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 (H_3Y^-) 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 wave length for maximum absorbance of $\lambda_{max}=241nm$, but the maximum absorbance for calcium $HCK^+;CaHY^-$ was $\lambda_{max}=278nm$ 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 $\Delta H_{ex}=0.058kJmol^{-1}$, $\Delta G_{ex}=-47.28$ $kJmol^{-1}$, $\Delta S_{ex}=158.86J.mol^{-1}$ K^{-1} for Mg(II) and for Ca(II) was $\Delta H_{ex}=0.0892kJmol^{-1}$, $\Delta G_{ex}=-54.66$ $kJmol^{-1}$, $\Delta S_{ex}=180.69J.mol^{-1}$ K^{-1}.

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

INTRODUCTION

Cloud point extraction method has been applied for Mg^{2+} ions extraction. The extracted solvated species have $\lambda_{max}=249nm$. The study includesthe determination of all optimum conditions for extraction, as well as the determination of Mg^{2+} ions in different samples[1]. Extraction of ^{45}Ca(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-100[3]. 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[4]. 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 CH_3COONa 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 CH_3COONa salts[5]. The distribution of alkaline earth cations between CCl_4 and aqueous sodium perchlorate solutions has been studied by thenoyltrifluoro acetone and adduct forming ligand trioctylphosohlne oxide. The separation of alkaline earth cations is explained by solvent extraction with H^+ ion in aqueous solutions. The selectivity in the order is, $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ [6].

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 farther 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 $MgCl_2$ (Merck) and (0.0275g) of $CaCl_2$ (Merck) respectively in 10 ml distilled water, so that 0.1M EDTA was prepared by dissolving (3.7224g) of Na_2EDTA (B.D.H) in 100 ml distilled water, Cinchonine((S)-[(2R,4S,5R)-5-ethenyl-1-azabicyclo[2.2.2]octan-2-yl]-quinolin-4-ylmethanol) (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 Mg^{2+} or Ca^{2+} 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 5minutes 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 λ_{max}=241nm for the ion pair complex of Mg^{2+} and at λ_{max}=278nm for the ion pair complex of Ca^{2+}.

The aqueous solution of extracted Mg^{2+} was treated according to the Eriochrom black T[7] spectroscopic method for determining the remaining quantity of Mg^{2+} 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 Mg^{2+} ions in the aqueous phase to determine the transfer quantity of metal cation afterward calculate D values for extraction.

For determining the Ca^{2+} ions in the aqueous solution after extraction, the new method was used as detailed below:

5ml of aqueous solution contains the remaining quantity of Ca^{2+} 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 $\lambda_{max}=283nm$ against the DB18C6 solution as blank solution. This was limited through spectroscopic study.
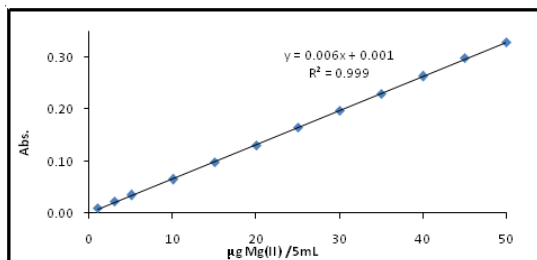
(a)
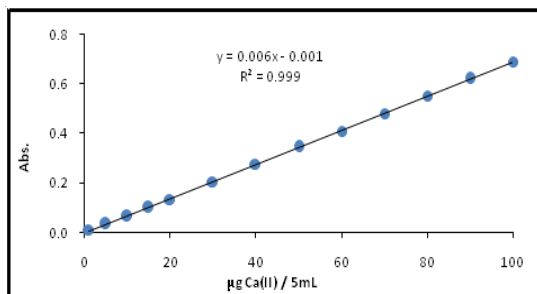
(b)

Fig.1. Calibration Curves for the Determination of Mg²⁺ and Ca²⁺ in the Aqueous Phase
a/ According to Eriochrom Black T Methods for Mg²⁺
b/ DB18C6 Crown Ether Method for Ca²⁺

RESULTS AND DISCUSSION
Spectroscopic Studies

The spectrophotometric study shows wavelength for maximum absorbance was $\lambda_{max}=283nm$ for spectrophotometric determined of Ca²⁺ in aqueous solution by DB18C6 method, so that for extracted complexes were $\lambda_{max}=241nm$ for Mg(II), $\lambda_{max}=278nm$ for Ca(II).
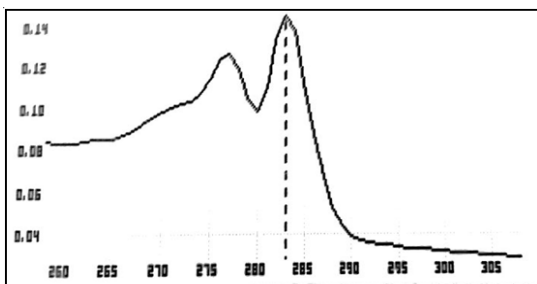
Fig. 2 . UV-Vis. Spectrum of Ion Pair Complex for CaDB18C6²⁺; 2Cl⁻for Determination of Remaining Quantity of Ca²⁺in the Aqueous Phase.

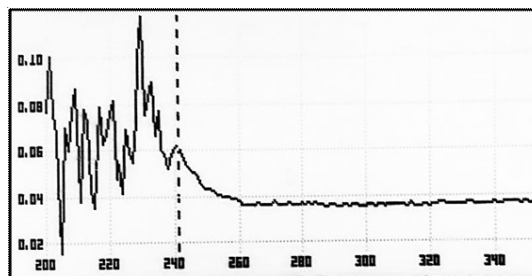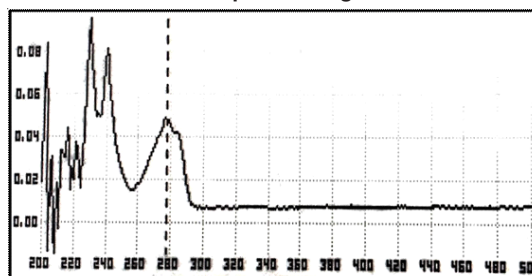**Fig. 3. UV-Vis. The Spectrum of the Ion Pair Complex for Mg²⁺**

Fig. 4. UV-Vis. The Spectrum of an Ion Pair Complex for Ca²⁺

Effects of HCl Concentration

The Mg²⁺ and Ca²⁺ was extracted according to the fundamental method after a 5mL solution of 1×10^{-4} 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).
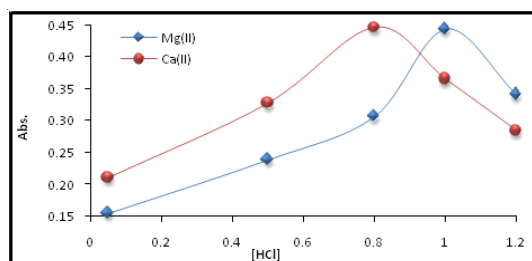

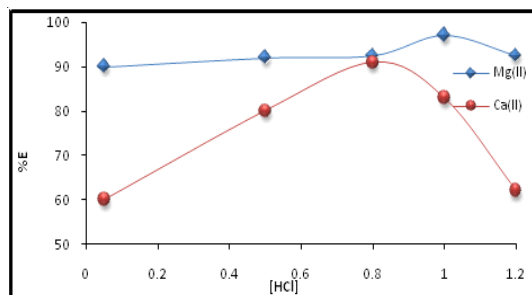**Fig. 5. Effects of HCl Concentration on Ion Pair Complex Formation and Stability.**

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[8].

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.
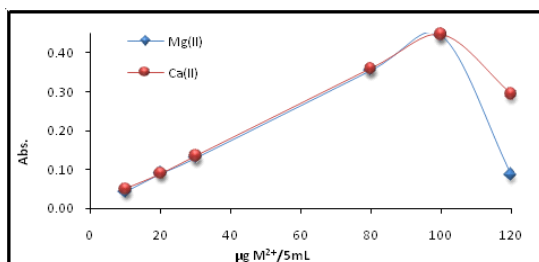

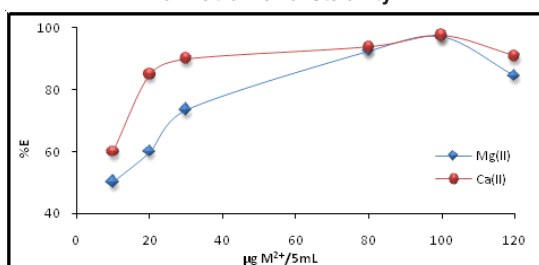**Fig. 7. Effects of metal cation on ion pair complex formation and stability.**

Fig. 8. Effects of metal cation on extraction efficiency and D values

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[9].

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.
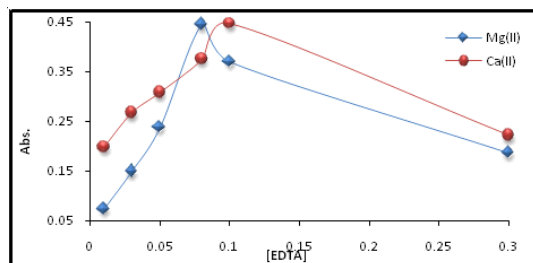

Fig. 9. Effects of EDTA Concentration on Ion Pair Formation and Absorbance.
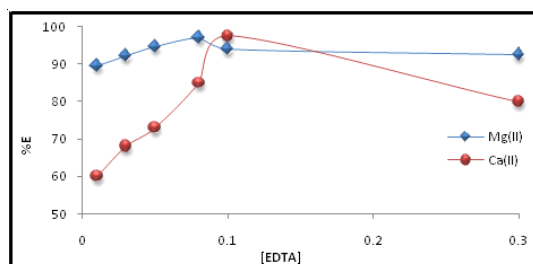

Fig. 10. Concentration of EDTA's effects on Extraction Efficiency and D Values.

From the results, it appears that 0.08M, 0.10M EDTA was the optimum concentration for extractionof Mg^{2+} and Ca^{2+} respectively, because at these concentrations, they reached the ideal thermodynamic equilibrium to formanion complex species $MgHY^-$ and $CaHY^-$. Any concentration less than optimum isnot 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[9].

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.
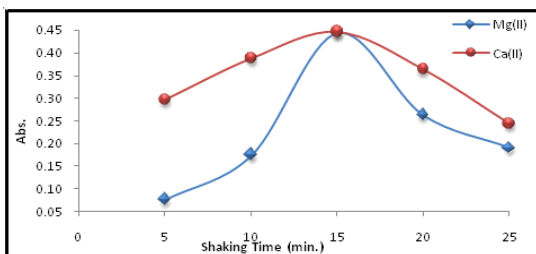

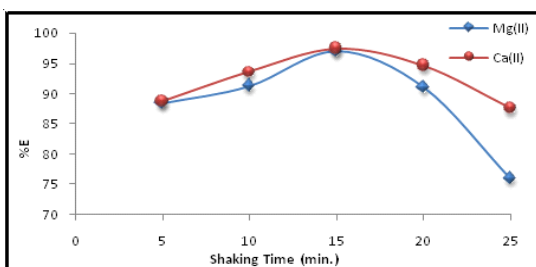**Fig. 11. Effect of shaking time on ion pair complex formation.**

Fig. 12. Effect of shaking on extraction efficiency and D values.

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 $CK^+;[Ca(EDTA)]^-$ [8,11].
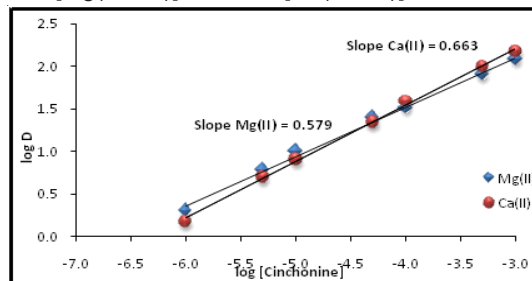

Fig. 13. The effect of different concentrations of Cinchonine on D values.
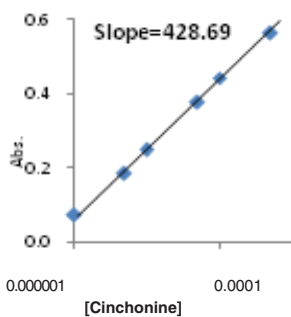

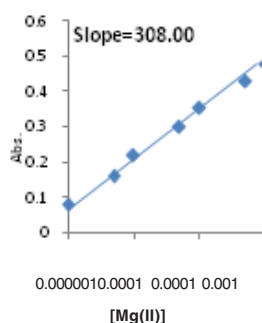**Fig.14. Effect of CK Concentrations on absorbance value**

Fig.15. Effect of Mg (II) Concentrations on absorbance value
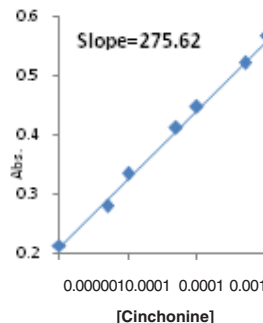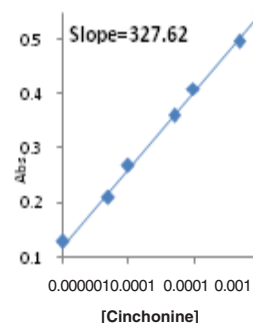
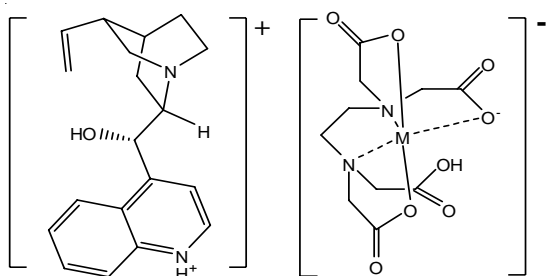

Fig.16. Effect of CK Concentrations on absorbance value

Fig.17. Effect of Ca (II) Concentrations on absorbance value

The slope ratio value for Mg^{2+} was 1.392

But for Ca^{2+} it was 0.841

More probable structures of extracted complexes, Where M= Mg²⁺ or Ca²⁺

Fig. 19. Effects of the percentage of CH₃OH presence on extraction efficiency and D values.

Percentage of Methanol Effect

Mg²⁺ and Ca²⁺ were extracted according to the fundamental method in presence of different percentages of methanol in aqueous solutions; the results are shown in Figures 18 and19.
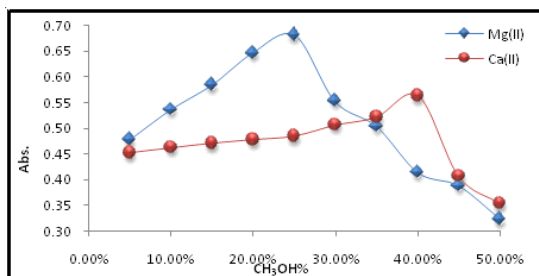

Fig. 18. Thermodynamic relationship between percentage of CH₃OH and ion pair formation.

The results show that 25% CH3OH is suitable for Mg2+ extraction and 40% CH3OH is suitable for Ca2+, as well as the presence of CH3OH enhancing the extraction efficiency. But once the optimum values for absorbance and D values were reached, the presence of CH3OH 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
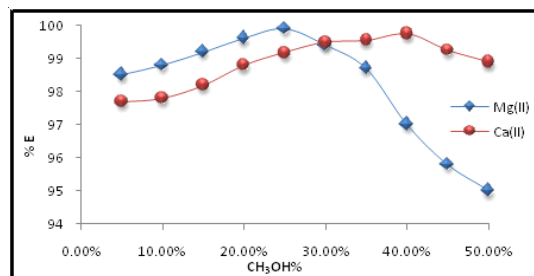
anion complex, as well as increase the transfer to the organic phase to form the ion pair association complex with higher concentration and stability. Any percentage of CH3OH less than the optimum values appear to cause a decline in extraction efficiency by decreasing the effectiveness. Also when the CH3OH% 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 [12,13].

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 Mg2+ and Ca2+ through formation of the ion pair complexes with EDTA and Cinchonine. These interferences cause the concentration of H3Y- and

Table. 1: Interferences effect.

Interferences	Mg²⁺			Ca²⁺		
	Abs. at λ_{max}=241nm	D	%E	Abs. at λ_{max}=278nm	D	%E
Ba²⁺	0.341	29.30	96.69	0.396	30.25	96.80
Sr²⁺	0.218	16.24	94.19	0.366	25.32	96.70
Zn²⁺	0.233	19.83	95.19	0.345	22.26	95.70
Ni²⁺	0.311	22.81	95.80	0.302	16.86	94.40
Cd²⁺	0.345	25.32	96.20	0.268	10.24	91.10

Cinchonine to decrease to less than optimum values for extraction of Mg2+ and Ca2+ which appear to cause a decrease in extraction efficiency of the metal cations[14].

Variation of Temperature

Extractions of Mg2+ and Ca2+ 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 Mg2+ and the optimum of 35 °C for Ca2+, as in Figure 20 and 21.
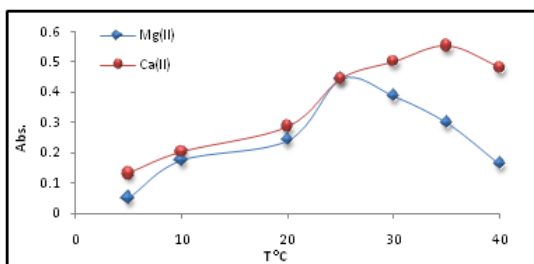

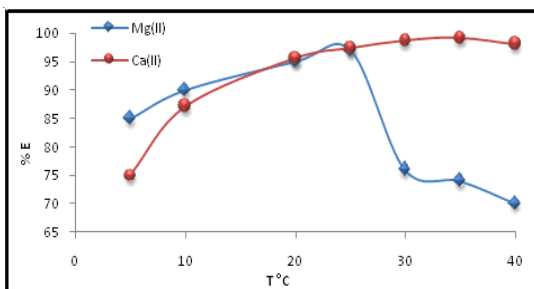**Fig. 20. Effects of temperature on complex formation and stability.**

Fig. 21. D= *f* (T°C).

$$K_{ex} = \frac{D}{[M^{2+}][CK]}$$
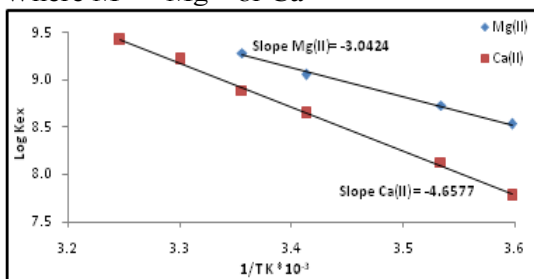
Where $M^{2+}= Mg^{2+}$ or Ca^{2+}

Fig. 22. K$_{ex}$ = *f* (T K)

Then calculations were done for the extraction constant Kex by relation below[8,9].

$$\text{Slope} = \frac{\Delta\text{-Hex}}{2.303\ R}$$

$\Delta G_{ex}= -RT \ln K_{ex}$ $\Delta G_{ex}= \Delta H_{ex} - T\, \Delta S_{ex}$

Table. 2: Thermodynamic data for extraction Mg^{2+} and Ca^{2+}

Metals	ΔH_{ex} (KJmol^{-1})	ΔG_{ex} (KJmol^{-1})	ΔS_{ex} (Jmol^{-1}K^{-1})
Mg^{2+}	0.058	-47.28	158.86
Ca^{2+}	0.0892	-54.66	180.69

Afterward plotted log Kex vis 1/T K giving straight line relation as in Figure (22) from the slope of this straight line and application thermodynamic relations[15] determined thermodynamic data as in Table 2.

The results show a small value of ΔHex 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 ?Sexwhich demonstrated dependence of the extraction method on entropy to formation and extraction ion pair association complex which means the method is entropic in region[8,9].

Organic Solvent Effect

Extraction of Mg2+ and Ca2+ 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[16].

Variation of Extractants

By using different extractants with the procedures detailed in the fundamental method for extraction of Mg2+ and Ca2+ 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[17].

Table. 3: Organic solvent effect.

Organic Solvent	ϵ_r	Mg^{2+}				Ca^{2+}			
		λ_{max}	Abs.	D	%E	λ_{max}	Abs.	D	%E
Nitrobenzene	35.74	362	0.350	19.00	95.00	322	0.378	28.41	96.60
1,2-Dichloro ethane	10.65	310	0.215	6.14	85.99	285	0.512	75.92	98.70
Chloroform	4.806	241	0.444	32.33	97.00	278	0.447	39.00	97.50
Toluene	2.438	303	0.118	4.71	82.49	294	0.221	16.86	94.40

Table. 4: Extractant kind effect.

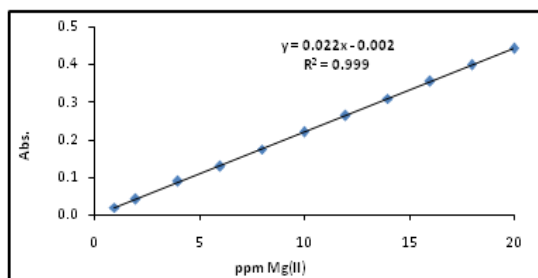| Organic reagent	Mg^{2+}				Ca^{2+}			
	λ_{max}	Abs.	D	%E	λ_{max}	Abs.	D	%E
Cinchonine	241	0.444	32.33	97.00	278	0.447	39.00	97.50
*PAN	495	0.374	19.83	95.19	496	0.332	22.814	95.80
Brilliant green	582	0.316	22.81	95.80	411	0.385	27.57	96.50

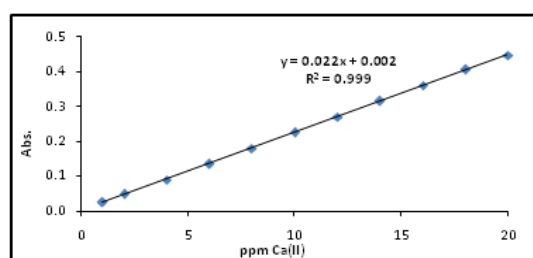**Fig. 23. Calibration curve of Mg^{2+} for spectrophotometric determination.**

Fig. 24. Calibration curve for spectrophotometric determination of Ca^{2+}.

Table. 5: Parameters for the determination of $PbCl_3^-$ or $PbCl_4^=$ via liquid ion exchange method.

Parameter	Mg(II)	Ca(II)
RSD% (n=3)	0.7207	0.7715
Molar absorptivity ($L.mol^{-1}.cm^{-1}$)	785.8746923	1378.114133
Sandell's sensitivity	3.0539×10^{-8}	2.9025×10^{-8}
Limit of Detection (μgmL^{-1})	1.8017×10^{-5}	1.15728×10^{-5}

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).

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