Liquid – liquid Extraction of Palladium by Dibenzo-18-Crown-6 from Salt's Media.

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Abstract

Liquid-Liquid extraction of palladium by using Dibenzo-18-Crown-6 (DB18C6) dissolved in 1,2-dichloroethane (1,2-DCE) has been investigated. The distribution ratio (DPd) and percent of extraction (E_{Pd} %) were determined as a function of crown ether and palladium concentration, pH value, shaking time ,presence of salt media (NH4Cl ,KCl, NaCl) and solvent polarity. Depending on the mole ratio analysis method, it was suggested that the most tolerable categories were [(M^+DB18C6)2 (PdCl4)$^{-2}$] where M^+ are (NH4$^+$,K$^+$,Na$^+$)

The thermodynamic extraction data indicated that the extraction was dependent on the temperature and the Vant Hoff plot was linear over the temperature range studied (283-313 K). The result is ΔHex. has a positive value (endothermic) due to the extend of bonding between cation and the donor atoms of crown ether cavity and solvation energy changes, ΔSex. has a positive value, and ΔGex. has a negative value (spontaneous process) and the complex was stable at higher temperature.

(DB18C6) 6-   -18-

(1,2-DCE)   -2,1

(D_{ex})   (E%)

.

(2:1)

. (Na$^+$,K$^+$, NH$_4^+$)   (M$^+$)   [(M$^+$ C.E)$_2$ PdCl$_4^{-2}$] (Sandwich)

(283-313)

(ΔHex.)

(ΔGex.)   (ΔSex.)

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Introduction

Microcyclic crown ethers, first reported by Pederson in the 1967s,[1] constitute an important class of host molecules that are used in studies of molecular recognition and inclusion phenomena.[2]

The macrocyclic compound (crown ethers) are regarded an important compounds in extraction process for trace quantity of elements of the (IIIA-VIA) group via an ion-dipole interaction.[3-5]

Kuds [6] has reviewed the extraction of alkali metals with crown ethers, Salon and Krylov[7] are regarded from the first researchers to extract the complexes by macrocyclic compounds as a negative part such as Au(III) as $[AuCl_4]^-$.

The complexation process between crown ether and cation is controlled by several structure factors, such as the ring size , number of donor atoms and stereochemistry.[8]

Hossain and Honjo[9] are separated trace amounts of palladium from hydrochloric acid and potassium thiocyanate media based on the formation of ion-pair complex of palladium thiocyanate anion $Pd(SCN)4^{-2}$ and the cationic potassium complex of dicyclohexyl-18-crown-6 (DC18C6) in chloroform.

Shu-Yuan and co-worker [10] describe the synthesis and characterization of novel Schiff base liquid crystalline crown ethers prepared from the intermediates 4-(4'-alkoxylbiphenyl-4-carbonyl) benzaldehyde, cis- and trans-4, 4'-diaminodibenzo-18-crown-6.

AL-Haidarei and co-worker[11] studied the extraction of (Mn^{+2}) as $(MnO4)^-$ by (DB18C6) in atomic absorption technique, AL-Shirify and co-worker[12] extract of Al(III) by employing of polydibenzo-18-crown-6-resin (PDB18C6) in acidic and alkaline media .In the present work the extraction of Pd (II) by DB18C6 dissolve in 1,2-DCE has been studied under various conditions, such as pH of aqueous phase, shaking time, and different concentration of some salt's (NaCl, KCl, NH_4Cl) .

Experimental

A- Instruments:

1) Double beam U.V-Visible spectrophotometer, (Cintra 5 –Austral).
2) Flask shaker, (Griffin –England).
3) Digital pH-meter, (Knick –England).
4) Digital balance (Sartorios, Bp- 3015- Germany).

B- Reagents:

The crown ether (DB18C6) 98% purity was supplied by Merck an Fluka, and used without further purification .

Stock solution of crown ether 0.1 $mol.dm^{-3}$ in 1,2-DCE was prepared by dissolving (0.9000 gm) in 25ml of 1,2-DCE .Standard stock solution of palladium (II) (1mg Pd / ml) was prepared from $Pd(NO_3)_2$ (Analar – Riedel – Dehaen). Other chemicals (Analar grade and 99%) were supplied by

(BDH, Hopkins and Williams).

C-Procedure

Molar distribution coefficient Kd and percent of extraction E% of DB18C6 dissolved in 1,2-DCE for Pd (II) were determined by batch method by mixing 10ml of organic DB18C6 dissolved in 1,2-DCE (1.1×10^{-4} $mol.dm^{-3}$) in separating funnel with 15ml of aqueous (1×10^{-3} $mol.dm^{-3}$) palladium nitrate solution.

The separating funnel was shacked vigorously on a Burrell wrist-action shaker set at (280) oscillation per minute, for (30) minute (a time was found to be sufficient to reach equilibrium).

Palladium (II) concentration in the aqueous phase was determined spectrophotometrically [14] at λ_{max} 410 nm. The concentration of Pd (II) in the organic layer was obtained either by stripping or by difference from the initial concentrations.

The value of distribution ratio (D_{Pd}) and   .
(E_{pd} %) were determined by the relations

$$D_{Pd} = \frac{\text{Total Pd concentration in the organic phase}}{\text{Total Pd concentration in the aqueous phase}} \quad \text{........(1)}$$

$$E_{pd}\% = \frac{D_{Pd}}{D_{Pd} + (V_{aq.} / V_{org.})} \times 100 \quad \text{......(2)}$$

Where :- $V_{aq.}$ is the volume of aqueous solution (15ml).
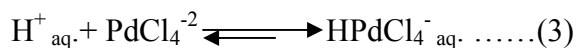 $V_{org.}$ Is the volume of organic solution (10ml).

The value of D_{Pd} as a function of temperature (283 – 313) K was obtained as described above using Lewis cell connected with thermostatic circulator.
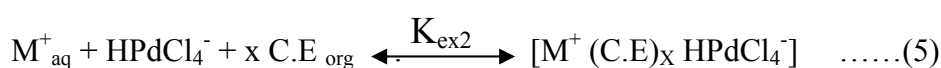
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Results & Discussion
Extraction conditions of Pd (II).

The optimum conditions for the extraction of Pd (II) using DB18C6 in 1,2-DCE as extractant were determined by studying the effect of concentration of Pd (II) , pH, concentration of crown ether, solvent polarity and kind of cation present. The result is the extraction power of Pd (II) at different pH value as in Table (1) show that the lightest value of D_{Pd} is at pH = 7, the possible formation of [$(M^+ : C.E)_2 : (PdCl_4)^{-2}$] and/or protonation of $(PdCl_4)^{-2}$ at lawer pH as in equations (3-4) can be account to the influence of pH on the extraction.

$$H^+_{aq.} + PdCl_4^{-2} \rightleftharpoons HPdCl_4^-{}_{aq.} \quad \text{......(3)}$$

$$Keq = \frac{[HPdCl_4^-]_{aq.}}{[H^+]_{aq.} [PdCl_4^{-2}]_{aq.}} \quad \text{.........(4)}$$

$$M^+_{aq} + HPdCl_4^- + x \, C.E_{org} \xrightarrow{K_{ex2}} [M^+ (C.E)_X \, HPdCl_4^-] \quad \text{......(5)}$$

Arrangements equation 1,2 give

$$D_{Pd} = K_{ex2} K_{eq}[M^+]_{aq} [PdCl_4^{-2}] . [C.E]^x_{org.} \quad \text{.....(6)}$$

$$Log \, D_{Pd} = Log \, K_{ex2} K_{eq}[M^+]_{aq} [PdCl_4^{-2}]_{aq.} + Log \, [H^+]_{aq.} + x \, Log \, [C.E]_{org.} \text{ (7)}$$

Table (1). Value of EPd% at different pH.

pH	Epd%
1	40
2	48
3	49
4	51
5	59
6	83
7	92
8	91
9	90
10	86
11	82
12	68

The extraction mechanism of kinetic reaction between Pd (II) ions and DB18C6 that dissolved in 1,2-DCE at pH (7) was investigated, by batch method . Rapid stirring of the mixing solution was essential to minimize the film diffusion effect. The results obtained are shown in Table (2), revealed that a shaking period (30 minute) was required to reach equilibrium at each extraction temperature.
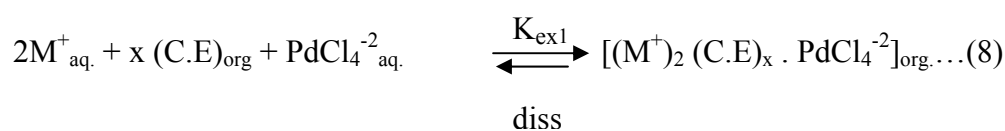
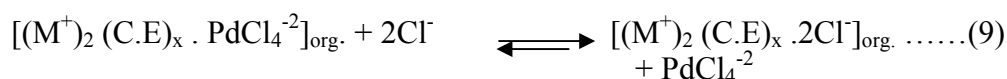## Table (2). Value of EPd% at different shaking time at pH= 7.

t/min	EPd%
5	94
10	94
15	94
20	94
25	97
30	97
35	97
40	97
45	97
50	97

The extraction has also been studied at various concentration of salts solutions (NH$_4$Cl, KCl and NaCl).

The results obtained are shown in Table (3), the E$_{Pd}$% value of DB18C6 in 1,2-DCE for Pd (II) were increase with an increasing of these salts concentration in the aqueous phase (0.001 – 0.1) mol.dm^{-3} of NH$_4$Cl solution and from (0.001 – 0.01) mol.dm^{-3} of KCl and NaCl solution respectively, large value of 0.1 mol.dm^{-3} of NH$_4$Cl or/and 0.01 mol.dm^{-3} of KCl and NaCl solutions the E$_{Pd}$% will be decrease, this could be interpreted in the terms of dissociation of the complexes according to the following equations

$$2M^+_{aq.} + x (C.E)_{org} + PdCl_4^{-2}{}_{aq.} \xrightarrow[\text{diss}]{K_{ex1}} [(M^+)_2 (C.E)_x . PdCl_4^{-2}]_{org} \ldots (8)$$

$$[(M^+)_2 (C.E)_x . PdCl_4^{-2}]_{org.} + 2Cl^- \quad \longleftrightarrow \quad [(M^+)_2 (C.E)_x .2Cl^-]_{org.} \ \ldots\ldots(9)$$
$$+ PdCl_4^{-2}$$

Were M^+ is (Na^+, K^+ and NH_4^+)

As indicated from Table (3) presence of alkali metals (as chlorides) in the aqueous phase shows that $E_{Pd}\%$ maximum is achieved at the best size matching NH_4^+ to the crown cavity[3] of DB18C6.

The result of Table (3) indicate that improve extractabilities are obtained by using NH_4^+ ions counteraction for $PdCl_4^{-2}$ instead of K^+ and Na^+ ions.

Table (3) effect of salts concentrations on the extraction of Pd

Salt concentrations (M)	EPd% with NH4Cl	EPd% with KCl	EPd% with NaCl
0.001	57.69	70.46	53.02
0.005	60.15	89.64	57.41
0.01	62.43	73.66	72.61
0.1	91.00	72.62	66.87
0.5	57.02	57.70	45.33
1	56.82	54.02	43.76
1.5	55.18	43.35	42.43
2	55.33	39.92	40.28

Concerning the effect of solvent polarity upon the extraction of $PdCl_4^{-2}$ by DB18C6 at pH (7); there is a substantial influence of increasing the polarity upon D_{Pd} value as in Table (4) .

A relative linear relation can be obtained between $E_{Pd}\%$ and $1/\varepsilon$ (were (ε) is the dielectric constant of the solvent) in order 1,2-DCE $\cong$ Benzen > Tolune > C.B > DCM > N.B+T $_{(50:50)}$ > N.B+T $_{(30:70)}$.

Table (4) effect of different solvents on the extraction of Pd (II) (1.1 x10^{-4} mol.dcm^{-3}) by (1 x10^{-3} mol.dcm^{-3}) DB18C6 in different solvents, at pH (7).

Solvents	ε	$1/\varepsilon$	EPd%
1,2-DCE	10.61	0.09	98.70
DCM	9.10	0.10	85.70
Benzene	2.28	0.43	98.50
C.B	5.70	0.17	89.70
N.B	35.70	0.02	55.40
Toluene	2.40	0.41	95.50
N.B+T 30:70	10.70	0.09	50.60
N.B+T 50:50	15.60	0.06	59.20

Where (C.B) is Chlorobenzene and (N.B) is Nitrobenzene and (N.B+T) is Nitrobenzene + Toluene.

The enthalpy for complexation reactions depending on the temperature coefficient method for the relation Ln D_{Pd}

against (1/T) which is found to be linear in Figure (1).

The enthalpy of extraction ($\Delta H_{ex.}$) is determined from Vant-Hoff equation[15].

The values of ($\Delta G_{ex.}$) and ($\Delta S_{ex.}$) are listed in Table (5), it is obvious that the extraction process is an endothermic,

thus the positive enthalpic value means that the heat of solvation ($\Delta H_{solv.}$) exceeds the heat of hydration ($\Delta H_{ex} = \Delta H_{solv} - \Delta H_{hyd}$), $\Delta S_{ex.}$ value reflect the possibility of the conformational change of the crown ether in the extracted system [16].

Table (5) Thermodynamic data for the extraction of Pd (II) (1.1×10^{-4} mol.dcm^{-3}) by (1×10^{-3} mol.dcm^{-3}) DB18C6 dissolve in 1,2-DCE, at pH (7).

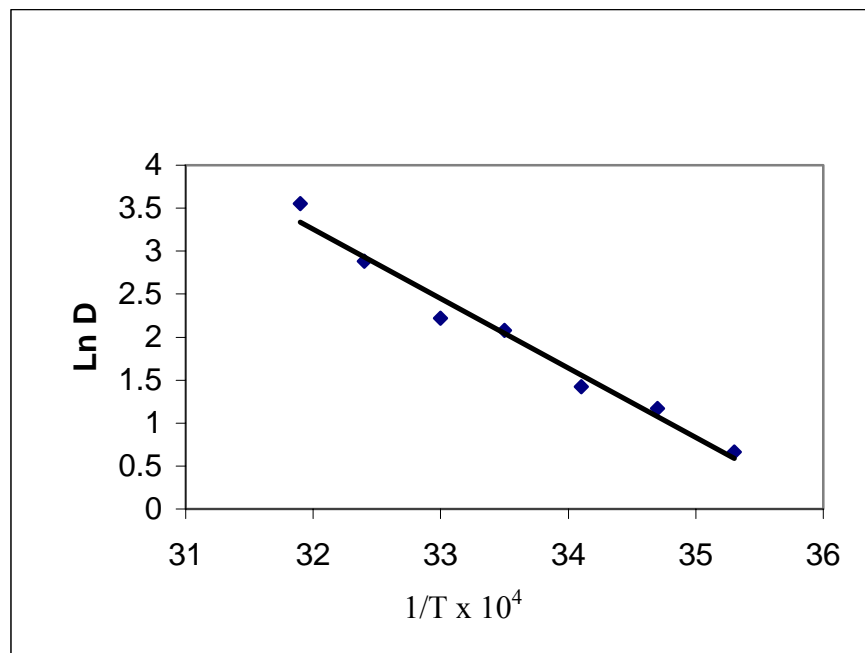| $\Delta H_{ex.}$ KJ.Mol^{-1}	$\Delta G_{ex.}$ KJ..Mol^{-1}	$\Delta S_{ex.}$ J..Mol^{-1}
69.50	-1.55	251.06
	-2.80	251.04
	-4.75	253.41
	-5.15	250.51
	-5.59	247.80
	-7.09	248.60
	-10.05	254.17

Figure (1)Effect of temperature on Ln D$_{Pd}$ values for the extraction of Pd (II) (1.1×10^{-4} mol.dcm^{-3}) by (1×10^{-3} mol.dcm^{-3}) DB18C6 dissolve in 1,2-DCE, at pH (7).

Stoichiometric Study

The stoichiometric study of the expected formation of the complexes for Pd (II) with DB18C6 dissolved in 1,2-DCE at pH (7) aqueous solution was curried out by using mole ratio method.

The results were reported in Figure (2) which proved that the expected ratio of the complex formation is (2:1) from the reagent (DB18C6) to Pd (II) and the structure has **sandwich** $[(M^+ C.E)_2 (PdCl_4)^{-2}]$
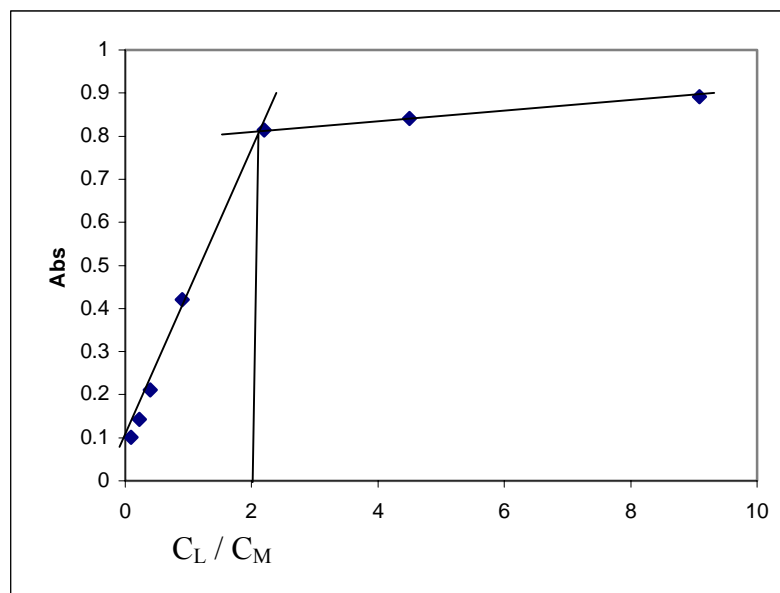

Fig (2) Mole ratio method for DB18C6 to Pd (II).

Conclusion

The extraction process of Pd (II) from different salts media by using DB18C6 is endothermic and spontaneous at higher temperature .

The best solvents are (1,2-DCE, C.B, and Toluene).

The structure of the extracted complex was (2:2:1) for $[M^+DB18C6]_2$ $[PdCl4]^{-2}$ and sandwich structure .

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