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Extraction and Separation of Aluminum (III) as $AlCl_4^-$ from Neutral Media via Liquid ion exchange method

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Abstract: Extraction of Al^{3+}chloroanion complex $AlCl_4^-$ from NaCl media using the crown ether 15C5 as complexing agent. The concentrations of NaCl and Al^{3+}ions in addition to shaking time, organic solvent effect, and cavity size effect. Thermodynamic show the ion exchange reaction was endothermic. The stoichiometry shown on the basis of slope analysis and slope ratio methods the extracted species was 1:1:1 $[Na15C5]^+$; $AlCl_4^-$.The extracted complex having λ_{max}=241nm. The proposed method used for the spectrophotometric determination of Al^{3+} in environmental and vital samples, %RSD=0.008136, D.L= 1.78×10^{-5} ppm, ε= 300.191 $L.mol^{-1}.cm^{-1}$,Sandell's sensitivity= 0.00899μg/cm^2.

Key Words: Liquid ion exchange, aluminum (III), spectrophotometric determination, crown ether.

I. INTRODUCTION

Al compounds occur in ionic form in the environment and are therefore not expected to volatilize. In the environment, Aloccur in only one oxidation state (+3), and does not undergo oxidation-reduction reactions [1, 2]. Extraction of Pt (II) as $PtCl_4^=$ from HCl media on the basis of CPE method by using Janus green (JG) and in presence TritonX-100. Ion pair complex extracted having λ_{max}= 690nm. The stoichiometric illustrate the extracted species was $[JG^+;HPtCl_4^-]$[3].CPE method applied for extracted of Zn (II) as chloroanion complex from HCl media by using organic reagent 3-[(2-Pyridyl azo)]-1-nitroso-2-naphthol (PANN) in presence 1%TritonX-100. The ion association complex show λ_{max}=414nm. Stoichiometry illustrate the extracted species was 1:1$[HPANN]^+$; $ZnCl_3^-$, $[2H\text{-}PANN]^{2+}$; $ZnCl_4^=$, $[HPANN]^+$; $HZnCl_4^-$[4].Liquid-Liquid extraction of Al (III) by curcumin in the presence of picric acid using UV-vis. spectrophotometry method. The 1:2 molar ratio of Al:Cur was obtained in MIBK and in phosphate buffer (pH 9.00). The resulting complex having λ_{max}= 378nm[5].CPE methodology used for the separation of Al (III) ion after the complex formation with Quinizarin, using Triton X-114 as surfactant[6].Trace amounts of Au(III) as $AuCl_4^-$separated from HCl media by formation an ion association complex of with 18C6 oxoniumcation in 1,2-dichloroethane based on solvent extraction method. From slope analysis method, the extracted species was $[H_3O.18C6]^+AuCl_4^-$[7].

II. EXPERIMENTAL

A. Apparatus:

The spectrophotometric measurements were made by double beam UV-Vis. spectrophotometer, (Biochrom Libra S60) (UK) is used by 1cm quartz cells and pH was measured with pH-meter, WTW (Germany). For shaking HY-4 vibrator with AD Just about speed multiple (Italy) was used.

B. Chemicals and Solutions:

The solution 1×10^{-2}M of crown ether 15C5 (Merck) were prepared by dissolving suitable quantity of 15C5 in chloroform. Al(III) solution at a concentration of 1mg/mL prepared by dissolving 1.127gm of $AlCl_3.6H_2O$ (LAB-SCAN) in 100mL distilled water. 1%8-Hydroxyquinoline(B.D.H) solution was prepared by dissolving 1.000gm in 100mL chloroform.

III. COMPREHENSIVE METHOD FOR EXTRACTION

Aqueous solution of 5mL in volume contain known amount of Al^{3+} at optimum concentration of NaCl shaking this solution for 10min. afterward adding 5mL of 1×10^{-4}M crown ether 15C5 dissolved in chloroform and shaking the two layers 10min. at 25°C in electrical shaker, then separate organic phase from aqueous phase, as well as measure the absorbance of organic phase at λ_{max} against crown ether 15C5 as blank, and determine distribution ratio (D) values after treated aqueous phase according to spectrophotometric method 8-hydroxyquinoline method[8] and return to calibration curve Fig. (3) to determine remainder and transfer quantity of aluminum.

IV. RESULTS AND DISCUSSION

A. Spectrophotometric studies

Absorption spectra of crown ether 15C5 and its ion pair association complex with Al(III) as chloroanion complex $AlCl_4^-$ were performed as in Fig. (1,2):

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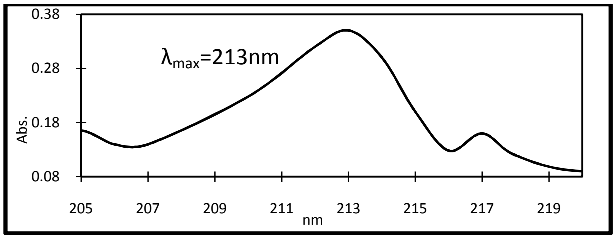


Figure 1: Absorption spectra of crown ether 15C5 in chloroform

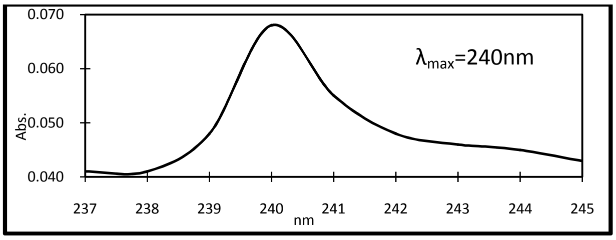


Figure 2: Absorption spectra of ion pair association complex

From the UV-Vis. absorption spectrum in Fig. (1,2) show λ_{max}=213nm for crown ether 15C5 and for ion pair complex was 240nm with ε=302.18L.mol^{-1}.cm^{-1}.

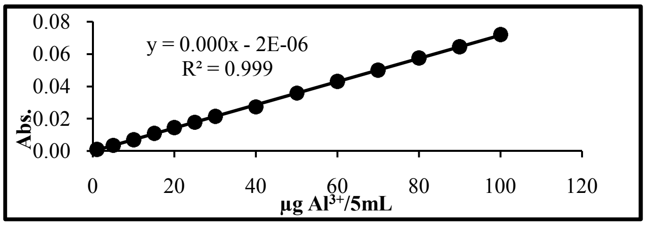


Figure 3: Calibration curve of Al (III) ion in aqueous solution by 8-Hydroxy quinoline method.

B. NaCl Concentration Effect

5mL aqueous solutions contain 100µg Al^{3+}, and varying concentration of NaCl ranging from (0.1-2.0M), shaked with 5mL of 15C5 solution at 1×10^{-4}M, according to procedure detailed in comprehensivemethod for extraction. The results obtained were as in Fig. (4, 5):

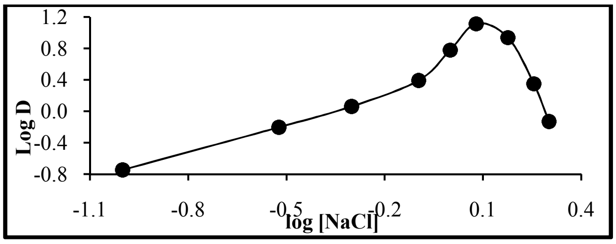


Figure 4: D=F [NaCl].

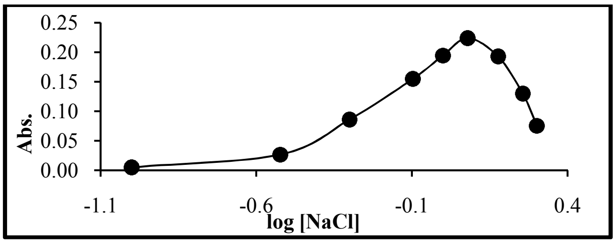


Figure 5: Effect of NaCl concentration on ion pair complex formation and extraction.

The results show 1.2M NaCl was the optimum concentration giving favorable thermodynamic equilibrium for produce ion exchanger and exchange $AlCl_4^-$ instead of Cl^- ion. Any concentrations less than 1.2M not allowreaching thermodynamic equilibrium and giving low concentration of ion exchanger which is decrease extraction efficiency. Any concentration more than 1.2M NaCl also effect to decline extraction efficiency, by electrophoretic effect in aqueous solution and restriction $AlCl_4^-$ in aqueous solution and prevent $AlCl_4^-$ to participate in liquid ion exchange to produce ion pair complex for Al^{3+}.

C. Aluminum (III) Concentration Effect

Increasing concentrations of Al^{3+} ranging from (1-120µg) extracted from 5mL aqueous solutions in presence 1.2M NaCl. These solutions shaked with 5mL of 1×10^{-4}M 15C5, according to procedure detailed in comprehensive method for extraction. The results were as in Fig. (6,7):

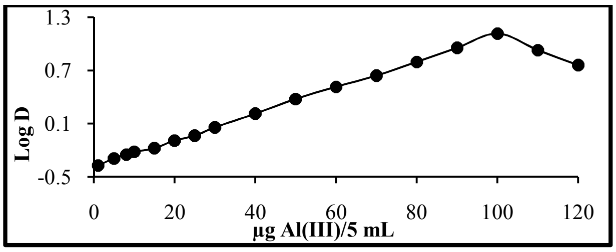


Figure 6: D= F(Al^{3+} concentration)

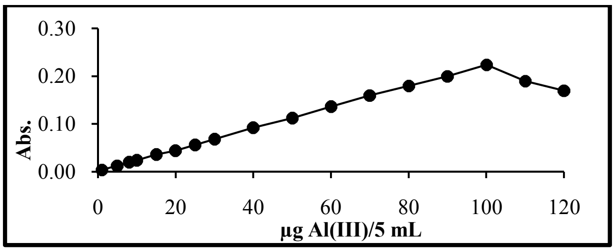


Figure 7: Effect of Al^{3+} concentration on ion pair complex formation and extraction.

The result illustrates the optimum concentration of Al3+ was100µg, giving the best thermodynamic equilibrium and produced more stable chloroanion complex $AlCl_4^-$of Al^{3+}:

$$Al^{3+} + 4\ Cl^- + 4\ Na^+ \rightleftharpoons AlCl_4^- + 4\ Na^+$$

$$[Na15C5]^+; Cl^- + AlCl_4^- \rightleftharpoons [Na15C5]^+; AlCl_4^- + Cl^-$$

Any concentration less than 100µg doesn't allow to reach thermodynamic equilibrium to produce $AlCl_4^-$, then the concentration of $AlCl_4^-$ produced is very small and not enough to formation ion pair complex extracted then giving low absorbance and D values. As well as Al^{3+} concentration more than 100µg effect to decrease absorbance and D values also by effect of mass action law and Le chatelier principle, because the high concentration of Al^{3+} at constant other parameters effect to increase the rate of backward direction of reaction for formation $AlCl_4^-$ whereas this effect to decline extraction efficiency.

D. Shaking Time Effect

5mL aqueous solutions at optimum conditions shaking with 5mL of (1×10^{-4} M) 15C5, according to procedure detailed in comprehensive method for extraction.The results demonstrate as in Figures (10,11):

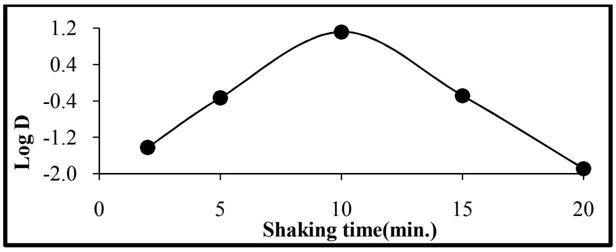


Figure 8: D=F (Shaking time).

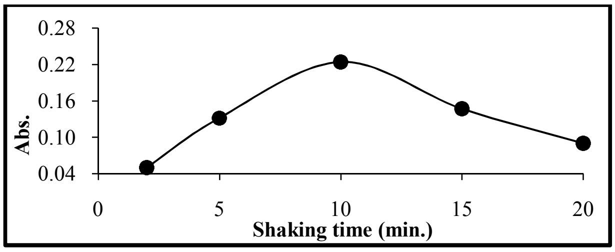


Figure 9: Effect of shaking time on complex formation and absorbance value.

The results show optimum shaking time which allow to reach the equilibrium of higher extraction efficiency was 10min., that is mean the kinetic energy beside thermodynamic control the extraction ability and shaking time less than optimum mean the kinetic energy less than needed as well as shaking time more than optimum mean the kinetic energy is more than needing and in the both case effect to decline extraction efficiency.

E. Stoichiometry:

To know and limitation the structure of ion pair association complex extracted applied spectrophotometric method which is slope analysis method. The result as in Fig.(10). The more probable structure of extracted complex was 1:1:1 $[Na15C5]^+$; $AlCl_4^-$.

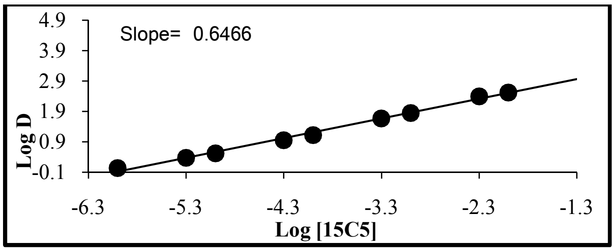
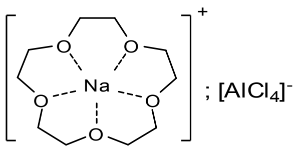


Figure 10: Slope analysis method



More probable structure of complex extracted

F. Crown Ethers Cage Size Effect

5mL aqueous solution at optimum conditions shaking with 5mL of 1×10^{-4} M solution of different crown ethers, according to procedure detailed in comprehensive method for extraction. Also taken the spectrum of organic phase against the same crown ether used solution. The results show as in Table (1):

Table1: Effect of Agreement Between Crown Ethers Cavity Size And Na^+ Cation Diameter.

Crown ether	Cavity size (Å)	R_{Na^+} (1.96Å)/R_{Crown} (Å)[9]	D	%E	λ_{max}	Absorbance	Molar absorptivity $L.mole^{-1}.cm^{-1}$
12C4	1.35	1.45	11.5	92.00	243	0.118	159.18
15C5	1.95	1.01	13.1	92.91	241	0.224	302.18
18C6	2.9	0.68	4.00	80.01	253	0.215	290.04
DB18C6	2.9	0.68	1.70	63.02	248	0.200	269.80
DCH18C6	2.9	0.68	6.32	86.34	260	0.200	316.67
DB24C8	5.05	0.39	3.82	79.26	287	0.458	617.84

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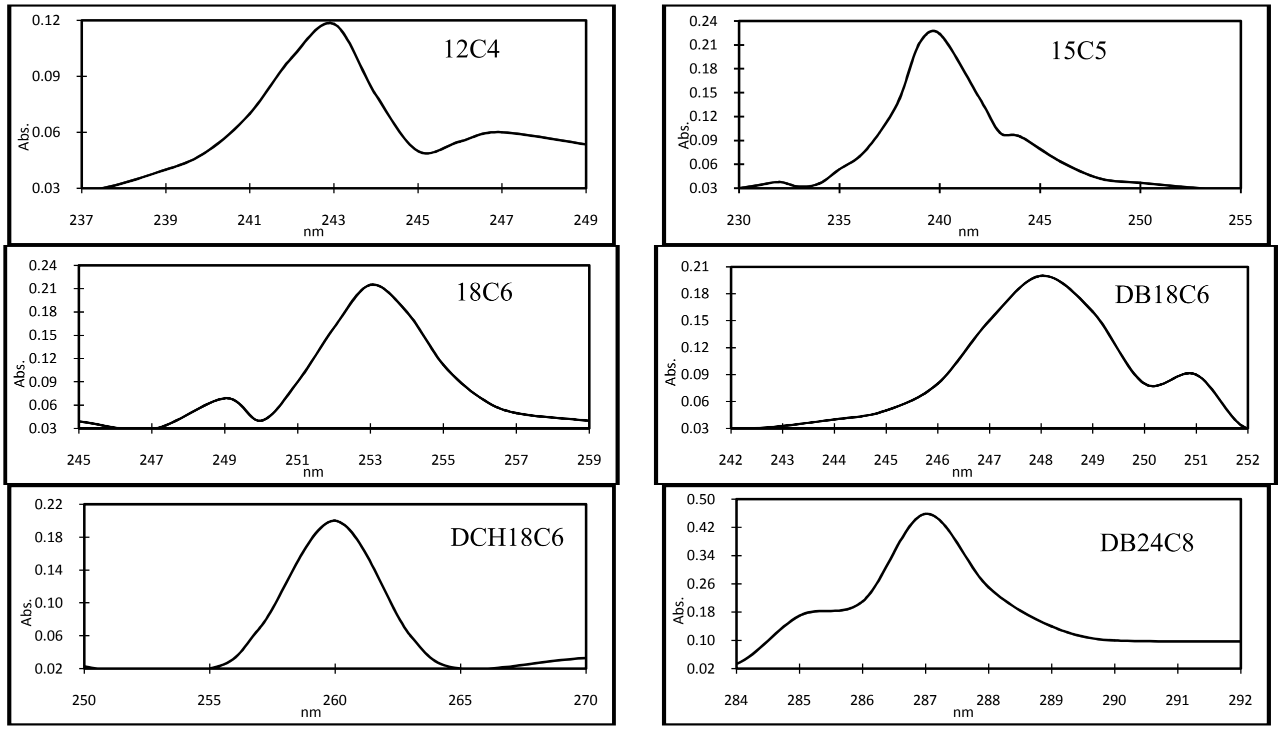

Figure 11: Effect of agreement between Na+ diameter and crown ethers cavity size.

The cavity is not the only parameter in determining which cation could be complexed, but generally, it giving a good idea of which crown ether can be used as complexing agent with desired cation. The results illustrate higher agreement between 15C5 with Na^+ giving higher Dand absorbance values at λ_{max}=241nm, all that due to the fitting interaction between 15C5 crown ether which is having five oxygen atoms and Na^+ cation, and provide higher stability of ion pair complex[9].

G. Spectrophotometric determination of Aluminum (III) in different samples

For spectrophotometric determination of Al^{3+} in different samples such as soil, water, vegetable, fruit etc. The samples digestion by using wet digestion method[10]. Prepared calibration curve at λ_{max}=241nm to the determination Al^{3+}in different samples as in Fig. (12) according to liquid ion exchange method. %RSD=0.008136, D.L= 1.78×10^{-5} ppm, ε= 300.191L.mol^{-1}.cm^{-1} ,Sandell's sensitivity= 0.00899µg/cm^2.

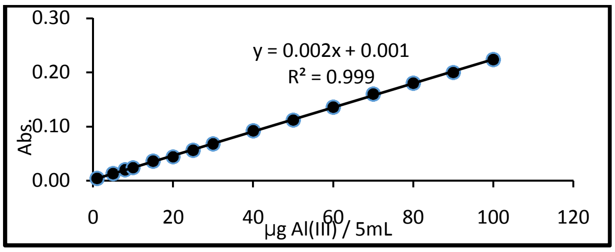

Figure 12: Calibration curve for spectrophotometric determination of Al^{3+} in different samples.

Table 2: application

Sample No.	Sample	Al quantity (ppm)
1	Al-Mishikhab roadside street	52.96
2	Sediment of drainage	58.13
3	Sediment of Euphrates river	87.55
4	Najaf sea (agriculture)	20.37
5	Soil of Al-Salam Valley	20.44
6	Al-Ameer Neighborhood	29.34
7	Water of Nassar's Spring	25.70
8	Al-Hafar drainage water	230.25
9	Euphrates river	0.049
10	Tap water	1.631

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