Electrochemical Study of the Complexes and Electrode Kinetics of Palladium(II) at D.m.e.

J. N. GAUR, S. C. BAGHEL and (MISS) R. S. SHARMA

Chemical Laboratories, University of Rajasthan, Jaipur-302004, India

Received December 28, 1977

Polarographic study of Pd(II) reveals that it reduces quasi reversibly at d.m.e. in 0.2M pyridine + 0.1 NHCl medium. The effect of the concentration of meta toulic acid on the kinetics of the reduction of Pd(II) has been explained. The DeFord and Hume's graphical method and Mihailov's mathematical method have been employed for the evaluation of overall formation constants of the complexes formed by Pd(II) with meta toulic acid. The values obtained by the two methods agree well with each other. Thermodynamic parameters were also calculated.

Introduction

Palladium does not give waves in aqueous medium. A well defined wave of Pd(II) has been reported in pyridine + HCl medium [1]. We have obtained a well defined wave in 0.2M pyridine + 0.1 NHCl medium and found that the reduction at d.m.e. is quasi reversible. Magee and Douglas [2] showed the reversible reduction of palladium in pyridine medium with sodium sulphate as base electrolyte. The DeFord and Hume [3] method for evaluation of overall formation constants of metal ion complexes is well known. The mathematical method of Mihailov [4] suggests that

$$\beta_n = A \frac{a^n}{n!} \tag{1}$$

where A and a are constants. The values of A and a are obtained by solving the following two equations:

$$(F' - 1) \sum_1^n \frac{[X'']^n}{n!} a^{n-1} - (F'' - 1)$$

$$\sum_1^n \frac{[X']^n}{n!} a^{n-1} = 0 \tag{2}$$

and

$$A = \frac{F - 1}{\sum_1^n \frac{a^n}{n!} [X]^n} \tag{3}$$

where F' and F'' are the values of the experimental F functions at ligand concentrations [X'] and [X''] respectively.

Using equations (2) and (3) the values of A and a are calculated and then using equation (1) the β values for corresponding consecutive complexes are calculated.

The Gellings [5] method is used for the determination of $E_{1/2}^r$ (reversible half wave potential) by graphical extrapolation of $E + RT/nF \ln i(i_d - i)$ vs. i to i = 0. The $E_{1/2}^r$ values are then used to calculate the kinetic parameters (K_s and α).

Experimental

All chemicals used were of reagent grade purity. KNO_3 was used as supporting electrolyte to keep ionic strength constant at 1.0M. 5 × $10^{-4}M$ Pd^{2+} ion concentration requires 0.001 per cent gelatin as maxima suppressor.

The temperatures were maintained constant at 298 ± 0.1 and 308 ± 0.1 °K using a U_3GerNer 8354 type thermostat. The capillary of d.m.e. had the following characteristics: m = 1.62 mg/sec, t = 3.9 sec at the height of 70 cm of the mercury head.

Just prior to polarographic examination of each solution, purified nitrogen gas was passed through it for about fifteen minutes to expel dissolved oxygen. Polarograms were taken manually.

Results

Study of Complexes

Palladium(II) in 0.2M pyridine + 0.1 NHCl medium with the ligand gives a two electron reduction wave which on further analysis shows quasi reversible nature of reduction of Pd(II). The slopes of the plots of log i(i_d − i) vs. $E_{d.e.}$ were found between 50 to 60 mV. The reduction was diffusion controlled as revealed from the proportionality of diffusion current to the square root of effective height of mercury column.

$E^r_{1/2}$ values of Pd(II) were found to shift towards more cathodic side as the concentration of *meta*-toulic acid increased.

From the shifts in $E^r_{1/2}$ as a function of ligand concentration the DeFord—Hume function $F_0(X)$ is calculated and then the derived functions are obtained by graphical extrapolation. The polarographic measurements and DeFord—Hume derived functions are recorded in Tables I and II at 298° and 308 °K respectively.

TABLE I. Polarographic Measurements and F_j Functions of Pd—*meta*-Toulic Acid System at 298 °K. i_d = 68 div of Simple Metal Ion. $-E^r_{1/2}$ = 0.1685 Volts of Simple Metal Ion.[a]

C_X	$-E^r_{1/2}$ V *vs.* S.C.E.	i_d	$F_0 \times 10^{-3}$	$F_1 \times 10^{-4}$	$F_2 \times 10^{-4}$
0.00	0.1685	68	–	–	–
0.02	0.2435	68	0.3286	1.6430	–
0.04	0.2630	67	1.4890	3.7225	43.06
0.06	0.2715	66	2.7940	4.6566	44.27
0.08	0.2765	65	4.1640	5.2050	40.06
0.10	0.2800	63	5.6180	5.6180	36.18
0.12	0.2850	61	8.5230	7.1025	42.52
0.14	0.2880	60	10.9000	7.7857	41.32
0.16	0.2920	59	15.0700	9.4187	46.36

[a] $\beta_1 = 2 \times 10^4$; $\beta_2 = 41.97 \times 10^4$.

TABLE II. Polarographic Measurements and F_j Functions of Pd—*meta*-Toulic Acid System at 308 °K. i_d = 80 div of Simple Metal Ion. $-E^r_{1/2}$ = 0.1650 Volts of Simple Metal Ion. [a]

C_X	$-E^r_{1/2}$ V *vs.* S.C.E.	i_d	$F_0 \times 10^{-3}$	$F_1 \times 10^{-4}$	$F_2 \times 10^{-4}$
0.00	0.1650	80	–	–	–
0.02	0.2380	80	0.2290	1.1450	–
0.04	0.2570	79	0.9530	2.3825	22.06
0.06	0.2650	77	1.7740	2.9566	24.27
0.08	0.2700	76	2.6070	3.2887	21.98
0.10	0.2735	75	3.4280	3.4280	19.28
0.12	0.2785	73	5.1130	4.2608	23.00
0.14	0.2815	72	6.4800	4.6286	22.35
0.16	0.2845	70	8.3370	5.2106	23.19

[a] $\beta_1 = 1.50 \times 10^4$. $\beta_2 = 22.30 \times 10^4$.

Using $F_0(X)$ values corresponding to different ligand concentrations the values of Mihailov constants A and a are calculated and recorded in Tables III and IV at 298 °K and 308 °K respectively.

Using average values of A and a the stepwise fomation constants of the complexes are calculated. Stability constants as calculated from DeFord—Hume's and Mihailov's method are summarised below:

Temperature	DeFord—Hume's Method		Mihailov Method	
	log β_1	log β_2	log β_1	log β_2
298 °K	4.3010	5.6229	4.3181	5.5988
308 °K	4.1761	5.3483	3.9063	5.1673

TABLE III. Mihailov Constant 'a' for Various Combinations of *m*-Toulic Acid Concentrations and 'A' at Various *m*-Toulic Acid Concentrations at 298 °K.

Combination of *meta*-Toulic Acid Concentrations	'a'	Concentration of *m*-Toulic Acid	'A'
0.04 0.06	49.82	0.04	5.53×10^2
0.04 0.08	33.17	0.06 0.08	4.88×10^2 5.39×10^2
0.04 0.10	33.89	0.10 0.12	5.05×10^2 5.65×10^2
0.04 0.12	41.49	0.14 0.16	5.55×10^2 6.08×10^2
0.06 0.12	36.92	Average 'A' = 5.45×10^2	
0.08 0.12	67.22		
0.14 0.16	44.83		
0.06 0.14	33.87		
	Average 'a' = 38.19		

The overall formation constants of the complexes are in good agreement as calculated by the two methods. Small deviations may be due to different approaches.

Study of Electrode Kinetics

The slope and intercept of the 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 $K_s = \Lambda \times D^{1/2}$ where D is the diffusion coefficient and is determined from the diffusion currents using the Ilkovič equation. The ionic strength was kept constant at 1.0*M*. Table V records the kinetic parameters Pd^{2+} calculated by Gellings method in various concentrations of *meta*-toulic acid.

Effect of Ligand Concentration on Electrode Kinetics

Table V shows no regularity in the variation of the value of standard rate constant K_s. The value of K_s for the reduction of metal ion in solutions containing

TABLE IV. Mihailov Constant 'a' for Various Combinations of *m*-Toulic Acid Concentrations and 'A' at Various *m*-Toulic Acid Concentrations at 308 °K.

Combination of *m*-Toulic Acid Concentrations	'a'	Concentration of *m*-Toulic Acid	'A'
0.04 0.06	46.26	0.04 0.06	295.68 284.00
0.04 0.08	29.21	0.08 0.10	256.50 228.00
0.04 0.10	20.70	0.12 0.14	245.50 235.00
0.04 0.12	32.55	0.16	237.00
0.08 0.14	31.89	Average 'A' = 254.00	
0.08 0.12	39.91		
0.12 0.16	33.64		
0.08 0.16	37.34		
Average 'a' = 34.09			

TABLE V. Kinetic Parameters at 298 °K.

Conc.	α	Λ	$D^{1/2} \times 10^3$ $cm^2 \, sec^{-1}$	$K_s \times 10^3$ $cm \, sec^{-1}$
0.02	0.378	0.3369	1.221	0.4113
0.04	0.425	0.4049	1.203	0.4871
0.06	0.550	0.3218	1.179	0.3794
0.08	0.400	0.4442	1.161	0.5157
0.10	0.525	0.3959	1.126	0.4458
0.12	0.650	0.2868	1.090	0.3115
0.14	0.575	0.3139	1.072	0.3365
0.16	0.550	0.4544	1.057	0.4789

TABLE VI. Thermodynamic Parameters.

Complex Species	Thermodynamic Parameters		
	ΔF° Kcal/deg/ mol	ΔH° Kcal/deg/ mol	ΔS° cal/deg/ mol
[Pd(mTA)]$^+$	−5.903	−5.280	+2.00
[Pd(mTA)$_2$]	−7.718	−11.609	−13.00

different concentrations of the ligand shows that the reduction is quasi reversible. In first instance the value of K_s increases with increasing ligand concentration from 0.02*M* to 0.08*M* except a decrease at 0.06*M*. The variation in K_s value may be understood by taking into consideration the thermal changes occurring while complex formation in the solution takes place. The metal ion in absence of ligand is in the solvated form. The addition of ligand will be associated with thermal changes. When the ligand molecules replace the solvent molecules from the solvation sphere of the solvated metal ion there may be either absorption or release of heat.

In case there is change in enthalpy in the formation of M−L (metal−ligand) bond on breaking the M−S (metal−solvent) bond, the resulting complex may reduce either with a faster or a slower rate depending on the effect of temperature on reaction rates. An increase in temperature generally increases the value of rate constants. Therefore, the increase in the rate constant value in first instance on 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 ligand decreases the value of the rate constant up to a ligand concentration of 0.12*M*. Probably in this concentration variation the viscosity increases which offsets the effect of enthalpy change and therefore a decrease in rate constant value occurs. Still further increase in ligand concentration increases the rate constant value which may be due to the abnormal thermal changes which may occur during the change in the stoichiometric number of ligands bound to the metal ion in the resulting complex. The abnormal thermal changes may excite the outermost orbital electrons of the metal ion of the complex to some higher energy state.

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