

Via Cloud Point Extraction Methodology and Acidic HCl media Extracted of Iron (III) by DB18C6

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الخلاصة

بواسطة استخدام الايثر التاجي DB18C6 وفي وسط حامضي HCl استخلص ايون الحديد (III) كمعقد ترابط ايوني باستخدام تقنية استخلاص نقطة الغيمة بعد تغيير Fe^{3+} الى $FeCl_4^-$ ، هذه الدراسة وضحت 1.2 M HCl هو التركيز الامثل في وجود $5 \times 10^{-2} M$ من كلوريد الصوديوم NaCl و $1 \times 10^{-4} M$ من الايثر التاجي DB18C6 وكذلك 0.5mL من سطح لا ايوني TritonX-100 1% اللازمة للحصول على اعلى كفاءة استخلاص ، وكذلك وضحت الدراسة الحرارية $85^\circ C$ هي الدرجة الحرارية الملائمة للاستخلاص وفق تقنية استخلاص نقطة الغيمة CPE بالإضافة الى الحاجة لتسخين المحلول في حمام مائي كهربائي عند $85^\circ C$ ولمدة 15 دقيقة . الدوال الترموديناميكية هي انشالبي الاستخلاص $\Delta H_{ex} = 0.159 \text{ kJmol}^{-1}$ و الطاقة الحرة للاستخلاص $\Delta G_{ex} = -62.43 \text{ kJmol}^{-1}$ واما قيمة انتروبي للاستخلاص $\Delta S_{ex} = 174.83 \text{ J mol}^{-1} \text{ K}^{-1}$ ، التطبيق التجريبي بين ان التركيب الاكثر احتمالاً لمعقد الترابط الايوني المستخلص هو $[Na DB18C6]^+ ; FeCl_4^-$ ، وهناك تطبيق عملي لهذه الدراسة في نماذج حقيقية مختلفة.

Abstract

By use crown ether DB18C6 and from acidic HCl media extracted Fe^{3+} ion as ion association complex by application cloud point extraction methodology after change Fe^{3+} into $FeCl_4^-$, this study show 1.2M HCl was the optimum concentration in precence $5 \times 10^{-2} M$ NaCl and $1 \times 10^{-4} M$ Crown ether DB18C6 as well as show 0.5mL of Nonionic surfactant 1% TritonX-100 was necessary to obtained higher extraction efficiency, so that thermodynamic study illustrate $85^\circ C$ was favorable temperature for extraction according to CPE method in addition to needing heating the solution in electrostatic water bath at $85^\circ C$ for 15 minutes . Thermodynamic data was $\Delta H_{ex} = 0.159 \text{ kJ mol}^{-1}$, $\Delta G_{ex} = -62.43 \text{ kJ mol}^{-1}$, $\Delta S_{ex} = 174.83 \text{ J mol}^{-1} \text{ K}^{-1}$, experimental application offer the more probable structure of ion pair association complex extracted was $[Na DB18C6]^+ ; FeCl_4^-$, there are another empirical application for this study in real samples .

Keywords: Iron; cloud point extraction; crown ether; liquid ion exchange.

Introduction

CPE method is based on the distribution ion pair association complex formed between surfactant and aqueous phase and when the solution is heated to fixed temperature the micelles formed cloud point layer with smallest volume and higher density containing ion pair association complex of Ni^{2+} in equilibrium with aqueous solution^[1,2]. A previous study used CPE methodology for separating Cu(II), Co(II), Pb(II) from different samples after complex formation with 1-phenyl thiosemicarbazide by used TritonX-114 coupled with flame atomic absorption with detection limit 3.42 $\mu\text{g/L}$ for Pb(II) 1 $\mu\text{g/L}$ Co(II) and 0.67 $\mu\text{g/L}$ Cu(II). Extraction Cu(II), Ag (I) and Ni(II) after complexation with two ligand 2-[(4-formyl phenyl)azo]-4,5-diphenyl imidazole and 2-[(2-methylphenyl)azo]-4,5-diphenyl imidazole at optimum condition which is restricted experimentally^[3]. By used CPE methodology coupled with flame atomic absorption determined micro amount of lead in different samples of soil and water after complexation with 1-[2-pyridyl azo]-2-naphthol and Triton X-114 at pH=8^[4]. By application of CPE methodology coupled with spectrophotometric technique for extraction and determination of Pb^{2+} , Cd^{2+} , Ni^{2+} in different samples^[5]. Study for separation and determination of cadmium (II) by cloud point extraction coupled with flow injection atomic absorption by used methyltrioctyl ammonium to formation ion pair association complex with CdI_4^- with using Triton X-114^[6]. By used BHIS as complexing agent for extraction Ag(I) at pH=8 in CPE methodology with Triton X-114 with detection limit 1.9 $\mu\text{g/L}$ ^[7]. Separation and determination Pb(II), Cd(II), Pd(II) in some vital samples by CPE method coupled with flame atomic absorption by used IPAI as complexing agent at pH=8 with Triton X-114 this study illustrate D.L.=1.6 $\mu\text{g/L}$ ^[8] by application of CPE methodology for separation and preconcentration small quantities of nickel(II) without using complexing agent as first step for determination by flame atomic absorption by used nonionic surfactant (PONPE7.5)^[9].

Experimental

It is important to note spectrophotometrically and absorbance measurements was carry out by employed biochrome spectrophotometer (80-7000-11) Libra 560 Cambridge CB40FJ, Jaban. So was used electrostatic water bath (WNB7-45 England) for maintain temperature.

Undoubtedly all chemicals used as received from trustworthy commercial company without further purification stock solution of Fe³⁺ ion 1000 ppm prepared by dissolved 0.2922 g of FeCl₃ in 100mL distilled water contain 1mL of hydrochloric acid in volumetric flask, other working solution prepared by dilution with distilled water by used suitable volumetric flask, 20% potassium thiocyanate solution prepared by dissolved 20g in distilled water and acidify the solution with HCl into (pH=2).

The Fundamental Method

10 mL aqueous solution contain 50µg Fe³⁺ and optimum concentration of NaCl with suitable concentration of DB18C6 with 0.5mL nonionic surfactant 1% TritonX-100 then heating the solution in electrostatic water bath for suitable temperature and time until formation cloud point layer CPL separated this layer from aqueous solution and dissolved in 5ml ethanol afterword measure absorbance of ethanolic solution against blank prepared at the same manner in absence metal ion as well as aqueous solution treated according to spectrophotometer method^[11] and after returned to calibration curve **Figure 1** Calibration curve to determined remainder quantity to metal ion in aqueous solution after extraction and subtraction this quantity from main quantity to determine the transfer quantity to the CPL as ion pair complex and by dividing there quantities each over other to calculate distribution ration (D) such as below:

$$D = \frac{[\text{Fe}^{3+}]_{\text{CPL}}}{[\text{Fe}^{3+}]_{\text{aq}}}$$

to determine the transfer quantity of Fe³⁺ ion to the CPL follow another procedure which called stripping method involved shaking CPL after separation with two portion each one 5mL in volume of 0.5M NaOH to destroyed the ion pair complex and remain Fe³⁺ ion in aqueous basic solution then used spectrophotometric method (thiocyanate method)^[10]. The experiments show the transferred quantity of Fe³⁺ ion to CPL as ion pair determined by stripping method was equal the quantity determined by subtraction remainder Fe³⁺ ion from origin quantity so that in all experimental studies determined the transfer Fe³⁺ to CPL by subtraction method because easier and faster .

Results and discussion

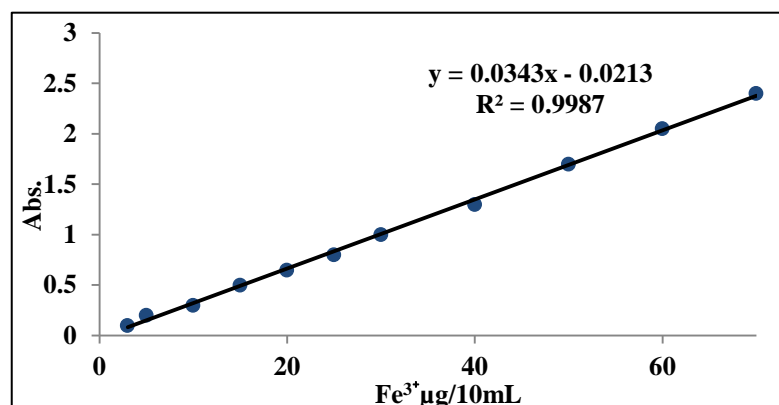


Figure 1: Calibration curve for determination remainder Fe³⁺ ion in aqueous solution.

Spectrophotometric Studies

10mL aqueous solution contain 50µg Fe³⁺ ion and 1.0M HCl 5×10⁻² M NaCl and 1×10⁻⁴ M DB18C6 shaking the solution for 5 minutes then added 0.5mL 1% TritonX-100 and heating the solution in electro static water but at 85°C for 15 minutes until complete formation cloud point layer with smaller volume and higher density separated this layer from aqueous solution and dissolved in 5ml ethanol and taken the Absorption UV-visible spectrum for ethanolic solution against blank prepared at the same manner without Fe³⁺ ion the result was illustrated in **Figure 2**.

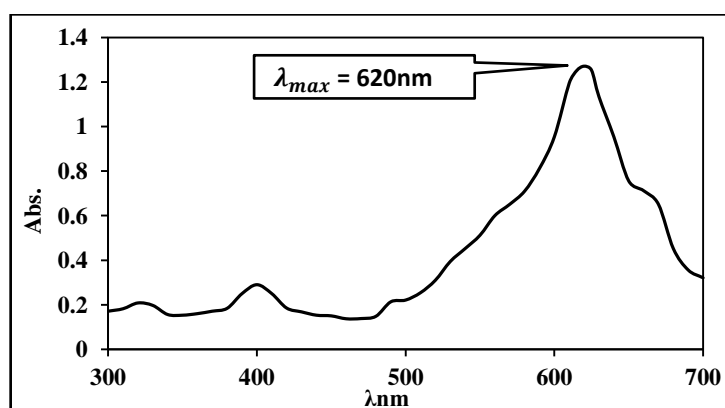


Figure 2: UV-VIS spectrum of the ion-pair complex extracted to cloud point

The spectrum show maximum absorbance for ion pair complex extracted to CPL was $\lambda_{\text{max}}=360$ nm.

Alteration HCl Concentration

10mL aqueous solution each one contain $50\mu\text{g Fe}^{3+}$ ion rising concentrations of HCl, 5×10^{-2} M NaCl, 1×10^{-4} M DB18C6 shaking all there solutions for 5 minutes then added 0.5mL of 1% Triton X-100, heating there solutions in electrostatic water bath at 85°C for 15 minutes until formation CPL, separate CPL from aqueous solution and follow the procedure detailed in fundamental method, the results was as in **Figures 3** and **4**.

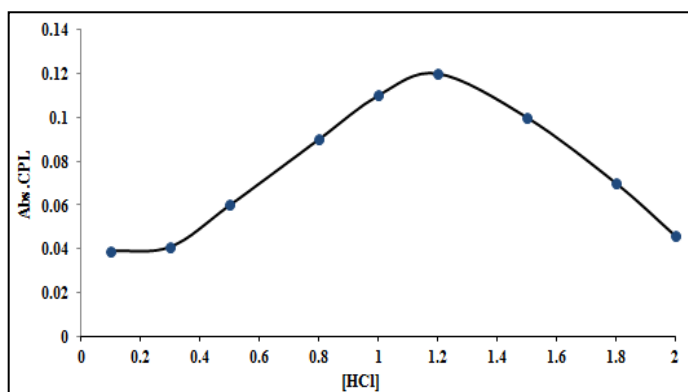


Figure 3: Effect of HCl concentration on complex concentration in CPL

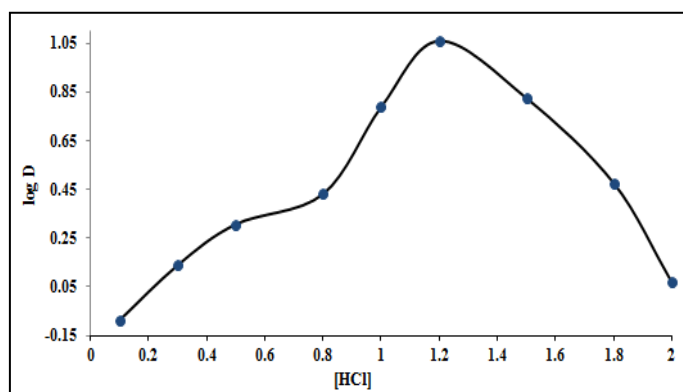
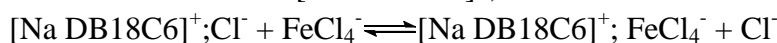
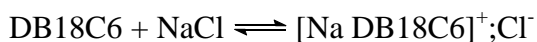
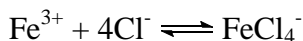


Figure 4: Effect of HCl concentration on extraction efficiency and D-values

The results show 1.2M was the optimum concentration of HCl which is suitable for giving best thermodynamic equilibrium to form FeCl_4^- as well liquid ion exchange to formation ion pair association such as below.



Any concentration less than optimum not allow to reach thermodynamic equilibrium and decrease extraction efficiency undoubtedly decline absorbance and D-value but any concentration more than optimum value effect to decline absorbance and D-value also because increase dissociation equilibrium and increase the species H_3O^+ , FeCl_4^- which being stable with increase acidity of solution and minimizing ion pair complex formation and extraction .

Variation NaCl Concentration

Extracted $50\mu\text{g Fe}^{3+}$ ion from 10mL aqueous solution in presence 1.2M HCl and rising concentrations form NaCl 1×10^{-4} M DB18C6, shaking these solution for 5 minutes then added 0.5mL 1% TritonX-100 and heating these solutions in electrostatic water bath at 85°C for 15 minutes until formation CPL separated and dissolved in 5ml ethanol the complex as detailed in fundamental method, the results shows as in **Figures 5 and 6**.

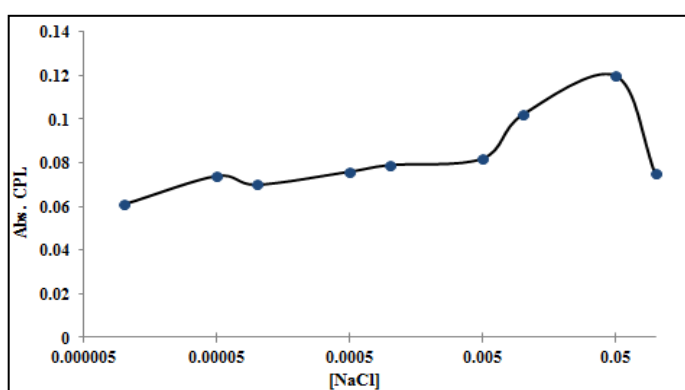


Figure 5: Effect of NaCl concentration on formation and stability of liquid ion exchanger

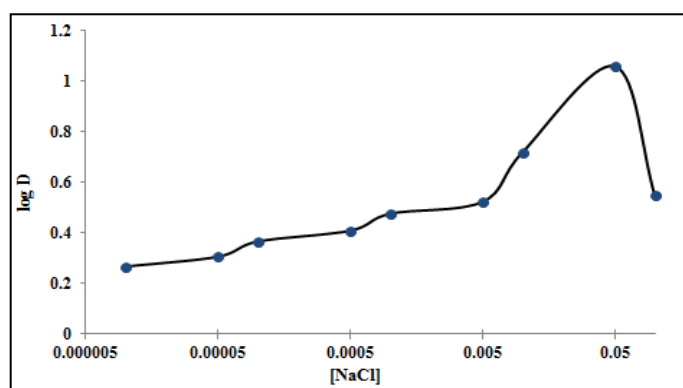
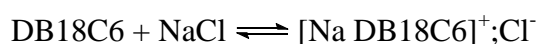


Figure 6: $D=F[\text{NaCl}]$

The results show 5×10^{-2} M NaCl was optimum value appear higher extraction efficiency because effect to reach thermodynamic equilibrium for formation ion exchanger. With high concentration and stability as bellow



This formation and stability help to increase extraction of FeCl_4^- by liquid ion exchange, any concentration less than optimum value decrease concentration and stability of liquid ion exchanger $[\text{NaDB18C6}]^+; \text{Cl}^-$ and reflect decline in extraction efficiency, but any concentration more than optimum value decrease extraction efficiency also because increase dissociation equilibria by effect of mass action law and Le Chatlier principle.

Changing DB18C6 Concentration

10mL aqueous solution contain $50 \mu\text{g Fe}^{3+}$ ion and 1.2 M HCl, 5×10^{-2} M NaCl, different concentrations of DB18C6 shaking these solutions for 5 minutes and then added 0.5mL 1% TritonX-100 after ward heated these solutions in electrostatic water bath at 85°C for 15minutes after complete formation CPL separated and dissolved in 5ml ethanol there complete as in the procedure detailed in fundamental the results was as in **Figures 7 and 8**.

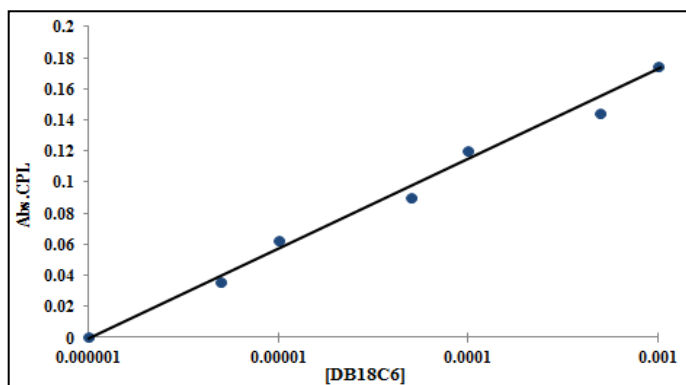


Figure 7: Increasing complex formation with increasing DB18C6 concentration.

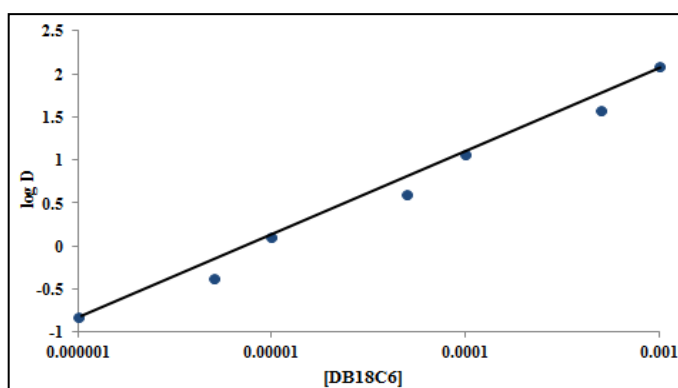


Figure 8: Increasing extraction efficiency and D-value with increasing DB18C6 concentration

The results show there is linear relation for effect of DB18C6 concentration on absorbance and D-values which is mean increasing extraction efficiency as a function for DB18C6 concentration.

Fluctuation TritonX -100 Volume

Extracted 50 μ g Fe³⁺ ion from 10mL aqueous solution at optimum condition in presence different volume of 1% TritonX-100 according to procedure detailed in fundamental method the results as in **Figures 9** and **10**.

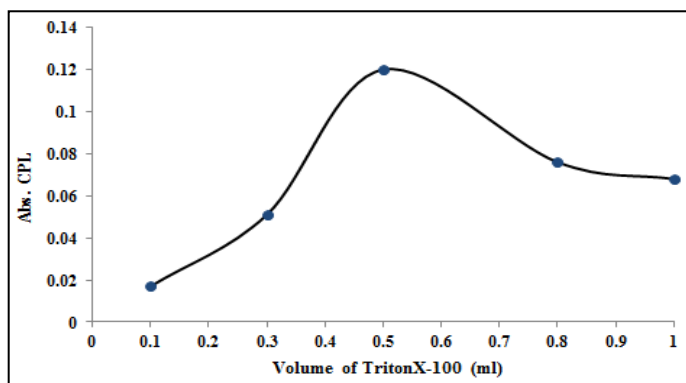


Figure 9: Effect of surfactant volume on ion pair transfer and absorbance

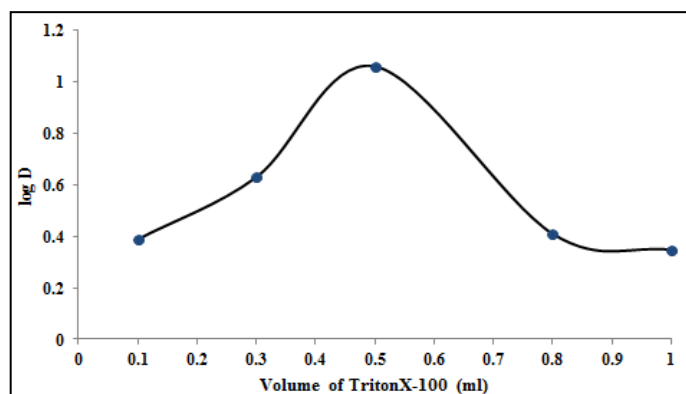


Figure 10: Effect of surfactant volume on extraction efficiency and D-value

The results show 0.5mL was the optimum volume which is more suitable for higher extraction efficiency because this volume applicability form good cloud point layer hold larger quantity of ion pair complex, any concentration less than optimum not enough to form this layer effect to decrease extraction efficiency, as well as any volume more than optimum increasing diffusion of micelles and decline extraction efficiency also.

Thermodynamic

Extracted 50µg Fe³⁺ ion from 10ml aqueous solutions at all optimum conditions according to procedure detailed in fundamental method except heating at different temperatures the results was as in **Figures 11** and **12**.

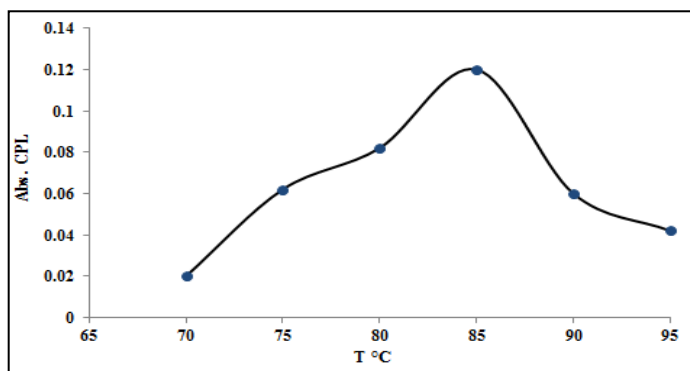


Figure 11: Effect of temperature on concentration of complex extraction and absorbance

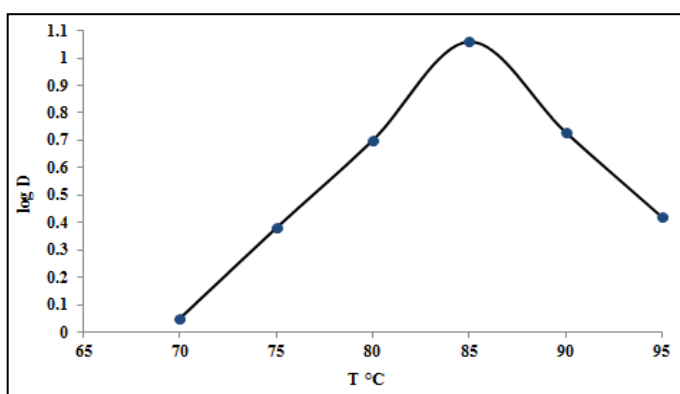


Figure 12: Effect of temperature on extraction efficiency and D-values

After calculated extraction constant temperature by application relation below.

$$K_{ex} = \frac{D}{[Fe^{3+}][DB18C6]}$$

Plotted $\log K_{ex}$ against $1/T$ K, the result was as in **Figure 13**.

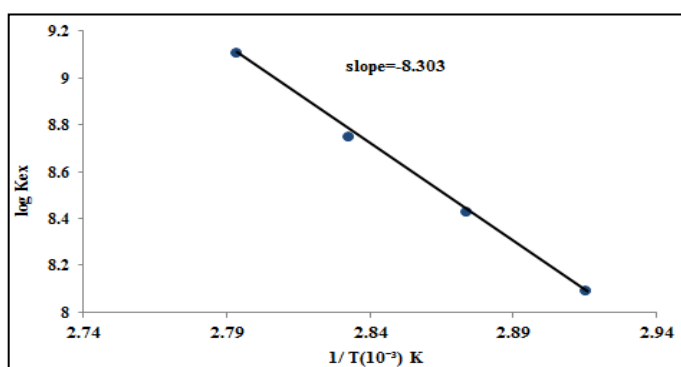


Figure 13: Effect of temperature on extraction constant value

From slope of straight line relation in **Figure 13** and thermodynamic relation calculate thermodynamic.

$$\Delta H_{\text{ex}} = 0.159 \text{ KJ mol}^{-1}$$

$$\Delta G_{\text{ex}} = -62.43 \text{ KJ mol}^{-1}$$

$$\Delta S_{\text{ex}} = 174.83 \text{ J mol}^{-1} \text{ K}^{-1}$$

Results show extraction of Fe^{3+} by cloud point extraction method was endothermic as well as the very small value of enthalpy offer the two ions of ion pair complex is closely near to each other whereas the large value of entropy reflect the nature of extraction method in entropic in region.

Effect of heating time

Extracted $50\mu\text{g Fe}^{3+}$ ion from 10mL at optimum condition except heating the solutions for different time according to the procedure detailed in fundamental method the results shows in the **Figures 14** and **15**.

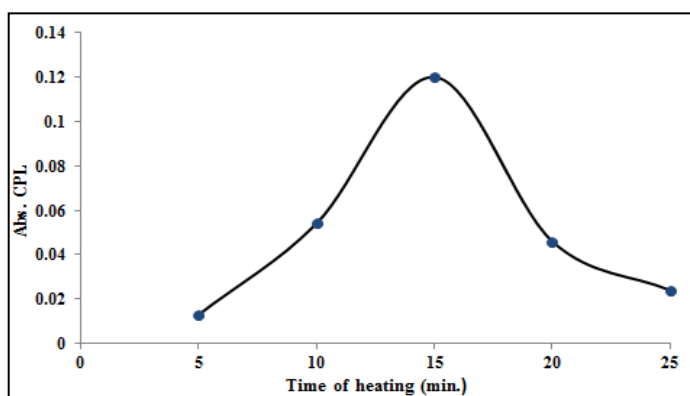


Figure 14: Effect of heating time on partition ion pair complex to CPL and absorbance

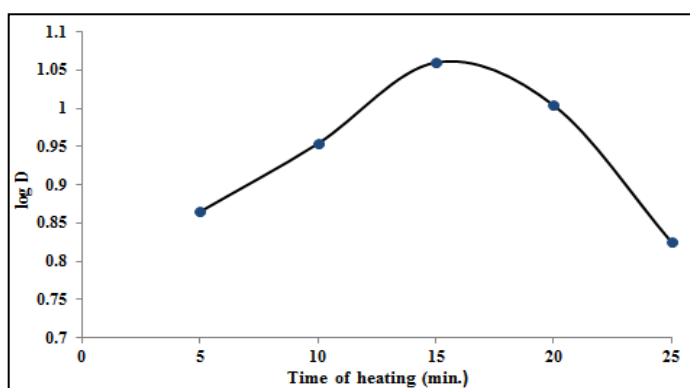


Figure 15: Effect of heating time on extraction efficiency and D- values

The results appear 15 minutes was the optimum heating time which is giving best aggregation for micelles to from CPL at CMC state to from best layer with smallest volume and higher density and layer efficiency for extraction any time less than optimum not suitable for extraction and effect to decline extraction efficiency so that any time more than optimum increase diffusion of micelles and decrease extraction efficiency.

Stoichiometry

To limitation the more probable structure of ion pair complex for Fe^{3+} ion extracted to CPL followed two spectrophotometric accurate methods which are named. Slope analysis method and slope ratio method by application the procedure detailed in fundamental method. Whereas the first method involved extracted Fe^{3+} at different concentration of DB18C6 at latter plot absorbance of $\log D$ against $\log[\text{DB18C6}]$. The second method involved to experiments one extracted different concentration of Fe^{2+} in 10mL under all optimum condition at latter plot absorbance against molar concentration of Fe^{3+} ion by different concentration of DB18C6 at latter plot absorbance against molar concentration of DB18C6 .The results was as in **Figures 16, 17 and 18**.

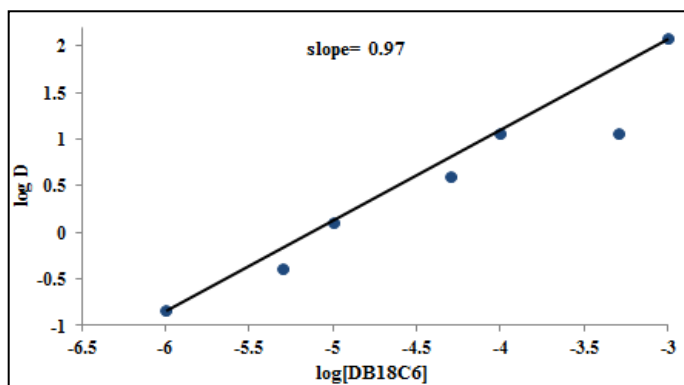


Figure 16: Slope analysis method

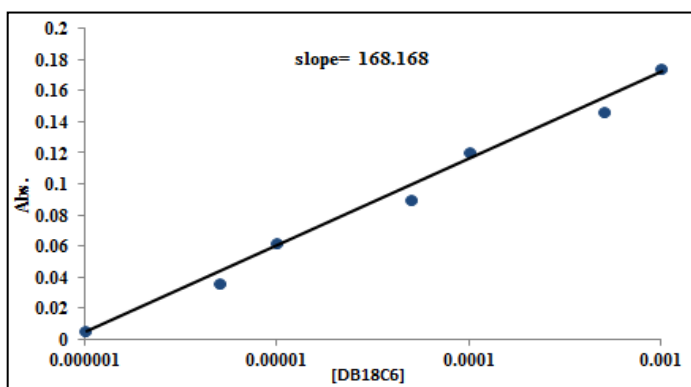


Figure 17: Effect of DB18C6 concentration on absorbance

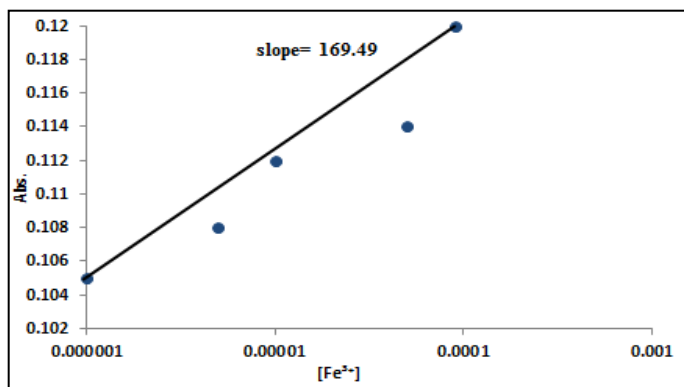
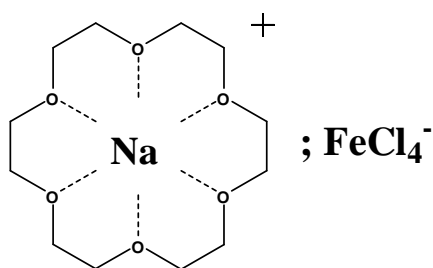


Figure 18: Effect of Fe³⁺ ion concentration on absorbance

Slope ratio = 0.99

The results show more probable structure of ion pair complex extracted was 1:1



Grown ether kind effect

Extracted 50 μg Fe^{3+} ion from 10mL aqueous solution at optimum conditions by different crown ethers and cryptand C222 according to procedure detailed in fundamental method the results was as in **Table 1**.

Table 1: Effect of type extractant

<i>Extractant</i>	<i>Abs.360nm</i>	<i>D</i>
12C4	0.015	3.36
15C5	0.077	8.54
18C6	0.186	20.82
DB18C6	0.120	11.5
DB24C8	0.103	9.64
C222	0.08	7.35

The results show 18C6 giving highest extraction efficiency more than DB18C6 because phenyl group effect to decrease electron density on oxygen atom by effect of withdrawing. Which is increasing stability of ion exchanger $[\text{Nacrow}]^+; \text{Cl}^-$ in addition to agreement of Na^+ diameter with cavity size of crown ether and cage of cryptand.

Electrolyte effect

Extraction 50 μg Fe^{3+} ion from 10mL aqueous solution at optimum condition and in presenter 0.05M different electrolytes according to procedure as mentioned earlier the results was as in **Table 2**.

Table 2: Effect of electrolyte

<i>Electrolytes</i>	<i>Abs.360nm</i>	<i>D</i>
LiCl	0.110	6.692
NaCl	0.120	11.500
KCl	0.275	24.000
NH ₄ Cl	0.154	2.333
MgCl ₂	0.257	19.000
CaCl ₂	0.255	15.666
SrCl ₂	0.115	8.285
BaCl ₂	0.081	5.666

Extraction efficiency differ by different electrolyte salt of alkali and alkali earth elements because metal cations of their salts giving different agreement between metal cation and cavity size of DB18C6 The results show KCl giving higher distribution ratio with higher agreement between K⁺ and DB18C6 .

Effect of interferences

Extracted 50µg of Fe³⁺ ion from 10mL aqueous solution of optimum condition in presence 0.05M some interference according to procedure detailed in fundamental method the results was as in **Table 3**.

Table 3: Effect of interferences

<i>Interferences</i>	<i>Abs.360nm</i>	<i>D</i>
Cd ²⁺	0.012	7.333
Hg ²⁺	0.106	8.090
Ni ²⁺	0.070	9.000
Cr ₂ O ₇ ²⁻	0.076	10.111
MnO ₄ ⁻	0.103	6.692

The results show metal cation and anions used all the giving interferences but in different degree because each one need specific optimum condition as well as there is appear different behavior in aqueous solution.

Spectrophotometric determination

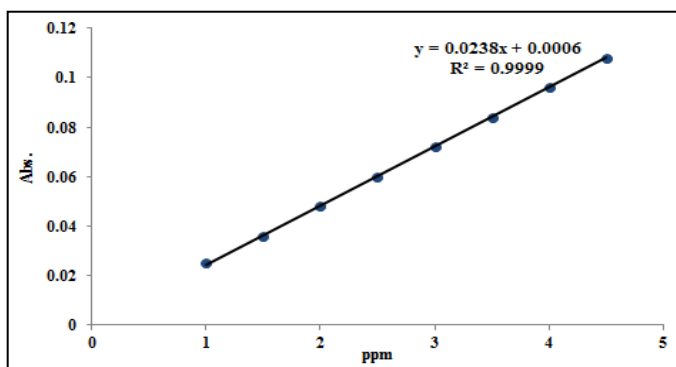


Figure 19: Calibration curve for spectrophotometric determination of Fe(III)

Table 3: Determination of Fe(III) in various samples

<i>S. No.</i>	<i>Sample</i>	<i>Fe(III)</i>
1	Soil Shatt al-Kufa	23
2	Agriculture soil of Al.Mishkab	4.5
3	Orange	5
4	Fragaria x ananassa	5.8
5	Apiumgraveolens	27
6	Solanum lycopersicum	7.2
7	Allium cepa	21
9	Lens culinaris	38.5
10	Chickens meat	12

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