Liquid Ion Exchange Application for Micro Amount Separation and Determination of Ca(II) and Mg(II) as Anions Species with EDTA

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ABSTRACT

Extracted Mg(II) and Ca(II) each one alone after combined with EDTA (H₃Y⁻) as (MgHY⁻) and (CaHY⁻) after preparing ion pair complexes according to liquid ion exchange method by using Cinchonine (CK) after changing to liquid ion exchanger HCK⁺;Cl⁻ in HCl medium, spectrophotometric studies showed that the ion pair magnesium complex HCK⁺;MgHY⁻ had a wavelength for maximum absorbance of \( \lambda_{\text{max}} = 241\text{nm} \), but the maximum absorbance for calcium HCK⁺;CaHY⁻ was \( \lambda_{\text{max}} = 278\text{nm} \) to determine the remaining quantity of Mg(II), the Eriochrome black T method was used, but for Ca(II) the crown ether DB18C6 method was used as new spectrophotometric method. Limitations to the study include optimum conditions for extraction ions in this study show a need for 1M HCl for Mg(II) and 0.8M HCl for Ca(II), to be present 100µg for each ion, 0.08M EDTA for Mg(II) and 1.0M EDTA for Ca(II), 1×10⁻⁴ M CK, after shaking for 10 min. Thermodynamic study shows \( \Delta_{H}^o = 0.058\text{kJmol}^{-1}, \Delta_{G}^o = -47.28\text{kJmol}^{-1}, \Delta_{S}^o = 158.86\text{J.mol}^{-1}\text{K}^{-1} \) for Mg(II) and for Ca(II) was \( \Delta_{H}^o = 0.0892\text{kJmol}^{-1}, \Delta_{G}^o = -54.66\text{kJmol}^{-1}, \Delta_{S}^o = 180.69\text{J.mol}^{-1}\text{K}^{-1} \).

Keywords: Calcium, Magnesium, EDTA, Cinchonine, Liquid Ion Exchange, Solvent extraction.

INTRODUCTION

Cloud point extraction method has been applied for Mg²⁺ ions extraction. The extracted solvated species have \( \lambda_{\text{max}} = 249\text{nm} \). The study include the determination of all optimum conditions for extraction, as well as the determination of Mg²⁺ ions in different samples¹. Extraction of ⁴⁵Ca(II) was performed into toluene solutions of HTTA, HDEHP, HTTA+TBP and HDEHP+ BP. Thermodynamic parameters are used to explain no change in the coordination number of Ca(II)². Cloud point extraction method was used for separation of Mg(II) as anion with oxine. The method involved formation of an ion pair complex between Rhodamin–B and oxine anion complex of magnesium [Mg(OX)₃] in basic media, in presence of Triton X-100³. 1-(2- Pyridyl azo)-4-Benzene naphthol was used...
as reagent for determination of Mg(II) in different environmental and vital samples, after Mg(II) conversion to anion complex with oxine, as well as micro amount determination of Magnesium(II) in different samples. The extraction of Ca(II) and Mg(II) with N, N-dioctyl-1-octan ammonium chloride from the mixture of elements (Ca and Mg) was prepared in a synthetic manner. The effects of HCl and NaCl, NaI and CH₃COONa concentration in extraction of Ca and Mg from water solutions were studied. All extractions were done from HCl solutions in the presence of NaCl, NaI and CH₃COONa salts. The distribution of alkaline earth cations between CCl₄ and aqueous sodium perchlorate solutions has been studied by thenoyltrifluoro acetone and adduct forming ligand trioctylphosphine oxide. The separation of alkaline earth cations is explained by solvent extraction with H⁺ ion in aqueous solutions. The selectivity in the order is, Mg²⁺ > Ca²⁺ > Sr²⁺ > Ba²⁺.

EXPERIMENTAL METHODS

Apparatus
The spectrophotometric measurements were carried out by using a double beam UV-Vis. spectrophotometer, (Biochrom Libra S60) (UK), and for shaking the solutions a HY-4 vibrator with AD at just about multiple speed was used (Italy). Electrical balance was used for the weight substance (A & D company, Limited, Dool, CE, HR 200), (Japan). The pH was measured by using a pH-meter, WTW (Germany). For regular temperature, a water bath (galvanothermy thermostatic bath) (Germany) was used.

Materials and Solutions
All chemicals used in experiments came from reliable commercial companies and were used without further purification, all solutions were prepared by using a suitable volumetric flask with distilled water stock solution of Mg(II) and Ca(II) at concentrations of 1000 ppm prepared by dissolving (0.0392g) of MgCl₂ (Merck) and (0.0275g) of CaCl₂ (Merck) respectively in 10 ml distilled water, so that 0.1M EDTA was prepared by dissolving (0.0392g) of MgCl₂ (Merck) and (0.0275g) of CaCl₂ (Merck) in 10 ml distilled water, Cinchonine((S)-[(2R,4S,5R)-5-ethenyl-1-azabicyclo[2.2.2]octan-2-yl]-quinolin-4-ylmethyl) (Fluka) solution 1×10⁻² M was prepared by dissolving (0.0294g) in 100 ml chloroform. The DB18C6 solution 1×10⁻² M was prepared by dissolving (0.0360g) in 10ml chloroform. Where applicable, all the other working solutions were prepared by dilution with solvents in a suitable volumetric flask.

Fundamental Method

- 5ml of aqueous solution contained 100µg Mg²⁺ or Ca²⁺ each, with 0.08M EDTA at pH=3 and these solutions were shaken for 5 min.
- 5ml of Cinchonine solution was dissolved in chloroform at 1×10⁻⁴ M and then shaken for 5 minutes with 5ml of 0.5M HCl, afterward the organic solution was separated from the aqueous solution.
- Afterward adding organic solution in second step to the aqueous solution at first step and then these two layers were shaken for 15 min. and later the organic phase was separated from the aqueous phase, then the absorbance of the organic phase was measured at λₘₐₓ=241nm for the ion pair complex of Mg²⁺ and at λₘₐₓ=278nm for the ion pair complex of Ca²⁺.

The aqueous solution of extracted Mg²⁺ was treated according to the Eriochrom black T’ spectroscopic method for determining the remaining quantity of Mg²⁺ in the aqueous phase after extraction by returning to a calibration curve in Fig. 1, so this quantity was subtracted from the original quantity of Mg²⁺ ions in the aqueous phase to determine the transfer quantity of metal cation afterward calculate D values for extraction.

For determining the Ca²⁺ ions in the aqueous solution after extraction, the new method was used as detailed below:

5ml of aqueous solution contains the remaining quantity of Ca²⁺ ion, which keeps the pH of the solution at pH=9 then 5ml of crown ether, DB18C6, dissolved in chloroform was added to make it 1×10⁻⁴ M, then the two layers were shaken for 10 minutes. Next, the organic phase was separated from the aqueous phase and the
absorbance of the organic phase was measured at \( \lambda_{\text{max}} = 283\text{nm} \) against the DB18C6 solution as blank solution. This was limited through spectroscopic study.

![Graph](image1)

(a)

![Graph](image2)

(b)

**Fig. 1.** Calibration Curves for the Determination of \( \text{Mg}^{2+} \) and \( \text{Ca}^{2+} \) in the Aqueous Phase

(a) According to Eriochrom Black T Methods for \( \text{Mg}^{2+} \)

(b) DB18C6 Crown Ether Method for \( \text{Ca}^{2+} \)

**RESULTS AND DISCUSSION**

**Spectroscopic Studies**

The spectrophotometric study shows wavelength for maximum absorbance was \( \lambda_{\text{max}} = 283\text{nm} \) for spectrophotometric determined of \( \text{Ca}^{2+} \) in aqueous solution by DB18C6 method, so that for extracted complexes were \( \lambda_{\text{max}} = 241\text{nm} \) for \( \text{Mg}^{2+} \), \( \lambda_{\text{max}} = 278\text{nm} \) for \( \text{Ca}^{2+} \).

**Fig. 2.** UV-Vis. Spectrum of Ion Pair Complex for \( \text{CaDB}18\text{C6}^{2+}; 2\text{Cl}^- \) for Determination of Remaining Quantity of \( \text{Ca}^{2+} \) in the Aqueous Phase.

**Fig. 3.** UV-Vis. The Spectrum of the Ion Pair Complex for \( \text{Mg}^{2+} \)

**Fig. 4.** UV-Vis. The Spectrum of an Ion Pair Complex for \( \text{Ca}^{2+} \)

**Effects of HCl Concentration**

The \( \text{Mg}^{2+} \) and \( \text{Ca}^{2+} \) was extracted according to the fundamental method after a 5mL solution of \( 1 \times 10^{-4} \text{M} \) Cinchonine dissolved in chloroform was shaken with 5mL of aqueous solutions of different concentrations of HCl, the results were as in Figures (5 and 6).

**Fig. 5.** Effects of HCl Concentration on Ion Pair Complex Formation and Stability.

**Fig. 6.** Effects of HCl Concentration on Extraction Efficiency and D Values
The results show 1M HCl was the optimum concentration for extraction of Mg$^{2+}$ ions, but for extraction of Ca$^{2+}$ ions, 0.8M HCl was necessary at these concentrations to reach a favorable equilibrium to form an ion exchanger that appears more suitable for an equalized ion exchange between Cl$^-$ and MHY to offer maximum concentration and more stable ion pair extraction. Any concentration of HCl less than optimum values prevented the solution from reaching thermodynamic equilibrium and minimized extraction efficiency, so that concentration more than optimum concentration effects was required to increase backward direction and dissociation of the ion exchanger. In addition, increasing the Cl$^-$ concentration in the solutions appeared to affect steric to metal ion for preparing complex with EDTA.

**Effects of Metal Ion Concentration**

5ml aqueous solutions contained different quantities of Mg$^{2+}$ or Ca$^{2+}$ with 0.08M of EDTA at pH=3 after these solutions were shaken for 5min. Another 5ml of Cinchonine was shaken for 5min. with 5ml of 1M HCl for Mg$^{2+}$ and 0.8M HCl for Ca$^{2+}$, then the organic phase containing the ion exchanger was separated, and then the solution of Cinchonine was added to the solutions of metal cation with EDTA which were shaken for 10min, and then completed using the fundamental method, the results are show in Figures 7 and 8.

![Fig. 7. Effects of metal cation on ion pair complex formation and stability.](image)

![Fig. 8. Effects of metal cation on extraction efficiency and D values.](image)

The results show that 100µg Mg$^{2+}$ and Ca$^{2+}$ was the optimum concentration of metal cation, allowing higher absorbance and D value, undoubtedly this concentration created the appropriate equilibrium, a concentration less than optimum would not be suitable to reach favorable thermodynamic equilibrium of ion pair formation, so an increase in metal cation causes a reduction in extraction efficiency, because it indicated an increase in backward direction of equilibrium and dissociation according to mass action law.

**Effects of EDTA Concentration**

According to the fundamental method, Mg$^{2+}$ and Ca$^{2+}$ were extracted at optimum conditions in the presence of different concentrations of EDTA; the results are shown in Figures 9 and 10.

![Fig. 9. Effects of EDTA Concentration on Ion Pair Formation and Absorbance.](image)

![Fig. 10. Concentration of EDTA’s effects on Extraction Efficiency and D Values.](image)

From the results, it appears that 0.08M, 0.10M EDTA was the optimum concentration for extraction of Mg$^{2+}$ and Ca$^{2+}$ respectively, because at these concentrations, they reached the ideal thermodynamic equilibrium to form anion complex species MgHY$^-$ and CaHY$. Any concentration less than optimum is not suitable for forming sufficient concentration and stability of the anion complexes with EDTA, which also minimizes absorbance and D values. Concentrations more than optimum cause a deviation in extraction by increasing backward direction of equilibrium and dissociation according to mass action law.
Shaking Time Effect

According to fundamental method, Mg$^{2+}$ and Ca$^{2+}$ were extracted at optimum conditions for each ion at different shaking times. The results are shown in Figures 11 and 12.

The results demonstrate that 10 min. was the optimum shaking time for both metal cations, as well as being the optimum time for favorable thermodynamic equilibrium for formation and extraction of high concentrations of ion pairs with high stability. Shaking time represents kinetic energy for transitioning the species to the organic phase$^9, 10$.

Structure of Extracted Species

According to fundamental method, extracted metal cation can be studied by using different concentrations of Cinchonine dissolved in chloroform. The distribution ratio (D) of extraction was calculated. The results are shown in Figure 11.

This procedure, which is known as the slope analysis method, found that the slope value is equal to 0.579 for Mg$^{2+}$ and 0.663 for Ca$^{2+}$.

The second procedure for detecting the structure of extracted species was the slope ratio method, which included extracted metal ion under study with different concentrations of Cinchonine, and another procedure for extracting different concentrations of different cations with fixed concentration of Cinchonine; the results are shown in Figures 14-17.

From the values of slope analysis and slope ratio methods, it was demonstrated that the ion pair association complex extracted was CK$^+;[Mg(EDTA)]^-$ and CK$^+;[Ca(EDTA)]^-$.

The slope ratio value for Mg$^{2+}$ was 1.392, but for Ca$^{2+}$ it was 0.841.
Percentage of Methanol Effect

Mg$^{2+}$ and Ca$^{2+}$ were extracted according to the fundamental method in presence of different percentages of methanol in aqueous solutions; the results are shown in Figures 18 and 19.

The results show that 25% CH$_3$OH is suitable for Mg$^{2+}$ extraction and 40% CH$_3$OH is suitable for Ca$^{2+}$, as well as the presence of CH$_3$OH enhancing the extraction efficiency. But once the optimum values for absorbance and D values were reached, the presence of CH$_3$OH in aqueous solution caused a decline in dielectric constant and polarity of aqueous solution, which means it destroyed the hydration shell of metal cation and helped to increase binding with EDTA to prepare anion complex, as well as increase the transfer to the organic phase to form the ion pair association complex with higher concentration and stability. Any percentage of CH$_3$OH less than the optimum values appear to cause a decline in extraction efficiency by decreasing the effectiveness. Also when the CH$_3$OH% percentage is higher than the optimum level, it causes a decrease in extraction efficiency also because it leads to a decrease in polarity and dielectric constancy of the aqueous solution, which causes it to transfer some of the Cinchonine (CK) to the aqueous phase so that there is a decrease in the concentration of the ion pair complex extracted to the organic phase.

Interferences Effects

Metal cations under study were extracted according to the fundamental method at optimum conditions and in the presence of different interferences. The results obtained are shown in Table 1:

The results show that all foreign ions have a range of interferences with metal cation of Mg$^{2+}$ and Ca$^{2+}$ through formation of the ion pair complexes with EDTA and Cinchonine. These interferences cause the concentration of H$_3$Y$^-$ and 

<table>
<thead>
<tr>
<th>Interferences</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Abs. at $\lambda_{max}=241$nm</td>
<td>D</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>0.341</td>
<td>29.30</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>0.218</td>
<td>16.24</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>0.233</td>
<td>19.83</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.311</td>
<td>22.81</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>0.345</td>
<td>25.32</td>
</tr>
</tbody>
</table>
Cinchonine to decrease to less than optimum values for extraction of Mg\textsuperscript{2+} and Ca\textsuperscript{2+} which appear to cause a decrease in extraction efficiency of the metal cations\textsuperscript{14}.

**Variation of Temperature**

Extractions of Mg\textsuperscript{2+} and Ca\textsuperscript{2+} were completed from aqueous solutions according to the procedure detailed in the fundamental method; just at different temperatures. The results appear to increase absorbance and D values along with increasing temperatures to the optimum of 25 °C for Mg\textsuperscript{2+} and the optimum of 35 °C for Ca\textsuperscript{2+}, as in Figure 20 and 21.

![Fig. 20. Effects of temperature on complex formation and stability.](image1)

![Fig. 21. D= f (T°C).](image2)

\[ K_{ex} = \frac{D}{[M^{2+}][CK]} \]

Where \( M^{2+} = \text{Mg}^{2+} \) or \( \text{Ca}^{2+} \)

Then calculations were done for the extraction constant \( K_{ex} \) by relation below\textsuperscript{8,9}.

\[
\text{Slope} = \frac{\Delta \text{Hex}}{\Delta \text{G}_{ex}} = -\frac{RT}{\Delta \text{S}_{ex}} \ln K_{ex} \]

\[
\Delta \text{G}_{ex} = \Delta \text{H}_{ex} - T \Delta \text{S}_{ex} \]

![Fig. 22. \( K_{ex} = f (T\ \text{K}) \)](image3)

<table>
<thead>
<tr>
<th>Metals</th>
<th>( \Delta \text{H}_{ex} ) (KJmol\textsuperscript{-1})</th>
<th>( \Delta \text{G}_{ex} ) (KJmol\textsuperscript{-1})</th>
<th>( \Delta \text{S}_{ex} ) (Jmol\textsuperscript{-1}K\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg}^{2+} )</td>
<td>0.058</td>
<td>-47.28</td>
<td>158.86</td>
</tr>
<tr>
<td>( \text{Ca}^{2+} )</td>
<td>0.0892</td>
<td>-54.66</td>
<td>180.69</td>
</tr>
</tbody>
</table>

Afterward plotted log \( K_{ex} \) vis 1/T K giving straight line relation as in Figure (22) from the slope of this straight line and application thermodynamic relations\textsuperscript{15} determined thermodynamic data as in Table 2.

The results show a small value of \( \Delta \text{Hex} \) for both ions, which reflect the increased approach of ions in ion pair association complexes extracted which add high stability to the complexes, and it is important to note the large value of \( \Delta \text{Sex} \) which demonstrated dependence of the extraction method on entropy to formation and extraction ion pair association complex which means the method is entropic in region\textsuperscript{8,9}.

**Organic Solvent Effect**

Extraction of Mg\textsuperscript{2+} and Ca\textsuperscript{2+} from aqueous solutions was done according to the procedure detailed in the fundamental method by using different organic solvents to dissolve the organic reagent Cinchonine was the extractant. The results are shown in Table 3:

The results show there is not any linear relationship between dielectric constants of solvents used and D values, which means there is not any effect of polarity of organic solvents on the extraction efficiency, but it demonstrates that there is an effect on the structure of organic solvents in the formation of ion association complexes through the formation contact ion pair or solvent separated ion pairs\textsuperscript{16}.

**Variation of Extractants**

By using different extractants with the procedures detailed in the fundamental method for extraction of Mg\textsuperscript{2+} and Ca\textsuperscript{2+} in optimum conditions, the results are shown in Table 4.
The results demonstrate differences in the extraction efficiency when different extractants are used; this overshadowed the nature and behavior of the organic reagent to form the ion pair association complex in addition to the conclusion that each organic reagent needs optimum conditions for extraction.

Table. 3: Organic solvent effect.

<table>
<thead>
<tr>
<th>Organic Solvent</th>
<th>( \varepsilon_i )</th>
<th>( \lambda_{\text{max}} )</th>
<th>Abs.</th>
<th>D</th>
<th>%E</th>
<th>( \lambda_{\text{max}} )</th>
<th>Abs.</th>
<th>D</th>
<th>%E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrobenzene</td>
<td>35.74</td>
<td>362</td>
<td>0.350</td>
<td>19.00</td>
<td>95.00</td>
<td>322</td>
<td>0.378</td>
<td>28.41</td>
<td>96.60</td>
</tr>
<tr>
<td>1,2-Dichloro ethane</td>
<td>10.65</td>
<td>310</td>
<td>0.215</td>
<td>6.14</td>
<td>85.99</td>
<td>285</td>
<td>0.512</td>
<td>75.92</td>
<td>98.70</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.806</td>
<td>241</td>
<td>0.444</td>
<td>32.33</td>
<td>97.00</td>
<td>278</td>
<td>0.447</td>
<td>39.00</td>
<td>97.50</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.438</td>
<td>303</td>
<td>0.118</td>
<td>4.71</td>
<td>82.49</td>
<td>294</td>
<td>0.221</td>
<td>16.86</td>
<td>94.40</td>
</tr>
</tbody>
</table>

Table. 4: Extractant kind effect.

<table>
<thead>
<tr>
<th>Organic reagent</th>
<th>( \varepsilon_i )</th>
<th>( \lambda_{\text{max}} )</th>
<th>Abs.</th>
<th>D</th>
<th>%E</th>
<th>( \lambda_{\text{max}} )</th>
<th>Abs.</th>
<th>D</th>
<th>%E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cinchonine</td>
<td>241</td>
<td>0.444</td>
<td>32.33</td>
<td>97.00</td>
<td>278</td>
<td>0.447</td>
<td>39.00</td>
<td>97.50</td>
<td></td>
</tr>
<tr>
<td>*PAN</td>
<td>495</td>
<td>0.374</td>
<td>19.83</td>
<td>95.19</td>
<td>496</td>
<td>0.332</td>
<td>22.81</td>
<td>95.80</td>
<td></td>
</tr>
<tr>
<td>Brilliant green</td>
<td>582</td>
<td>0.316</td>
<td>22.81</td>
<td>95.80</td>
<td>411</td>
<td>0.385</td>
<td>27.57</td>
<td>96.50</td>
<td></td>
</tr>
</tbody>
</table>

Spectrophotometric Determination

In order to determine the Mg\(^{2+}\) and Ca\(^{2+}\) in different samples, prepared calibration curves are created such as in Figures (23 and 24).

ACKNOWLEDGEMENT

"I would like to thank all those whose assistance proved to be a milestone in the accomplishment of my end goal."
REFERENCES