Electrode Kinetics and Thermodynamics Study of 2,3-Dihydroxy Pyridine Complexes of Pd(II) at DME in Vicinity of Khetri Copper Mines in Rajasthan

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The kinetic parameters and formation constant of palladium- pyridine complexes were determined polarographically by De Ford/Hume graphical extrapolation method and method Mihailov's mathematical method respectively. The thermodynamic parameters ($\Delta F°$, $\Delta H°$ and $\Delta S°$) were also determined.

INTRODUCTION

The pollution of ground water by copper industry in Khetri which lies at the intersection of 22° North latitude and 74° East longitude was studied by mine dewatering or pumping out the ground water from the wells in the surrounding area of the project and by observing pollutate quality.

Polarographic study of Pd(II) in water samples from ten wells different sites of the project reveals that it reduces the quasireversibility at DME in 0.2 M pyridine and 0.1 M HCl medium. Kinetic parameters of Pd^{2+} complexes with various concentrations of 2,3-dihydroxy pyridine were calculated by using Gellings method and thus the effect of concentration of 2,3-dihydroxy pyridine on the kinetics of the reduction of Pd(II) has been explained. De Ford/Hume extrapolation method and the mathematical method of Mihailov have been employed for the evaluation of overall formation constants of the complexes formed with 2,3-dihydroxy pyridine.

In aqueous medium palladium does not give a polarographic wave as such. Water samples from ten different wells adjoining the mine site were first evaporated to dryness and proper treatment of palladium was done in pyridine-HCl medium. In this medium a well-defined wave of Pd(II) has been reported[1]. Reversible reduction of palladium in pyridine medium, with sodium sulphate as base electrolyte, has been reported by Magee and Douglas[2].

In the present work, we have obtained a well defined wave in 0.2 N pyridine + 0.1 N HCl medium and found that reduction of Pd(II) in this medium at DME is quasireversible. For the sake of brevity only one sample out of ten with maximum palladium content is being reported.

EXPERIMENTAL

All chemicals used were of analytical reagent grade. Pure potassium nitrate

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was used as supporting electrolyte to keep the ionic strength constant at 1.0 M. 5×10^{-4} M Pd^{2+} ion concentration required 0.001 per cent gelatin as maxima suppressor.

The temperatures were maintained constant at 298 ± 0.1 and 308 ± 0.1 K using U_3 Ger Ner 8354 type thermostat. The capillary of DME had the following characteristics: m = 1.55 mg^{-1} s and t = 3.5 s open circuit at the height of 60 cm mercury head. Purified nitrogen gas was purged through each solution for about 15 min to expel dissolved oxygen. The polarograms were recorded using manually operated polarograph. Osaw slide wire potentiometer and galvanometer AJCO, model No. P-GI, Sr. No. P71049 having sensitivity 3.71 × 10^{-2} µa/div and H-type cell saturated with sodium chloride agar-agar bridge were used. Century CD 901 Digital pH meter with glass and calomel electrode was used for measuring pH of the solution. 2,3-Dihydroxy pyridine was used as commercially received.

RESULTS AND DISCUSSION

Palladium(II) in pyridine and HCl medium gives a two electron reduction wave. In all systems the nature of reduction remains the same with slopes of ion $(i/i_d - i)$ vs. E_{de} plots from 60–50 mv thus showing the quasireversible nature of reduction. The reduction of Pd(II) in all solutions of each system was diffusion controlled as revealed from the proportionality of diffusion current to the square root of the effective height ($h_{eff}^{1/2}$) of mercury column. Palladium concentrations in various samples of water collected from different wells are given in Table-1.

$E_{1/2}^r$ values of Pd(II) were found to shift towards the more cathodic side as the concentration of resorcyclic acid increased. From the shift in $E_{1/2}^r$ as a function of ligand concentration the De Ford/Hume[3] function $F_0(x)$ was calculated and then the derived functions were obtained by graphical extrapolation. The polarographic measurements and De Ford/Hume derived functions have been recorded in Tables 2 and 3 at 298 K and 308 K respectively.

TABLE-1
SAMPLES COLLECTED FROM VARIOUS WELLS AND THEIR PALLADIUM
CONSTANT

Site	Pd conc. in ppm
Nanu Wali Bawari	20
Discharge from copper plant (Main Gate)	35
Chawara river incoming	44
Koti Ki Dhani	39
Modi Wali Bagichi	210.
Jasrapur Well	128
Manota Well	216
Bab Dhando	14
Mishra Wali Dhani	32
Kharkhara	106

TABLE-2

POLAROGRAPHIC MEASUREMENTS AND $f_j(x)$ FUNCTION VALUES OF Pd(II)
(2,3-DIHYDROXY PYIDINE) SYSTEM AT 298 K ($\mu = 1.0$ M)

Cx (moles)	i_d (divs.)	$E^1_{1/2}$ (−v *vs.* S.C.E.)	$f_0(x) \times 10^{-8}$	$f_1(x) \times 10^{-7}$	$f_2(x) \times 10^{-8}$	$f_3(x) \times 10^{-8}$
0.00	72	0.1623	−	−	−	−
0.02	71	0.3212	0.1245	6.7250	12.4810	−
0.04	69	0.3259	0.2238	6.5151	6.8415	45.12
0.06	66	0.3441	0.4060	7.8825	6.8219	44.75
0.08	64	0.3445	0.7895	9.3565	8.8464	44.69
0.10	60	0.3568	1.2004	12.8625	9.2122	48.22
0.12	58	0.3685	1.6858	14.8414	9.1019	44.63
0.15	57	0.3905	2.8595	19.7521	11.4513	44.20
0.20	55	0.3980	5.9400	30.6812	14.2364	46.15

Sample of Manota well.

TABLE-3

POLAROGRAPHIC MEASURMENTS AND $f_j(x)$ FUNCTION VALUES OF Pd(II)
(2,3-DI HYDROXY PYRIDINE) SYSTEM AT 308 K ($\mu = 1.0$ M)

Cx (moles)	i_d (divs.)	$E^1_{1/2}$ (−v Vs S.C.E.)	$f_0(x) \times 10^{-8}$	$f_1(x) \times 10^{-7}$	$f_2(x) \times 10^{-8}$	$f_3(x) \times 10^{-8}$
0.00	84	0.1595	−	−	−	−
0.02	82	0.3014	0.0145	5.6811	11.1811	−
0.04	80	0.3045	0.2048	5.5014	5.2800	25.10
0.06	79	0.3315	0.3968	6.9210	5.7516	24.62
0.08	76	0.3356	0.6899	8.1861	7.2222	24.99
0.10	73	0.3614	1.0010	10.8213	8.1015	28.15
0.12	70	0.3728	1.5526	13.1653	8.1020	28.75
0.15	65	0.3811	2.0018	18.1496	10.3614	28.11
·0.20	60	0.3865	3.8464	28.5151	12.2891	30.02

Sample of Manota well.

Using $F_0(x)$ values corresponding to different ligand concentrations the values of Mihailov constants·"A" and "a" were calculated and recorded in Table-5.

Using average values of "A" and "a" the stepwise formation constants of the complexes are calculated. Stability constants are summarized in Table-4.

TABLE-4

Temp. (K)	De Ford/Hume Method			Mihailov Method		
	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
298	8.85	9.72	10.84	8.82	9.51	10.76
308	8.02	8.86	10.66	−	−	−

TABLE-5

MIHAILOV CONSTANT "a" FOR VARIOUS COMBINATIONS OF 2,3-DIHYDROXY PYRIDINE CONCENTRATION (C_x) AND "A" AT VARIOUS CONCENTRATIONS OF 2,3-DIHYDROXY PYRIDINE AT 298 K

C_x combinations (moles)	a	C_x combinations (moles)	A
0.14		0.04	7.76×10^5
0.06	24.67	0.06	7.28×10^5
0.04		0.08	7.69×10^5
0.08	28.80	0.10	7.70×10^5
0.04		0.12	7.92×10^5
0.10	18.84	0.14	8.86×10^5
0.04		0.16	13.55×10^5
0.12	30.12		
0.06		Average a = 27.39	
0.12	31.22		
0.08		Average A = 8.68×10^5	
0.12	30.74		

The overall formation constants of the complexes are in good agreement in both methods.

Electrode Kinetics: The slope and intercept of plots of $E - E^r_{1/2}$ vs. log $(z - 1)$ give the values of K_s and α. The standard rate constant K_s is given by the relation $K_s = \lambda \cdot D^{1/2}$, where $D^{1/2}$ is the diffusion coefficient and is determined from the diffusion currents using the llkovic equation. Table-6 records the kinetic parameters of Pd^{2+}. reduction calculated by Gellings method[5] in various concentrations of 2,3-dihydroxy pyridine.

TABLE-6

VARIOUS KINETIC PARAMETERS AT 298 K

C_x (moles)	$E^r_{1/2}$ (−v vs. S.C.E.)	α	λ (sec.$^{1/2}$)	$D^{1/2} \times 10^3$ cm^2 s^{-1}	$K_s \times 10^3$ cm s^{-1}
0.00	0.1613	0.60	0.5109	1.714	1.910
0.02	0.3200	0.55	0.4188	3.289	1.862
0.04	0.3258	0.52	0.4395	3.226	1.925
0.06	0.3439·	0.52	0.4092	3.179	1.815
0.08	0.3445	0.52	0.3685	3.108	1.626
0.10	0.3568	0.48	0.3546	3.100	1.754
0.12	0.3684	0.48	0.3500	3.008	1.622
0.15	0.3904	0.46	0.5418	3.106	1.984
0.20	0.3980	0.44	0.5440	3.120	1.026

From the values of K_s (which are of the order of 10^{-3}) it is seen that the reduction of the metal ion is quasireversible. The values of K_s are in general first

increasing and then decreasing regularly with the increasing ligand concentration. This suggests thermal charges taking place when the solvent molecules already attached to the metal ions are replaced by the stronger complexing ligands. An increase in temperature generally increases the value of rate constant. Therefore, the increase in the rate constant upon addition of ligand shows that the complex formation is an exothermic process. However, it is not always true, because the rate constant is governed by other factors like viscosity, electrostatic effects, etc. Further addition of ligands decreases the value of rate constant. Probably in this concentration range the viscosity increases which offsets the effect of enthalpy charge and, therefore, decrease in K_s occurs. Another possibility which is expected from the result is that as the ligand is added it forms a complex with metal ion, the ligand field of the complexing species may form an activated complex which reduces relatively fast.

Thermodynamic parameters were also calculated and are reported in Table-7.

TABLE-7

THEMODYNAMIC PARAMETERS OF Pd(II) 2,3-DIHYDROXY PYRIDINE
SYSTEM IN AQUEOUS MEDIUM

Complex species	Thermodynamic parameters		
	ΔF° kcal. deg^{-1} mol^{-1}	ΔH° kcal deg^{-1} mol^{-1}	ΔS° kcal deg^{-1} mol^{-1}
[Pd (2,3-dihydroxy pyridinate)]	−9.25	−35.12	−91.42
[Pd (2,3-dihydroxy pyridinate)]$^{-2}$	−10.60	−38.77	−88.36
[Pd (2,3-dihydroxy pyridinate)]$^{-4}$	−12.48	−6.84	+17.54

ACKNOWLEDGEMENTS

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