Synthesis and Spectro-Kinetic Study of the Complexes of Pd^{+2} Ion with 2-(5-Bromo-2- pyridylazo)-5diethylaminophenol Reagent in Ethanol – Water Solutions

Muayed khaleel Ibrahim

Dept. of Chemistry/ College of Science/ University of Baghdad

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Abstract

The complexes of Pd^{+2} ion with 2-(5-bromo-2-pyridylazo)-5-dieıhyl aminophenol (BPADAP) were studied kinetically and spectrophotometrically in aqueous ethanolic solutions. The reagent forms 1:1, 2:1 square planer and 1:1 bridged shape binuclear complexes with Pd^{+2} ion. All these complexes (violet colour) absorb light in the same region at 540, 575 and 618nm. The band at 618 nm seems to be specific for complexes of Pd^{+2}ion with BPADAP.

The rate constants of the growth in 93% H_2O + 7% ethanol of 1:1 and 2:1 complexes at 575 and 618 nm were followed the first order kinetics and are quite of the same values , 0.495 and 0.463 min^{-1} respectively. The rate constants of the decay of 2:1 complex at 618 and 575 nm were followed the first order kinetics; their values are 0.075 and 0.065 min^{-1} respectively which are slower than the rate of the decay of 1:1 complex. Whereas, the rate constants of the growth and decay of 1:1 bridged binuclear complex also followed the first order kinetics but they are much slower than those of 1:1 and 2:1 complexes: the values of the growth are 025min^{-1}at 575 nm , and 0.16 min^{-1} at 618 nm. And the values of the decay are 0.0476 min^{-1} at 575 nm and 0.008min^{-1} at 61 8 nm.

It was found that BPADAP can identify and detect in ethanol at 575 and 618 nm less than one microgram up to more than seven micrograms of Pd^{+2} ion . The interference of UO_2^{+2}, Th^{+4}, Pb^{+2} , Cd^{+2},Bi^{+3}, Hg^{+2} and Zn^{+2} in the detection of Pd^{+2} ion at 575 nm ranges between (25.3 - 67)%. Whereas, the interference of these ions with the detection at 618 nm is only between (2.3 -3.9) %, so it is reasonable to suggest that BPADAP is a specific reagent for Pd^{+2} ion at 618 nm.

Keywords: Palladium (II) ion, BPADAP reagent, UV-Visible spectrometer, Complexes of Pd(II), Kinetic study.

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Introduction

Previously the reagent 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol, BPADAP, was used for detection of micro amount quantities of UO_2^{+2} ion[1-3]. It was found that the ions Li^+ , NH_4^+, Cs^+, Sn^{+2}, Cd^{+2}, Hg^{+2}, Pb^{+2}, Be^{+2}, Mg^{+2}, Ca^{+2}, Mn^{+2}, Al^{+3}, Bi^{+3}, Nd^{+3}, Cr^{+3}, Th^{+4}, Mo^{+6} and W^{+6} interfere with the determination of uranyl ion by ±2% in the level of 5mg in the detection of 50µg of uranyl ion, it was also found that the ions Cu^{+2}, Ni^{+2}, As^{+5}, Zr^{+4}, Co^{+2}, $V^{+4}$and V^{+5} interfere in the range of 0.01- 4 mg[3] . In more recent studies [4] it was found that BPADAP forms 2:1 complex with uranyl ion in neutral aqueous ethanolic solutions, and forms also complexes with some heavy metal ions such as Bi^{+3}, Hg^{+2}, Pb^{+2}, Sm^{+3} and Th^{+4} as well as with some other metal ions such as Mg^{+2} , $Cd^{+2}$and Al^{+3} .The reagent was also found to be specific for Mg^{+2} ion among the alkaline earth metal ions group(4) . A large number of platinum and palladium complexes containing amine based ligands have become the subject of intensive research, since they are structurally related to cisplatin. The success of cisplatin and other Pt(II) complexes in the treatment of ovarian, testicular, neck and head, esophageal and non-small cell lung cancers and similar properties of Pt(II) and its congener Pd(II), have led to a large effort in the search to find Pd(II) antitumor drugs that are effective against Pt(II) resistant therapies and that have fewer side effects [5].

In this work, the complex of BPADAP with Pd^{+2} ion is studied spectrophotometric ally in neutral aqueous ethanolic solutions. The study is included the measurements of electronic spectra, interference of some other metal ions , determination of micro amount quantities of Pd^{+2} ion in the presence of the interfering metal ions, and kinetics study of the decay of Pd^{+2} complexes in aqueous solutions.

Experimental

Palladium chloride, $PdCl_2$, purity 99% was of "Aldrich". The metal ions used throughout this work of are nitrates from "Fluka" except Zn and Hg which are as chlorides, all purity > 98%, and ethanol was absolute. The reagent 2-(5- bromo-2- pyridylazo)-5-(diethyl amino) phenol, BPADAP (Scheme 1) purity > 95% was of "Fluka". Varian DMS 100 UVVisible spectrophotometer (computerized) was used to measure the electronic spectra, optical densities and kinetics data by using a quartz cell of 1 cm path length. The standard solutions of BPADAP were prepared in ethanol, and those of metal ions in distilled water. Palladium chloride was dissolved in distilled water containing 1-2 drops of concentrated hydrochloric acid. In the determination of the ratio of BPADAP to Pd^{+2} ion experiments, the concentration of Pd^{+2} ion was kept constant , $4.4x10^{-5}$ mol dm^{-3}, and the concentration of the reagent was variable in the range of $(0.44\text{-}1l)*l0^{-5}$ mol dm^{-3}. These concentrations give molar ratios of 0.1:1 to 2.5:1. Whereas , in the detection of micro amount quantities of Pd^{+2} ion experiments, the concentration of BPADAP was kept constant, 0.0001 mol dm^3 , and the concentration of Pd^{+2} ion was variable in the range of $(0.88\text{-}7.04)*l0^{-5}$ mol dm^3, these concentrations of Pd^{+2} ion give 0.85-6.78 mg of Pd^{+2} ion in 2 ml. In the other experiments, the concentrations of BPADAP and Pd^{+2}ion will be mentioned elsewhere. In all experiments, the reference cell, in every solution, was contained the same concentration of BPADAP as in the sample cell, this was done to eliminate electronically the absorption bands of the reagent and to obtain only the absorption bands of the complex of BPADAP with Pd^{+2} ion.

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Results

Figure (1) represents maximum wavelength absorption (λ_{max}) bands in the electronic spectra of the reagent BPADAP and its complexes (violet colour) with Pd^{+2} ion in ethanol - water mixture. Table (1) shows the colors and longer wavelength absorption bands in the electronic spectra of the complexes of BPADAP with some metal ions that interfere with the test of Pd^{+2},Table (3) exhibits the data of the most interfering metal ions with the detection of Pd^{+2} ions by BPADAP in ethanol. Figure (4) shows some of the electronic spectra of the complexes of the interfering study as typical examples. Tables 4 and 5 represent the values of the first order rate constants and half-life times of the growth and decay processes , and Figures 5 and 6 show a typical first order plots of the growth and decay of the complexes of B ADAP with Pd^{+2} ion .

Discussion

The electronic spectra of BPADAP and its complex with Pd^{+2} ions

Figure (1) illustrates that 1:1 complex is characterized by three transitions, shoulders at 540nm ($\mathcal{E}$ =1800 m^2 mol^{-1}) and at 618nm ($\mathcal{E}$ =1700 m^2 mol^{-1}), and at 575nm ($\mathcal{E}$ =2300 m^2 mol^{-1}), I, Scheme 2. The shoulder at 540nm and the band at 575nm interfere with the absorption bands of BPADAP complexes of many metal ions (Table 1), but the transition at 618nm seems to be unique for complex of the reagent with various metal ions [1-4]. The molar ratio method [6-9] was applied to our spectroscopic data, it seems from Figure 2 that BPADAP forms two kinds of complexes with Pd^{+2} ion in aqueous ethanolic solutions, the first is 1:1 , I (Scheme 2); and the other is 2:1, II (Scheme 3); both complexes absorb light at 540, 575, and 618nm (Figure 1). The structure I (Scheme 2) may be of a square planner configuration, since this leads to the increase force of the ligand field around the central ion owing to the large size of Pd^{+2}ion. This kind of coordination is very familiar in many palladium complexes such as $[Pd(H_2O)]^{+2}$, $[Pd(ClO_4)_2].2H_2O$, and $[Pd(CH_3COO)_2]3$[10,11].Whereas no sufficient information about the octahedral complexes of Pd^{+2} is available, but by comparison with the spectroscopic data of octahedral complexes of Pd^{+2} ion [10,11], we suggest that the structure of 2:1 complexes in solution II as shown in Scheme 3.

Detection of micro amount quantities of Pd^{+2} ion by BPADAP and recovery.

Owing to the data of Table 2 and Figure 3, it can be detectd from less than 1.0 µg of Pd^{+2} ion up to more than 7.0 µg. Apparently, the data of Table 2 indicate that the detection of Pd^{+2} ion by BPADAP at 575nm is greatly affected, (25.3-67)%, by the complexes of BPADAP with the ions $U0_2^{+2}$, Th^{+4}, Pb^{+2}, Cd^{+2}, Bi^{+3}, Hg^{+2} and Zn^{+2} since these complexes absorb light in the region of 510-577nm (Table 1). Whereas, the data exhibit clearly that the detection is affected only by (2.3 - 3.9) % when it is carried out at 618nm. Accordingly, it is reasonable to assume that the 618nm transition is specific for identification, determination and detection of Pd^{+2}ion among the complexes of BPADAP with thirty three metal ions (see the introduction).

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The kinetics of Pd^{+2} complexes in ethanol – water solutions

The complexes of Pd^{+2} ion with BPADAP are stable in pure ethanol and in 90% water + 10% ethanol, below 10% ethanol in water the complexes become unstable, their decay depends on (i) the molar ratio of BPADAP, and (ii) on the percent of ethanol in the solution. Initially before the decay, a species is grown within about the first two minutes, then the decay was commenced after about five minutes. During the period of the growth processes the color of the solution, was remained violet; this indicates that BPADAP is stile bonded with Pd^{+2} ion. When the decay occurs above 90% water in solution, BPADAP may be replaced by water molecules in one or two bonding positions of Pd^{+2} , this depending on the kind of complex if it is 1:1 or 2:1 as follows :

II $+2H_2O$-----> Pd (BPADAP) $CI_2.2H_2O$ (III) ------------(1)

I + H_2O -----> Pd (BPADAP) $Cl_2.3H_2O$ (IV) ------------(2)

The rate constant of formation of III at 618nm, molar ratio is about 2:1, is $0.463m^{-1}$; and that of IV at 575nm, molar ratio is about 1:1, is 0.495 m^{-1}. But when Pd^{+2}ion present in excess, $[Pd^{+2}]$: [BPADAP] is 1:0.46 (Table 4); the growth of II takes longer time. The data of Table 4 indicates clearly that formation of III and IV from II and I take approximately the same time, half-life times are 1.5 and 1.4 m respectively. While formation of IV when Pd^{+2} ion presents in excess takes longer time, half-life times are 2.77nm at 575nm and 4.33 m at 618nm; this point will be elucidated later. To confirm our suggestion from being water molecules may bond to Pd^{+2} ion instead of BPADAP when water is above 90% in solution, the followings should be considered : (i) the decay of molar ratio 0.92:1 complex at 575nm was done in 90% water + 10**%** ethanol, it is 9.6 times slower than that in 93**%** water +7% ethanol, $k_1 = 0.024\ min^{-1}$ and $t_{1/2} = 28.9$ min; (ii) the decay of the complexes in either 93% methanol, 93% acetone, or 93%> dimethyl form amide + 7% ethanol was investigated, no decay was observed at all in these solutions . Accordingly, III and IV may decay in 93% water + 7% ethanol by reactions 3 and 4:

III $+2H_2O$ ------> $PdCl_2.4H_2O$ (V) + BPADAP ....(3)
IV+H_2O-------> V + BPADAP ....(4)

As it was mentioned earlier the color of Pd^{+2} ion complexes with BPADAP in water - ethanol solutions is violet, after the decay is completed the color of all solutions becomes yellow. It well known that V and the dilute solution of BPADAP have yellow color in aqueous solutions, this indicates that BPADAP is unable to compete water in the coordination with Pd^{+2} ion in aqueous solutions, therefore it is reasonable to conclude that reactions 1-4 are irreversible reactions in these solutions. It is important at this moment to mention that after the growth of III and IV, there is a time in which both complexes seem to be stable before they decay to form V and BPADAP (Figure 6), this time ranges between 5-10 min .The time interval between the end of growth and beginning of the decay may be necessary for III and IV to rearrange their structures geometrically for completing the exchange of BPADAP by water molecules as shown by reactions 3 and 4. When Pd^{+2} ion presents in excess [BPADAP]: $[Pd^{+2}]$ is 0.47:1, it is obvious that the growth and decay of IV take longer times (Table 5). In this case a complex of 1:1 or 2:1 other than I or II may form, presumably a bridged binuclear complex, VI (Scheme 4) which hydrolyzed by water molecules in two steps as shown in equations 5 and 6:

VI+ $2H_2O$----> 2 [Pd (BPADAP) $CL_2.H_2O$] VII….. (5)
VII+ H_2O ----> $PdCL_2.2H_2O$ + BPADAP…….….. (6)

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This may explain the slow growth and decay of VII (Tables 4 and 5).It is well known that such bridged binuclear complexes of Pd^{+2} ion quite generally are subject to attack by other ligands whereby the bridges are split and two mononuclear species are formed [10-12]. When Cl^{-1} and Br^{-1} are the bridges, the equilibria lie toward the mononuclear complexes [12]. It might be supposed that such bridge splitting reactions should give the Trans mononuclear complexes.

Conclusion

BPADAP forms with Pd^{+2} ion 1:1, 2:1 and bridged binuclear complexes in ethanol water solution, all (violet in colour) absorb light at 540,575 and 618nm. The longer wavelength transition, at 618nm, is specific for Pd^{+2} ion among more than 25 metal ions which form coloured complexes with BPADAP. The rate constants of the growth in 93% water + 7% ethanol of 1:1 and 2:1 complexes at 575 and 618 nm are quite of the same values. The rate constants of the decay of 1:1 complex at 618 and 575nm are also close to each other but slower than the rate of decay of l:1 complex by about three times. Whereas, the rate constants of the growth and decay of the bridged binuclear complex are slower than those of 1:1 and 2:1 complexes in the same medium. Ali complexes hydrolyzed above 90% water + 10 % ethanol to give $PdCl_2.2H_2O$

The BPADAP reagent can detect in ethanolic solutions at 575 and 618nm, from less than one microgram of Pd^{+2}ion up to more than seven micrograms. The interference of uranyl, thorium, lead, cadmium, bismuth, mercuric and zinc ions in the detection of Pd^{+2} ion at 575 nm ranges between (25.3-67) %. Whereas, the interference of these ions with the detection at 618nm is between (2.3-3.9) %only. So it can be suggested that BPADAP is a specific reagent for Pd^{+2} at 618nm.

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Table (1): The longer wavelength absorption bands of BPADAP complexe with some metal ions in ethanol - water mixture.

Colour	λ_{max} /nm	Metal ion
Violet	540, 575,618	Pd^{+2}
Reddish- Pink	544, 571	UO_2^{+2}
Reddish- Pink	526, 562	Th^{+4}
Pink	540, 568	Pb^{+2}
Pink	543,575	Cd^{+2}
Deep Pink	550, 577	Bi^{+3}
Pink	533,550	Hg^{+2}
Pink	510, 540	Zn^{+2}

Table (2): Determination of micro amount quantities of Pd^{+2} by BPADAP in ethanol [BPADAP] = 0.0001 mol dm^{-3} which in constant.

$[Pd^{+2}]/10^{-5}$ mol dm^{-3}	Pd^{+2} /10^{-5} at 2 ml	OD/ 575nm	OD/18n m
0.88	0.85	0.44	0.31
1.76	1.74	0.84	0.63
2.64	2.54	1.16	0.84
3.52	3.40	1.58	1.14
4.40	4.24	1.75	1.23
5.28	5.09	2.23	1.59
6.16	5.94	2.59	1.83
7.04	6.78	2.88	2.09

Table (3): The data of the interfering metal ions with the detection of Pd^{+2}ion by BPADAP in ethanol.

interfering ion	575nm OD % interference		618nm OD %interference	
Pd^{+2}	1.82	—	1.28	—
$Pd^{+2}+U0_2^{+2}+Th^{+4}$	2.28	25.3	1.31	2.3
$Pd^{+2}+U0_2^{+2}+Th^{+4}+Pb^{+2}$	2.94	61.5	1.31	2.3
$Pd^{+2}+U0_2^{+2}+Th^{+4}+Pb^{+2}+Cd^{+2}$	2.93	60.9	1.33	3.9
$Pd^{+2}+U0_2^{+2}+Th^{+4}+Pb^{+2}+Cd^{+2}+Bi^{+3}$	3.04	67	1.33	3.9
$Pd^{+2}+U02^{+2}+Th^{+4}+Pb^{+2}+Cd^{+2}+B\dot{I}^{+3}+Hg^{+2}$	3.04	67	1.33	3.9
$Pd^{+2}+U0_2^{+2}+Th^{+4}+Pb^{+2}+Cd^{+2}+Bi^{+3}+Hg^{+2}+Zn^{+2}$	2.98	63.7	1.32	3.0

$[Pd^{+2}]$= $4.4x10^{-5}$ mol dm^{-3}, [BPADAP]= $10x10^{-5}$ mol dm^{3}, both are constants in all measurements. $[UO_2^{+2}J$ = $[Th^{+4}]$ = $2x10^{-5}$ mol dm^{-3}, $[Pb^{+2}]$ = $[Cd^{+2}]$ = $[Bi^{+3}]$ = $[Hg^{+2}]$= $2.2xl0^{-5}$ mol dm^{-3}, $[Zn^{+2}]$= $3.2x10^{-5}$ mol dm^{-3}. The reference cell contains the same concentration of BPADAP as in the sample cell.

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Table (4): Rate constants and half-life time of the first order growth.

[BPADAP]/10^{-5} mol dm^{-3}	[pd^{+2}]/10^{-5} mol dm^{-3}	$\frac{[BPADAP]}{[Pd^{+2}]}$	λ_{max} /nm	K_1/m^{-1}	$T_{1/2}$ /m
6.7	3.7	1.81:1	618	0.463	1.50
10	11	0.92:1	575	0.495	1.40
6.7	14.7	0.46:1	575	0.25	2.77
6.7	14.7	0-46:1	618	0.16	4.33

All solution of 93% Water + 7% ethanol, T=44 ^{0}c Reference cell contains the same concentration of BPADAP in every case.

Table (5): Rate constant and half-life time of the first order decay.

[BPADAP]/10^{-5} mol dm^{-3}	[pd^{+2}]/10^{-5} mol dm^{-3}	$\frac{[BPADAP]}{[Pd^{+2}]}$	λ_{max} /nm	K_1 /min^{-1}	$T_{1/2}$ /min
1.0	1.1	0.92:1	618	0.19	3.65
1.0	1.1	0.92:1	575	0.23±0.03*	3.17±0.34*
1.0	0.55	1.81:1	618	0.075	9.24
1.0	0.55	1.81:1	575	0.065	10.66
0.7	1.50	0.46:1	618	0.008	86.63
0.7	1.50	0.46:1	575	0.0474	14.55

All solution of 93% Water + 7% ethanol, T=44 ^{0}C Reference cell contains the same concentration of BPADAP in every case.

(*) Average of three experiments

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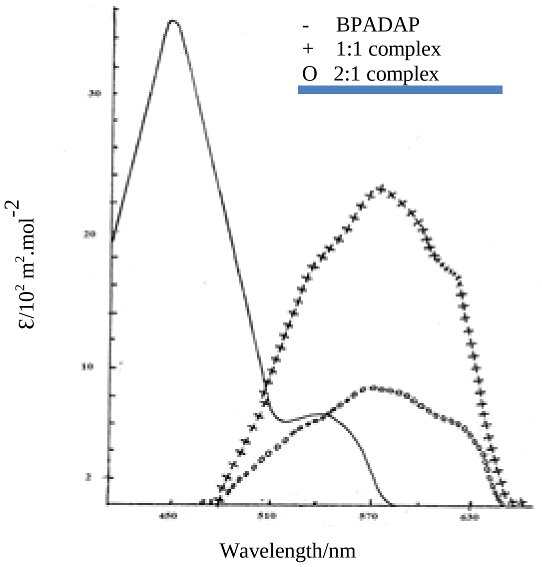

Figure (1)-The longer wave length absorption bands in the electronic spectra of BPADAP and its complexes with Pd^{+2} ion in ethanol-water mixture.

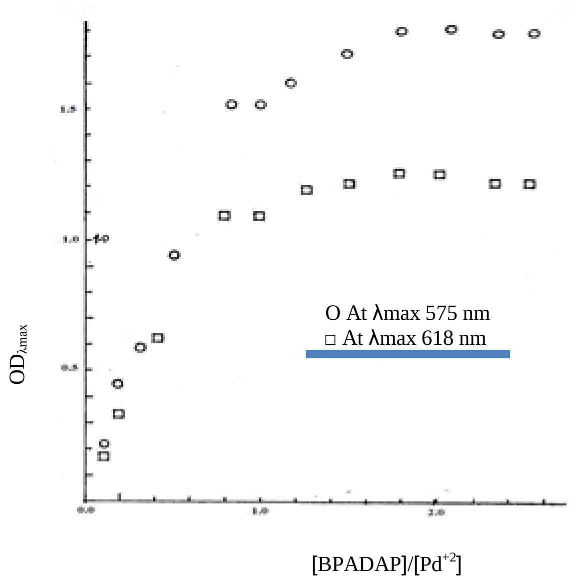

Figure (2)-The molar ratios VS optical at λmaxs plots of the complexes of BPADAP with pd^{+2} ion.$[PdCl_2]$=constant=$4.4*10^{-5}$ mol dm^{-3}

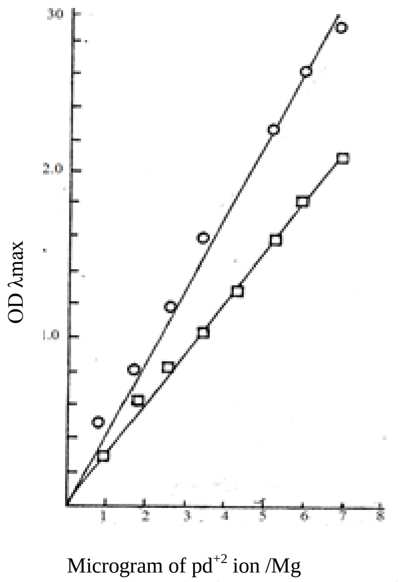

Figure (3)- the calibration curves of the determination of micro amount quantities of pd^{+2} by BPADAP. O-at λ_{max} 575 nm , □- at λ_{max} 618 nm

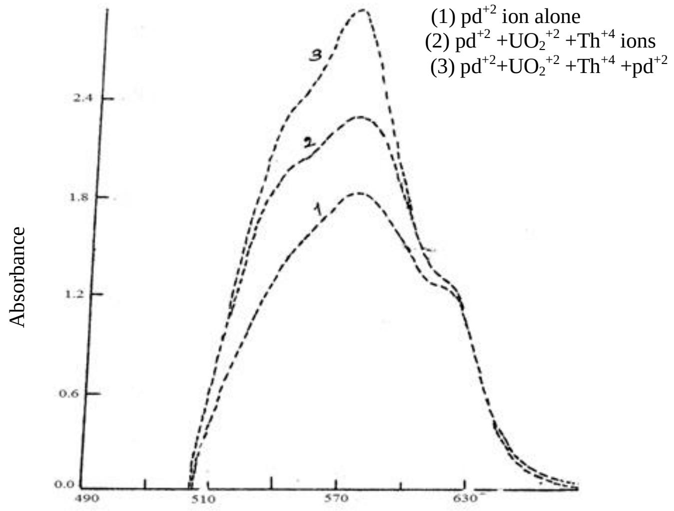

Figure (4)- The effect of some added interfering metal ions on the optical densities at λ_{max} 575&618 nm of the complexes of pd^{+2} ion with BPADAP in ethanol. The reference cell contains the same concentration of BPADAP as in the sample cell. [BPADAP]=$10x10^{-5}$ mol dm^{-3} , [pd^{+2}]=$4.4x10^{-5}$ mol dm^{-3} ,[UO_2^{-2}]=[Th^{+4}]=$2x10^{-5}$ mol dm^{-3} [pd^{+2}]=$2.2x10^{-5}$ mol dm^{-3}

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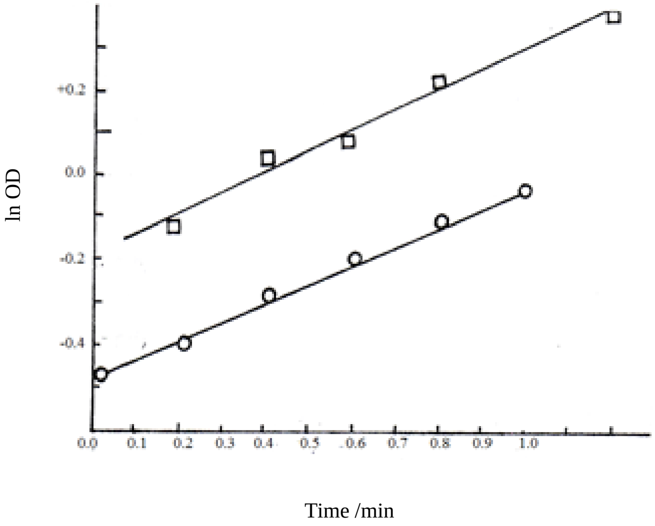

Figure (5)- typical first-order plots of the growth 93% water +7% ethanol. T=44 ^{0} C

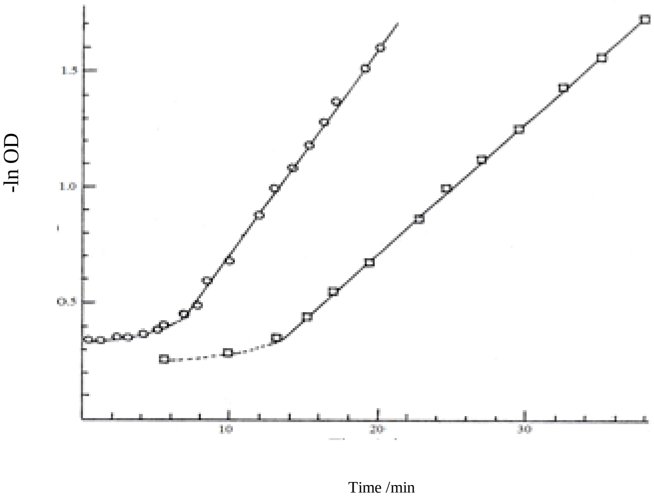

Figure (6)-- typical first-order plots of the growth 93% water +7% ethanol. T=44 ^{0} C o-at 618 nm, $[BPADAP] :[Pd^{+2}] =1.81:1$ □-at 575 nm , $[BPADAP] :[Pd^{+2}] =1.81:1$

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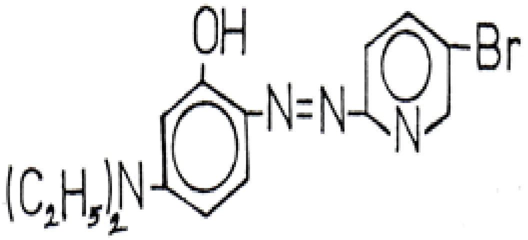
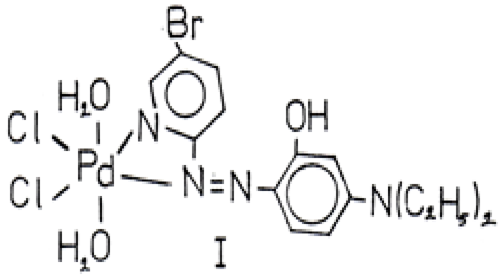
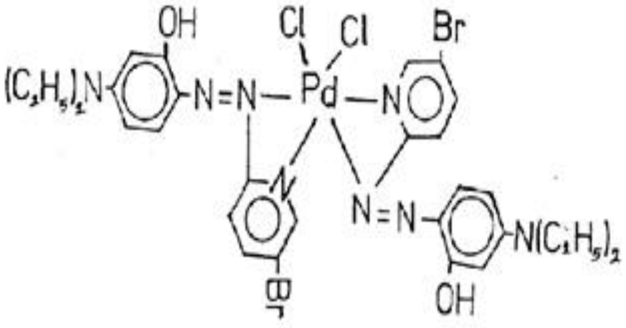


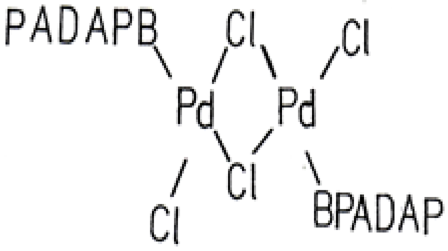
Scheme (1) BPADAP



Scheme (2) Square Planar



Scheme (3) Bridge



Scheme (4) Square Planar

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