Separation and Extraction Micro Amount of Cadmium (II) and Mercury (II) with Liquid Anion Exchange Method

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Abstract

For extraction chloro anion complexes of Cd^{2+} and Hg^{2+} used many organic agents as extractant according to liquid ion exchange method such as α-Naphthyl amine (α-NA), 4-Amino benzoic acid (4-ABA), 2-[(4-Carboxy methyl phenyl) azo]-4,5-diphenyl imidazole (4-CMePADPI) and Cryptand (C222). This study includes definition hydrochloric acid concentration in aqueous phase and shaking with organic phase necessary for extraction as well as shaking time, organic solvent effect, interferences and alkaline salt effect. Thermodynamic showed the ion exchange reaction was exothermic for α-NA, C222 and endothermic for 4-ABA, 4-CMePADPI for extraction $CdCl_4^=$, but for extraction $HgCl_4^=$ was exothermic with 4-ABA, 4-CMePADPI and C222 but endothermic with α-NA. In addition stoichiometry showed the ion pair complex extracted was 1:1:1 Cation: Ligand: Anion.

Key word: Liquid ion exchange, Cadmium, Mercury, Solvent extraction.

Introduction

Zn^{2+} was extracted from chloride ion media with (TPP) and the definition of all parameters effect on extraction method[1], Au^{3+} was extracted from hydrochloric acid media with amine alamine304 $[R_3N^+H,Cl^-]$ in Xylene, and calculate distribution ratio for complex $R_3N^+H,AuCl_4^-$ [2]. Different new liquid ion exchange [Ethylene bis (trioctyl phosphonium)](EBTOP) used for extraction of Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+} as well as Fe^{3+} and In^{3+}[3]. Hg^{2+} was separated from 0.5M acetic acid by Aliquat 336S as liquid ion exchange, and extracted species was $[2R_4N^+; Hg(OAC)_4^=]$, this method suitable for separation from Zn, Cd, Ni, Co, Cu, Bi, Mn [4]. Zn, Cd and Hg were extracted from chloride and sulphate media by solvation and liquid ion exchange methods and studied the extracted species [5]. Hg^{2+} extracted as chloro complexes anion by different high molecular weight amines and tetra ammonium salts with distribution the effective parameters and extracted species[6], Cd^{2+} extracted from sulphate media by di(2-ethyl hexyl)phosphoric acid (D2EHPA) dissolved in Toluene, at pH=5-6 and 0.1M of reagent in Toluene [7].

The present study was undertaken to investigate the effect of various extraction parameters on the extraction of Cd(II) and Hg(II) as chloro complex from hydrochloric acid media by (α-NA),(4-ABA), (4-CMePADPI) and (C222) parameters studied include the effect of hydrochloric acid concentration, metal concentration, foreign ion and temperature of extraction, organic solvent.
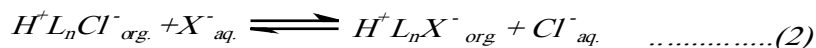
Experimental

Apparatus

For absorbance measurements shimadzu UV-1700 spectrophotometer is used with 1cm quartz cells (Japan), pH- measurements were carried out using WTW, listed 8F93(Germany), for shaking used HY-4 vibrator with AD just about speed multiple(Italy).

Reagents

A standard stock solutions 1mg/mL for Cd^{2+} and Hg^{2+} was prepared by dissolving drier (0.1631 gm) of $CdCl_2$ and (0.1354 gm) of $HgCl_2$ [Fluka] in 100mL distilled water contain 1mL HCl concentration in volumetric flask, other working solutions prepared by appropriate dilution of the stock solution with distilled water. Stock solution of dithiazone (1×10^{-2} M) was prepared by dissolving (0.0256 gm) in 10mL carbontetrachloride in volumetric flask, working solution (1×10^{-4} M) was prepared instantaneously by dilution with CCl_4. Standard solutions of different ligand prepared by dissolving weighed quantities of each one in chloroform.

General extraction procedure

Shaking fixed volume of ligand solution with HCl solution at optimum concentration in order to conversion ligand to liquid anion exchanger, as well aqueous phase contains suitable concentration of HCl to formation chloro anion complex for metal ion, after that shaking organic phase with aqueous phase to exchange small anion Cl^- in liquid anion exchanger with chloro complex in aqueous phase as in the equilibria below:-

$$nL_{org.} + H^+_{aq.} + Cl^-_{aq.} \rightleftharpoons H^+L_nCl^-_{org.} \qquad ....(1)$$

$$H^+L_nCl^-_{org.} + X^-_{aq.} \rightleftharpoons H^+L_nX^-_{org} + Cl^-_{aq.} \qquad ....(2)$$

$L = \alpha\text{-}NA, 4\text{-}ABA, 4\text{-}CMePADPI, C222$
$X^- = CdCl_4^=, HCdCl_4^-, HgCl_4^=, HgCl_3^-, HHgCl_4^-$

Afterwards determined reminder quantity of metal ion in aqueous solution and transferred quantity to organic solution at later calculate distribution ratio (D), according to dithiazone method [8].

Results and Discussion

Effect of HCl Concentration in Aqueous Solutions

The concentration of HCl in aqueous solutions at range (0.1-3.0M), the concentration of HCl shaked with ligand solution was 1M to forming liquid anion exchanger, the obtained results, reported in figure (3).

Effect of HCl Concentration on liquid ion pair formation

At optimum concentration of HCl for each ion in aqueous phase and organic phase of each ligand shaking with HCl solution in different concentrations (0.1-3.0M), the obtained results in figure (4).

Effect of Metal ion Concentration

Organic phase of ligand shaking with HCl optimum concentration, this organic phase shaking once again with aqueous solutions contain Cd^{2+} (5-100μg) and Hg^{2+} (5-150μg) at optimum HCl concentration, the results as in table (2) and figure (5).

Study about shaking time necessary for extraction, taken different times for shaking (2-20min), the obtained results, reported in table (3).

The stoichiometry of the probable extracted species was determined on the basis of slope analysis method by plotting logD versus log[L] graph and giving strait line relation with slope value demonstrate the stoichiometry of ion pair complex extracted was 1:1:1 $[HL^+]HCdCl_4^-$, $[HL^+]HHgCl_4^-$, $[HL^+]HgCl_3^-$, the results as in table (4).

Organic solvent effect on extraction method illustrates there is not any linear relation between dielectric constant (ε) of organic solvents and distribution ratio (D), obtain table (5).

Effect of electrolyte salt on distribution ratio investigated by use KCl and NaCl salts at different concentrations, the results show there is optimum concentration of electrolyte salt solution giving higher distribution ratio (D) as in Figure (7,8).

Extraction of $CdCl_4^=$ and $HgCl_4^=$ according to liquid anion exchange by C222 and 4-CMePADPI in foundation of cations appear interferences with hydrogen ions, these study and results shown the cations Na^+, K^+, Mg^{2+} and Ca^{2+} restrict the chloro complex anion $CdCl_4^=$ and $HgCl_4^=$ and decline distribution ratio by using C222 and transition metal cations Cu^{2+}, Ni^{2+} could not give stable coordination complex cation with 4-CMePADPI in acidic media because the protonation of 4-CMePADPI in acidic media decrease the chance of binding with Cu^{2+}, Ni^{2+} ions.

The study about temperature effect shows the reaction of anion exchange was endothermic for $CdCl_4^=$ with 4-ABA and 4-CMePADPI but exothermic with α-NA and C222, and the extraction of $HgCl_4^=$ was endothermic with α-NA but exothermic with 4-ABA, 4-CMePADPI, C222. Obtained results in table (6) and figure (8).And thermodynamic data for extraction demonstrate in table (7).

$$K_{ex} = \frac{D}{[HMCl_4^-]_{aq.} \, [L]_{org.}} \quad \ldots\ldots\ldots\ldots(3)$$

$$Slope = \frac{-\Delta H_{ex}}{2.303 \, R} \quad \ldots\ldots\ldots\ldots(4)$$

$$\Delta G_{ex} = -RT \ln K_{ex} \quad \ldots\ldots\ldots\ldots (5)$$

$$\Delta G_{ex} = \Delta H_{ex} - T \, \Delta S_{ex} \quad \ldots\ldots\ldots\ldots (6)$$

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Table (1): Sandyl Sensitivity

Ligand	Cd				Hg			
	α-NA	4-ABA	4-CMePADPI	C222	α-NA	4-ABA	4-CMePADPI	C222
S µg/mL	0.065	0.18	0.2	0.81	0.055	0.043	0.15	0.21

Table(2):Effect of Metal ion concentration on distribution ratio (D)

μg (Cd^{2+}, Hg^{2+})	D Cd				D Hg			
	α-NA	4-ABA	4-CMePADPI	C222	α-NA	4-ABA	4-CMePADPI	C222
5	No.Ex.	0.78	0.56	2.12	No.Ex.	.No.Ex	No.Ex.	No.Ex.
10	0.42	2.12	1.27	4.55	No.Ex.	.No.Ex	No.Ex.	0.47
20	1.17	3.76	2.56	9.52	0.29	0.06	0.53	1.85
30	1.77	5.81	4	14	0.82	0.54	1.34	2.94
40	2.57	7.69	4.71	18.04	1.22	1.02	2.12	4.31
50	4.55	11.5	7.92	49	1.45	1.47	3.23	6.14
60	3.83	9.34	5.26	25.08	1.97	1.88	3.61	6.87
70	2.5	4.38	4.88	21.74	2.3	2.27	4.3	7.25
80	1.7	3.12	4.37	19.05	2.47	2.66	4.88	8.3
90	1.36	1.5	4.06	16.29	2.54	3.16	5.92	8.58
100	1.22	1.22	3.84	14.12	3.03	2.62	6.63	9.99
110	-	-	-	-	3.1	-	7.2	12.41
120	-	-	-	-	3.51	-	7.69	12.95
130	-	-	-	-	3.85	-	8.92	10.76
140	-	-	-	-	4.26	-	8.58	9.42
150	-	-	-	-	4.1	-	8.37	7.39

Table (3):Effect of shaking time on distribution ratio (D)

Time (min.)	D Cd				D Hg			
	α-NA	4-ABA	4-CMePADPI	C222	α-NA	4-ABA	4-CMePADPI	C222
2	0.82	4.81	4.55	10.36	3.82	3.01	8.02	11.76
5	1.52	5.94	5.09	20.01	4.07	3.12	8.55	14.78
10	4.55	11.5	7.92	49	4.26	3.16	8.92	12.95
15	2.67	2.78	5.57	26.77	4	3.78	8.28	11.5
20	1.74	1.68	3.71	9.41	3.72	3.63	7.9	10.76

Conc. Of [L]	D Cd								D Hg							
	α-NA		4-ABA		4-CMePADPI		C222		α-NA		4-ABA		4-CMePADPI		C222	
	D	Slope	D	Slope	D	Slope	D	Slope	D	Slope	D	Slope	D	Slope	D	Slope
1×10^{-2}	6.14		49.16		31.63		832.3		6.21		5.08		13.93		20.03	
5×10^{-3}	5.94		37.82		22.59		682.4		5.79		4.84		12.66		19.09	
1×10^{-3}	5.41		24.68		15.52		251.4		5.14		4.35		10.81		17.21	
5×10^{-4}	5.09		17.53		11.53		154.6		4.78		4.17		10.2		16.13	
1×10^{-4}	4.55	0.062	11.5	0.3	7.92	0.3	49	0.602	4.26	0.085	3.78	0.057	8.92	0.097	14.78	0.065
5×10^{-5}	4.43		9.14		6.56		30.85		3.96		3.68		8.54		13.93	
1×10^{-5}	3.8		5.99		4.36		11.8		3.45		3.36		7.27		12.79	
5×10^{-6}	3.62		5.25		3.1		7.57		3.21		3.2		6.82		12.38	
1×10^{-6}	3.46		3.08		2.03		3.31		2.84		2.98		5.7		10.97	

Table (4): Effect of ligand concentration on distribution ratio (D)

Table (5): Effect of organic solvents on distribution ratio (D)

Organic Solvents	ε	D Cd				D Hg			
		α-NA	4-ABA	4-CMePADPI	C222	α-NA	4-ABA	4-CMePADPI	C222
Nitrobenzene	35.74	2.33	3.54	7.92	11.5	5.66	2.78	9.48	15.21
1,2-Dichloroethane	10.65	5.94	2.37	9	26.77	5.08	4.35	8.7	16.64
Dichloromethane	9.08	2.47	1.97	5.09	24	5.25	4.05	9.83	15.9
Chlorobenzene	5.708	2.42	8.61	6.81	21.72	5.08	3.83	8.15	16.14
Chloroform	4.806	4.55	11.5	7.92	49	4.26	3.78	8.92	14.78
Benzene	2.804	1.65	1.68	4.68	22.8	5.48	3.16	7.66	15.66
Toluene	2.438	3.46	1.84	8.61	19.83	4.93	3.45	8.42	14.58
Carbontetrachloride	2.38	1.68	2.52	9.41	12.15	5.14	5	8.28	11

Table (6): Effect of Temperature on distribution ratio (D)

T°C	Cd								Hg							
	α-NA		4-ABA		4-CMePADPI		C222		α-NA		4-ABA		4-CMePADPI		C222	
	D	$K_{ex} \times 10^9$	D	$K_{ex} \times 10^9$	D	$K_{ex} \times 10^9$	D	$K_{ex} \times 10^9$	D	$K_{ex} \times 10^9$	D	$K_{ex} \times 10^9$	D	$K_{ex} \times 10^9$	D	$K_{ex} \times 10^9$
5	6.57	0.74	8.77	0.99	5.94	0.67	124	14.09	3.24	2.31	4.69	0.52	12.26	9.5	16.61	13.84
10	5.94	0.67	9.41	1.07	6.35	0.72	99	11.25	3.4	2.43	4.48	0.5	11.74	9.1	16	13.33
15	5.41	0.61	10	1.13	6.93	0.78	82.33	9.35	3.6	2.57	4.17	0.46	10.6	8.22	15.54	12.95
20	4.95	0.56	10.4	1.18	7.33	0.83	61.5	6.98	3.92	2.8	4	0.44	9.65	7.48	15.29	12.74
25	4.55	0.51	11.5	1.3	7.92	0.9	49	5.56	4.26	3.04	3.78	0.42	8.92	6.91	14.78	12.32
30	4.31	0.49	12.2	1.38	8.25	0.93	40.66	4.62	4.46	3.19	3.63	0.4	8.42	6.52	14.45	12.04
40	3.71	0.42	13.7	1.55	9.41	1.07	30.25	3.43	4.98	3.55	3.41	0.38	7.55	5.85	13.88	11.57
50	3.31	0.37	14.6	1.66	10.36	1.17	19.83	2.25	5.42	3.87	3.12	0.35	6.83	5.29	13.28	11.07
60	3.03	0.34	15.7	1.78	11.5	1.3	15.66	1.78	6	4.28	2.98	0.33	6.47	5.01	12.55	10.46

Table (7): Thermodynamic data

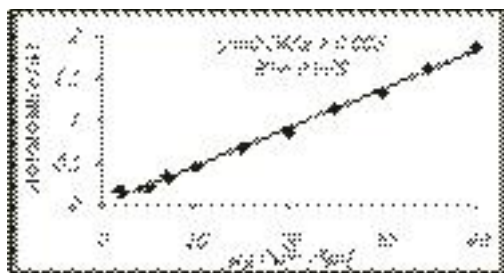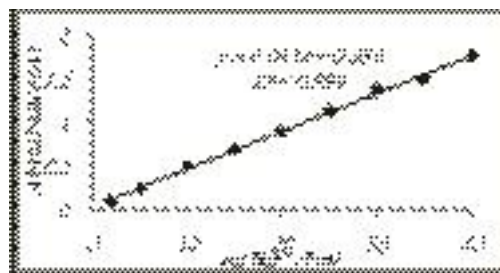| Ligand	Cd			Hg		
	ΔH_{ex} (KJ.mole^{-1})	ΔG_{ex} (KJ.mole^{-1})	ΔS_{ex} (J.mole^{-1}.K^{-1})	ΔH_{ex} (KJ.mole^{-1})	ΔG_{ex} (KJ.mole^{-1})	ΔS_{ex} (J.mole^{-1}.K^{-1})
α-NA	-0.0107	-46.15	165.96	0.0085	-53.80	161.58
4-ABA	0.0083	-57.66	173.17	-0.0063	-45.38	163.21
4-CMePADPI	0.0091	-56.81	170.62	-0.0085	-46.72	168.02
C222	-0.0028	-52.81	190.06	-0.0041	-47.57	171.12

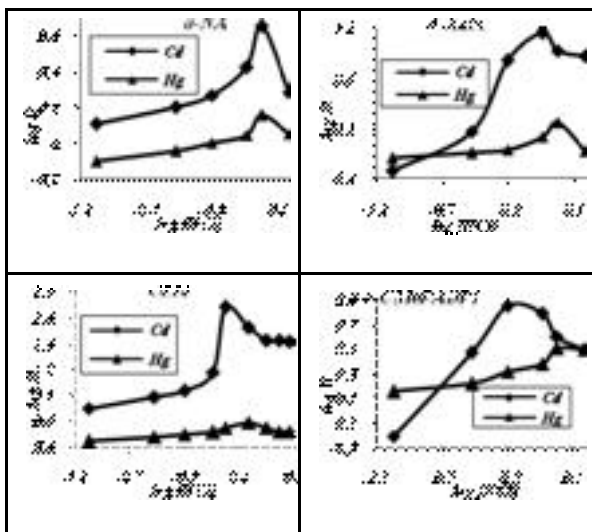**Fig. (1):Calibration curve of Cd(II)**

Fig. (2):Calibration curve of Hg(II)

Fig.(3): Effect of HCl concentration in aqueous solutions on distribution ratio (D) - $[Cd^{2+}]_{aq.}$, $[Hg^{2+}]_{aq.}$=50µg/5mL, [Ligand]=1x10^{-4}M in CHCl$_3$
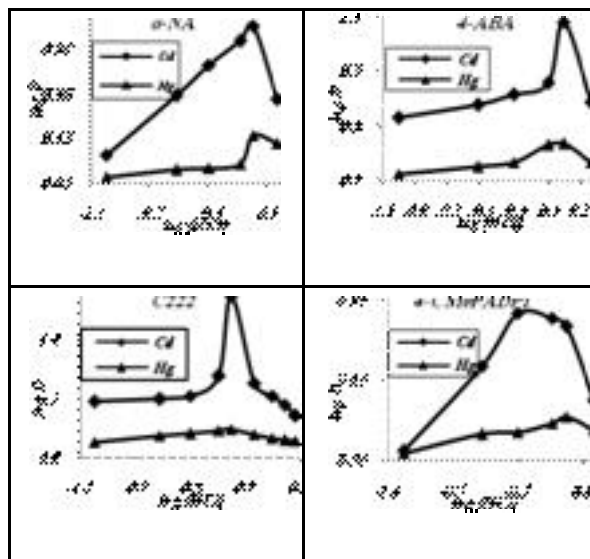
Fig. (4): Effect of HCl concentration on liquid ion exchanger formation-$[Cd^{2+}]_{aq.}$, $[Hg^{2+}]_{aq.}$=50µg/5mL, [Ligand]=1x10^{-4}M in CHCl$_3$
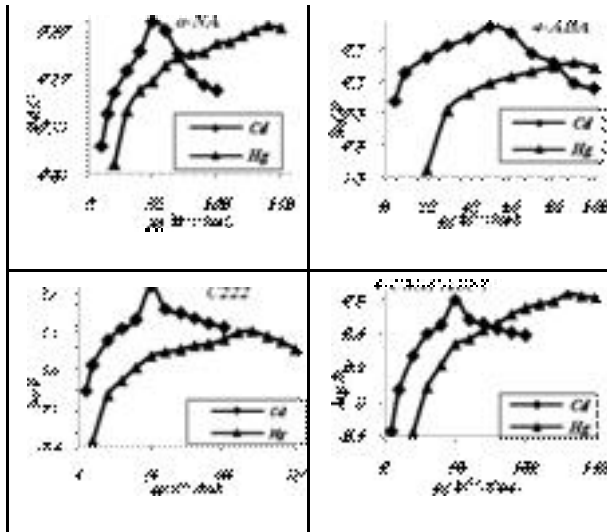
Fig. (5): Effect of Cd(II), Hg(II) ions concentration
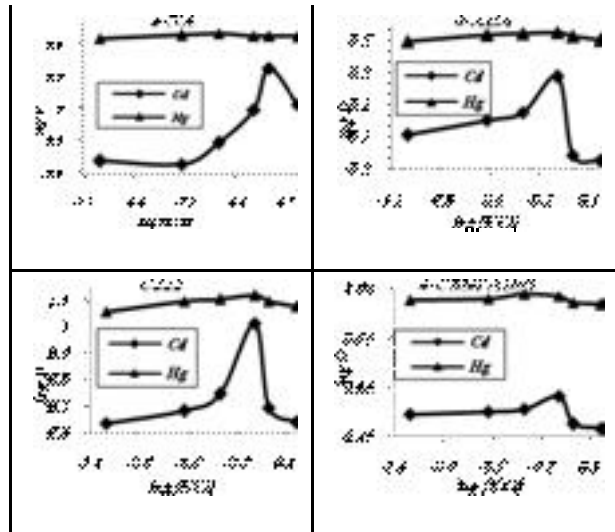
Fig. (6): Effect of KCl concentration on extraction of Cd(II), Hg(II).
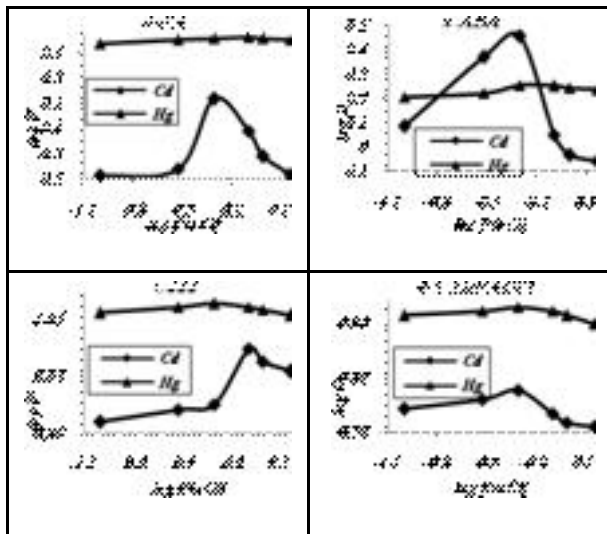

Fig. (7): Effect of NaCl concentration on extraction of
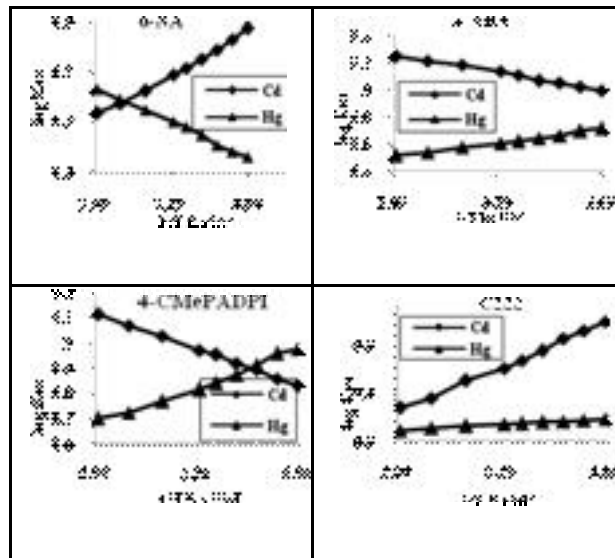

Fig.(8): Temperature effect on the extraction method of Cd(II), Hg(II).

فصل واستخلاص الكميات المايكروية من الكادميوم (II) و الزئبق (II) بوساطة طريقة التبادل الايوني السائل

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الخلاصة

لاستخلاص معقدات الكلورو السالبة للكادميوم (II) ،و الزئبق(II) استعملت كواشفا عضوية بوصفها مواد مستخلصة على وفق تقنية التبادل الايوني السائل، مثل α-Naphthyl amine (α-NA)، و 4-Amino benzoic acid (4-ABA)، و 2-[(4-Carboxy methyl phenyl) azo]-4,5-diphenyl imidazole (4-CMePADPI)، و Cryptand (C222). هذه الدراسة شملت تحديد تركيز حامض الهيدروكلوريك في الوسط المائي والتركيز المناسب للرج مع الطور العضوي واللازم لعملية الاستخلاص فضلا عن زمن الرج، وتأثير المذيب العضوي، والتداخلات،و تأثير الأملاح القلوية. الجانب الثرموديناميكي وضح إن تفاعل التبادل الايوني كان باعثا للحرارة exothermic لكل من α-NA و C222 وماصا للحرارة endothermic لكل من 4-ABA ، و 4-CMePADPI عند استخلاص $CdCl_4^=$ أما عند استخلاص $HgCl_4^=$ فكان التفاعل باعثا للحرارة exothermic مع كل من 4-ABA و 4-CMePADPI و C222 وماصا للحرارة endothermic مع α-NA. فضلا عن دراسة تركيب معقد الترابط الايوني المستخلص أثبتت انه Cation: Ligand: Anion 1:1:1.

الكلمات المفتاحية : التبادل الايوني السائل، الكادميوم، الزئبق، الاستخلاص بالمذيب.