Polarographic Investigation of Binary and Ternary Pd(II) Complexes with L-2-Amino-3-(4-Hydroxy Phenyl) Propanoic Acid, 2,2′-Bipyridine and 1,10-Phenanthroline

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Polarographic study of simple and mixed Pd(II) complexes with L-2-amino-3-(4-hydroxy phenyl) propanoic acid, 2,2′-bipyridine and 7,10-phenanthroline reveals that the reduction of these complexes involves two electron transfer, irreversible and diffusion controlled steps. The formal rate constants ($K°_{f,h}$) and the transfer coefficient (αn) are determined by Koutecky's method as extended by Meites and Isreal. Theromodynamic parameters have also been evaluated.

INTRODUCTION

Saxena and coworkers[1,2] have carried out comprehensive study on the electrochemical behaviour of some biologically important ligands and their complexation with metal ions. Considerable interest has recently been evinced in the complexes of Pt and Pd, mainly due to their possible utilization as potential anticancer drugs[3,4]. The anticancer drugs also may deactivate the carcinogensis by binding the abnormal nucleic acids via transition metal ions[5–11]. Recently the study at mixed ligand complexes is receiving considerable attention; as most of the biochemical and analytical reactions proceed via mixed ligand complex formation, it becomes important to study the thermodynamic properties of these complexes[12–18]. The present communication describes the results of polarographic study of binary and ternary Pd^{2+} complexes with L-2-amino-3-(4-hydroxyphenyl) propanoic acid, 2,2′-bipyridine and 1,10-phenanthroline at 25°, 35° and 45°C in aqueous media.

EXPERIMENTAL

L-2-Amino-3-(4-hydroxyphenyl) propanoic acid (referred here as L-tyrosine) was supplied by BDH Chemicals Ltd, Poole, England. 2,2′-Bipyridine (Bipy) and 1,10-phenanthroline (Phen) were supplied by E. Merck (India) Pvt. Ltd. Worli, Bombay. $Pd(II)Cl_2$ was supplied by Johnson Metthey and Co. Ltd., England. All other chemicals used were of AnalaR grade. Polarograms were recorded on a manual polarogram using an H cell and S.C.E. as reference electrode with following capillary characteristics in 0.1 M KNO_3 at −0.5 volts vs S.C.E. at $h_{Hg} = 80$ cm, m = 2.7359 mg/sec, t = 2.625 sec, $m^{2/3}t^{1/6} = 2.2971$ $mg^{2/3}s^{-1/2}$. Purified nitrogen was used for deaerating the solution and 0.002% prition X-100

as a maximum suppressor. KNO_3 was used as the supporting electrolyte
to maintain ionic strength constant (M = 0.1M).

RESULTS AND DISCUSSION

It is observed that simple and mixed ligand palladium(II) complexes
with L-Tyrosine, Bipy and Phen yield a single well defined cathodic wave
at pH = 9.0 and pH = 8.0 respectively and hence all subsequent studies
were made at these pH values. The plots of i_d vs $\sqrt{h_{eff}}$ were found to be
linear indicating the diffusion controlled nature of the electrode process.
The number of electrons involved in electrode process is determined by
millicoulometric method of Devries-Kroon[19] and found to be two. The
log analysis plot[20] *i.e.* log $\dfrac{i}{i_d - i}$ vs $- E_{d.m.e.}$ was carried out for the
simple and mixed ligand complexes of Pd^{2+} and was found to be linear
but slope values are much larger than the theoretical values expected for
two electron transfer reversible reduction process showed that the reduc-
tion is irreversible[21]. A perusal of polarographic data and various
criterion[21-24] of ascertaining the irreversibility of electrode reactions of
simple and mixed ligand Pd^{2+} complexes of L-Tyrosine, Bipy and Phen
indicate the irreversible nature of the electrode reduction process.

The Binary System

The cathodic shift of half wave potential coupled with decrease in
diffusion current with increasing ligand concentration indicating com-
plexation of Pd^{2+} with L-Tyrosine, Bipy and Phen. The values of kinetic
parameters viz transfer coefficient (αn) and formal rate constant ($K^\circ_{f,h}$) for
the electrode reaction have been determined by Koutecky's method[25] as
extended by Meites and Isreal[26] and are incorporated in Table 1. The
rate constant values lie in the order of 10^{-7} to 10^{-8} which confirms the
irreversible nature of electrode process[21].

It is evident from Table 1 that the values of αn decreases with increa-
sing ligand concentration that the transfer of electron is made increasingly
difficult with rise in ligand concentrations[27]. Decreasing value of $K^\circ_{f,h}$
also indicates[21] the increased irreversibility of the electrode reaction of
Pd^{2+} with increasing ligand concentrations.

The Ternary System

Polarograms were recorded when L-Tyrosine concentration was
varied and concentration of Bipy/Phen was kept constant with Pd^{2+}
solution. It is observed that half wave potential shift to cathodic side
coupled with decrease in diffusion current was more pronounced in
presence of L-Tyrosine than in absence of it, shows mixed ligand complex
formation. The transfer coefficient (αn) and formal rate constant (K°_{fh})

for the electrode reaction have been determined by Koutecky's[25] method as extended by Meites and Isreal[26] and are summarized in Table 1. The rate constant values lie in the order of 10^{-8} to 10^{-9} which confirms the irreversible nature of electrode process[21]. It is evident from Table 1 that the values of αn decrease with increasing L-Tyrosine concentration and the transfer of electrons is made increasingly difficult[27]. Decreasing value of $K^\circ_{f,h}$ also indicates[21] the increased irreversibility of the electrode reaction of Pd^{2+}-Bipy/Phen-L-Tyrosine system.

Thermodynamic Parameters

The enthalpy of activation (ΔH^*) for the electrode reaction has been calculated by equating the slope of the plot $\log K^\circ_{f,h}$ vs $1/T$ to $\dfrac{-\Delta H^*}{2.303\,R}$ at 35°C. The free energy of activation (ΔG^*) at 35°C can be determined from the equation[27]

$$K^\circ_{f,h} = \frac{KT}{h}\,\phi\,\exp\left[\frac{-\Delta G^*}{RT}\right]$$

TABLE 1

POLAROGRAPHIC CHARACTERISTICS AND KINETIC PARAMETERS OF THE ELECTRODE REACTION OF THE Pd^{2+} IN L-TYROSINE, Bipy AND Phen WITH Pd^{2+} AT 35°C

	$i_d(\mu A)$	$-E_{1/2}(V)$	αn	$K^\circ_{f,h} \times 10^{-8}$ cm/sec
(a) *Pd²⁺-L-Tyrosine system* [L-Tyrosine]				
0.0000	4.5	0.83	0.7932	———
0.0002	4.2	0.847	0.7849	3.1063
0.0004	3.9	0.865	0.7761	1.0293
0.0006	3.65	0.88	0.7680	0.499
0.0008	3.45	0.895	0.7601	0.2762
0.0009	3.3	0.901	0.7528	0.2372
0.0010	3.15	0.91	0.7453	0.1904
(b) *Pd²⁺-Bipy system* [Bipy]				
0.000	7.2	0.83	0.5704	———
0.002	6.9	0.95	0.5409	18.43
0.004	6.75	0.97	0.5136	12.8465
0.006	6.6	0.99	0.5081	5.59
0.008	6.25	1.025	0.5026	2.769
0.009	6.0	1.05	0.4971	1.7223
0.010	5.8	1.06	0.4911	1.494

TABLE 1 (Contd.)

	$i_d(\mu A)$	$- E_{1/2}(V)$	αn	$K^\circ_{f.h} \times 10^{-8}$ cm/sec
(c) *Pd²⁺-Phen-system* [Phen]				
0.00	7.2	0.83	0.5704	——
0.002	6.8	0.935	0.5634	13.57
0.004	6.5	0.96	0.5545	4.8096
0.006	6.25	0.99	0.5434	2.2285
0.007	6.12	1.02	0.5355	1.2594
0.008	5.9	1.04	0.5293	0.848
0.009	5.85	1.05	0.5263	0.669
0.01	5.8	1.07	0.5192	0.4983
(d) *Pd²⁺-Bipy-L-Tyrosine* system [L-Tyrosine]				
0.000	4.1	0.83	0.720	——
0.00015	3.9	0.96	0.714	0.8834
0.0003	3.7	0.975	0.707	0.3312
0.00045	3.55	1.005	0·700	0.1163
0.0006	3.4	1.035	0.692	0.0471
0.00075	3.25	1.055	0.685	0.0263
0.0009	3.05	1.065	0.682	0.0173
0.00105	3.00	1.075	0.679	0.0124
(e) *Pd²⁺-Phen-L-Tyrosine* system [L-Tyrosine]				
0.000	4.1	0.83	0.720	——
0.00015	3.8	0.95	0.7117	1.2113
0.0003	3.6	0.965	0.7028	0.4865
0.00045	3.45	0.99	0.692	0.2148
0.0006	3.32	1.02	0.684	0.0828
0.00075	3.05	1.04	0.677	0.0472
0.0009	2.95	1.055	0.675	0.0273
0.00105	2.80	1.08	0.673	0.0123

TABLE 1 (Contd.)

Temp. °C	$i_d(\mu A)$	$-E_{1/2}(V)$	αn	$K^\circ_{f,h} \times 10^{-8}$ cm/sec
Different Temperature				
(a) *Pd²⁺-L-Tyrosine system*				
25°	2.6	0.92	0.7359	0.1506
35°	3.15	0.91	0.7453	0.1904
45°	3.5	0.902	0.7519	0.2250
(b) *Pd²⁺-Bipy-system*				
25°	5.4	1.095	0.475	1.2164
35°	5.8	1.06	0.4	1.494
45°	6.0	1.00	0.526	1.7294cv
(c) *Pd²⁺-Phen-system*				
25°	5.6	1.09	0.5172	0.3489
35°	5.8	1.07	0.5192	0.4982
45°	6.15	1.05	0.5232	0.6980
(d) *Pd²⁺-Bipy-L-Tyrosine system*				
25°	2.6	1.115	0.672	0.00475
35°	3.0	1.075	0.679	0.01235
45°	3.4	1.065	0.684	0.01553
(e) *Pd²⁺-Phen-L-Tyrosine system*				
25°	2.4	1.110	0.671	0.00513
35°	2.8	1.08	0.673	0.01230
45°	3.3	1.055	0.675	0.02701

where K = Boltzman constant, h = Planck's constant and $\phi = 2.0 \times 10^{-8}$ and other terms have their usual significance.

The entropy of activation at 35°C is calculated from the relation

$$\Delta S = \frac{\Delta H^* - \Delta G^*}{T}$$

The values are summarized in Table 2.

The positive free energy change (ΔG^*) indicates that the reaction is endergonic[28]. The enthalpy changes are positive indicating the endothermic nature of the reaction. The negative ΔS^* value lends support to the irreversible nature of the electrode process. It is observed that the $-E_{1/2}$ is shifted to more positive side with rise in temperature showing easier

TABLE 2

VALUES OF THERMODYNAMIC FUNCTIONS IN AQUEOUS MEDIA AT 35°C
OF Pd^{2+}—SIMPLE AND MIXED LIGAND COMPLEXES

Complexes	ΔG^* (Kcals/mole)	ΔH^* (Kcals/mole)	$-\Delta S^*$ (Cals/deg/mole)
Pd^{2+}-L-Tyrosine	17.78	8.17	31.20
Pd^{2+}-2,2′-Bipyridine	16.69	10.40	20.42
Pd^{2+}-1,10-Phenanthroline	16.88	8.80	26.23
Pd^{2+}-2,2′-Bipyridine-L-Tyrosine	18.55	10.90	24.86
Pd^{2+}-1,10-Phenanthroline-L-Tyrosine	18.36	9.95	27.30

reduction and increased degree of reversibility of electrode process[29]. The
values of αn and $K°_{f,h}$ increase with the increase in temperature which
suggests that the electrode reaction tends to become less irreversible at
higher temperature.

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