}. Using these condition 90% of Calcium was in organic phase and all of magnesium remains in water phase.

Kimura (1960) has done the extraction of some metals including Calcium and Magnesium, from HCl solution with concentration 0.01, 0.1 and 1 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 mol L^{-1}, while Magnesium

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was extracted 36% from HCl solution with concentration 0.01moL L^{-1}.

Organic molecules as alamine 336 (Filiz, 2007; Sayar *et al*., 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.

In view of these observations and in continuation of our research programme on the extraction of Ca and Mg from water with different organic amines, we report herein the extraction of Ca and Mg with N, N-dioctyl-1-actan ammonium chloride.

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 $CaCl_2 \times 6H_2O$ and $MgCl_2$ in distillate water. Water solutions of Calcium and Magnesium with metal concentration of 1g L^{-1} were prepared using $CaCl_2 \times 6H_2O$ and $MgCl_2$. As organic phase we used 10% solution of N, N-dioctyl-1-octan ammonium chloride 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-octan ammonium chloride. The structural formula of N, N-dioctyl-1-octan ammonium chloride is shown in Fig. 1.

N, N-dioctyl-1-actan 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 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-octan ammonium chloride in methyl isobutyl ketone.
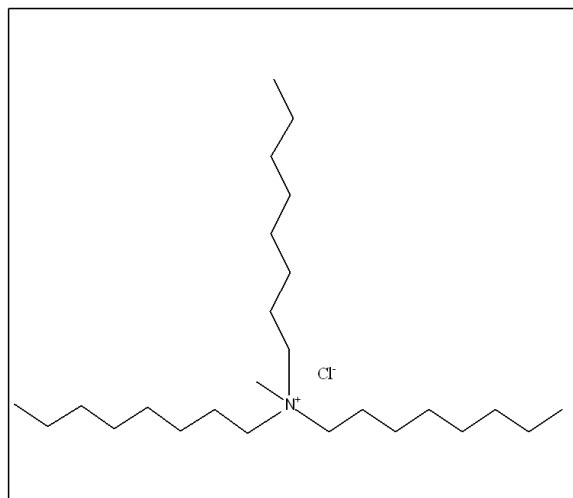

Fig. 1: Structure of N, N-dioctyl-1-actan ammonium chloride

All extraction was done from HCl water solutions with concentrations 3, 6 and 9 mol L^{-1} 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 Calcium and Magnesium was done with separator funnel of 150 mL^{-1}. 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^{-1} of water model and 10 mL^{-1} 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-octan ammonium chloride in presence of NaCl

c(HCl)/ mol L^{-1}	γ(NaCl)/ g L^{-1}	Ca	Mg
3	20	30.0	12.0
6	20	20.5	8.1
9	20	18.0	11.3
3	40	25.1	3.3
6	40	22.4	1.5
9	40	18.2	6.4
3	60	20.3	8.3
6	60	18.5	7.1
9	60	15.0	10.2

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

c(HCl)/ mol L^{-1}	γ(NaI)/ g L^{-1}	Ca	Mg
3	20	55.0	-
6	20	58.1	10.1
9	20	62.4	-
3	40	58.0	-
6	40	62.1	11.0
9	40	66.3	-
3	60	68.1	-
6	60	71.2	8.0
9	60	77.0	-

Table 3: Extraction of calcium and magnesium with N,N-dioctyl-1-octan ammonium chloride in presence of CH_3COONa

c(HCl)/ mol L^{-1}	γ(NaAc)/ g L^{-1}	Ca	Mg
3	20	51.0	-
6	20	62.1	-
9	20	65.4	8.0
3	40	50.0	4.0
6	40	68.1	5.2
9	40	71.0	6.0
3	60	55.4	3.1
6	60	57.3	5.3
9	60	63.1	6.2

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. As characteristic during the extraction of Calcium, from the NaCl solutions, is the percentage of Calcium decreases by increasing the concentration of HCl.

Extraction of Calcium from acidic solution containing NaI, is shown in Fig. 3a-c. From Fig. 3a-c we can see that in HCl solution with concentration of 3 mol L^{-1} extraction of Calcium is smaller and with increasing of acidities extraction of Calcium will increase continually till 77.0% (in solution of 9 mol L^{-1} HCl and in presence of NaI with concentration 60 g L^{-1}). Extraction curve of Calcium obtained from NaI solution are almost same.

Extraction of Calcium from acidic solution containing CH_3COONa, is shown in Fig. 4a-c. 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.

Extraction of Magnesium from acidic solution containing NaCl, is shown in Fig. 2a-c. Is found that extraction of Magnezium is 12.0% when extraction was done in HCl solution with concentration 3 mol L^{-1} and in presence of sodium chloride with concentration 20 g L^{-1} (Fig. 2a). Extraction curve of Magnesium obtained from sodium chloride solution are almost same.

Extraction of Magnesium from acidic solution containing NaI, is shown in Fig. 3a-c. From Fig. 3a-c we can see that in HCl solution with concentration of 3 and 9 mol L^{-1}, extraction of Magnesium is zero. Extraction curve of Magnesium obtained from NaI solution are almost same.

Extraction of Magnesium from acidic solution containing CH_3COONa, is shown in Fig. 4a-c. From Fig. 4a we can see that in HCl solution with concentration of 3 and 6 mol L^{-1}, extraction of Magnesium is zero and with increasing of acidities extraction of Magnesium will increase continually till 8.0% (in solution of 9 mol L^{-1} HCl and in presence of sodium acetate with concentration 20 g L^{-1}).

Extraction percentage of Magnesium from sodium acetate solutions will increase with increasing of HCl concentration (Fig. 4b and c). CH_3COONa and HCl concentrations have a little influence in extraction percentage of Magnesium.
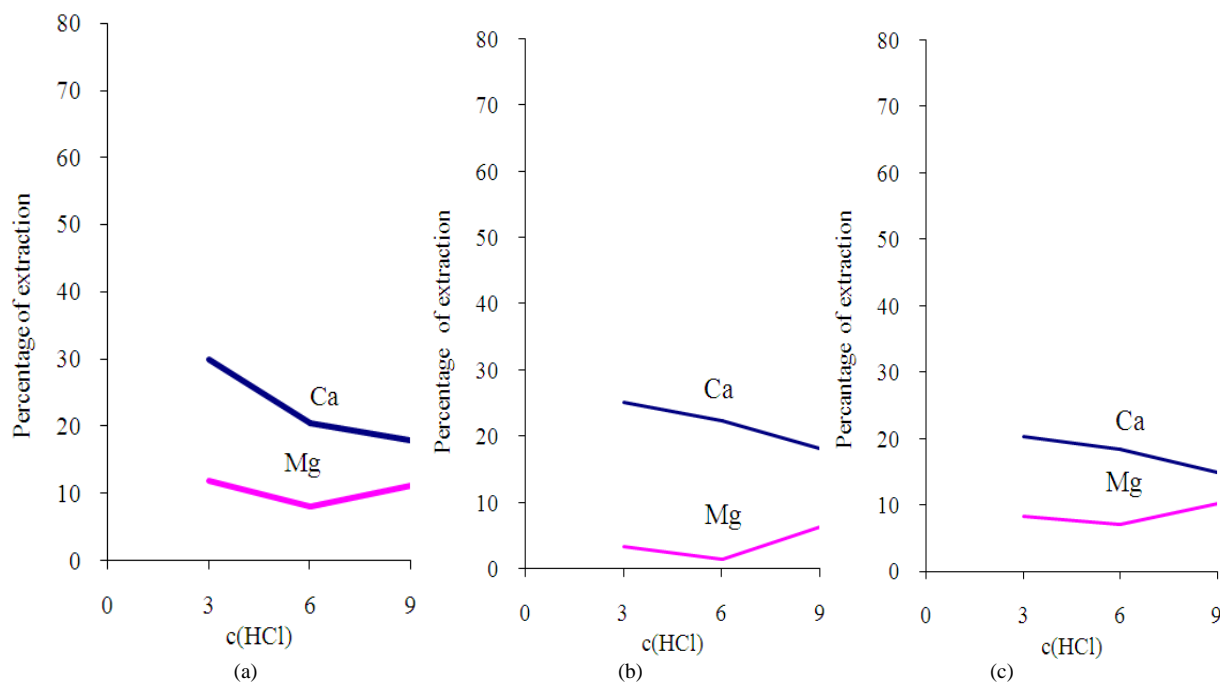

Fig. 2: Exraction curves, of elements with N,N-dioctyl-1-octan ammonium chloride shown, as function of HCl and NaCl concentrations: (a) γ (NaCl) = 20 g L^{-1} ; (b) γ (NaCl) = 40 g L^{-1} ; (c) γ (NaCl) = 60 g L^{-1}
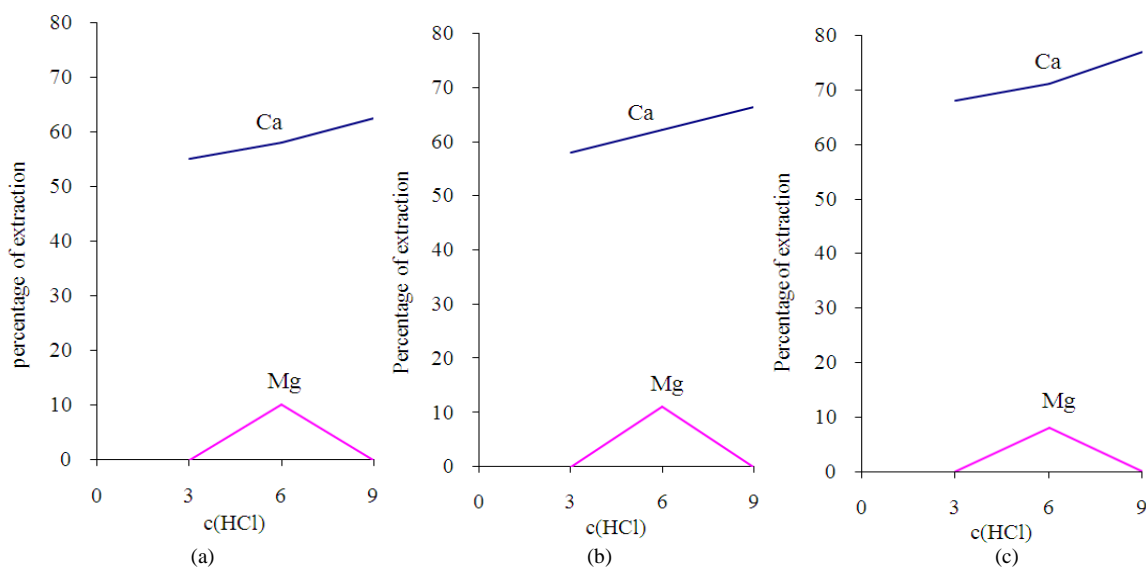
Fig. 3: Exraction curves, of elements with N,N-dioctyl-1-octan ammonium chloride shown, as function of HCl and NaI concentrations: (a) γ (NaI) = 20 g L^{-1} ; (b) γ (NaI) = 40 g L^{-1} ; (c) γ (NaI) = 60 g L^{-1}
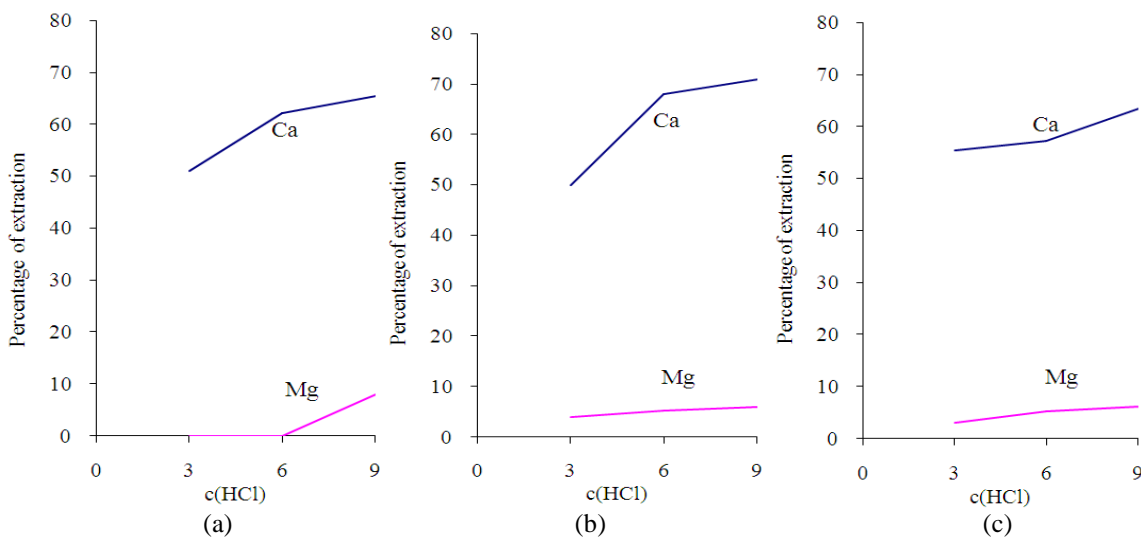

Fig. 4: Exraction curves, of elements with N, N-dioctyl-1-octan ammonium chloride shown, as function of HCl and NaAc concentrations: (a) γ (NaAc) = 20 g L^{-1}; (b) γ (NaAc) = 40 g L^{-1}; (c) γ (NaAc) = 60 g L^{-1}

CONCLUSION

From our results we can conclude:

- Extraction of Calcium from NaCl solution move from 18-30%, from NaI solution 55-77% and from CH$_3$COONa solution 50-71%.
- Extraction of Magnesium from NaCl solution move from 3-12%, from NaI solution 0-11% and from CH$_3$COONa solution 0-8%.

- Extraction of magnesium is small.
- In solution of 9 mol L^{-1} HCl and in presence of NaI with concentration 60 g L^{-1}, extraction of Calcium is higher (77.0%).
- As optimal condition to separate Calcium from Magnesium is the extraction of Calcium from HCl solution with concentration 9 mol L^{-1} in presence of NaI with concentration of 60 g L^{-1}. Using these

condition 77% of Calcium was in organic phase and all of magnesium remains in water phase.

- If we compare these results with the results from the previous work we can see that N, N-dioctyl-1-actan ammonium chloride is not effective as N,N-Dioctyl-1-Octanamine.

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