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Electrode Kinetics and Thermodynamic Study of Complexes of Palladium(II) at D.M.E.

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Polarographic study of Pd(II) reveals that it reduces quasireversibly at d.m.e. in 0.2 *M*-pyridine + 0.1 *N*-HCl medium. Kinetic parameters of Pd(II) in various concentrations of α-resorcyclic acid were calculated using *Gellings* method and thus the effect of concentration of α-resorcyclic acid on the kinetics of the reduction of Pd(II) has been explained. *DeFord/Hume* graphical extrapolation method and the mathematical method of *Mihailov* have been employed for the evaluation of overall formation constants of the complexes formed with α-resorcyclic acid. The logarithmic values of overall formation constants β_1, β_2 and β_3 obtained by the two methods are 7.47, 8.60, 9.66 (*DeFord* and *Hume* Method) and 7.44, 8.64, 9.66 (*Mihailov* Method) at 298 K. Thermodynamic parameters of these complexes are reported.

[Keywords: Electrochemistry; Pd(II)-complexes]

Elektrodenkinetik und thermodynamische Untersuchungen an Pd(II)-*Komplexen mittels Polarographie*

Pd(II) zeigt eine quasireversible Reduktion in 0,2 *M*-Pyridin/0,1 *N*-HCl. Kinetische Parameter wurden mittels der Methode von *Gelling* ermittelt und damit der Effekt verschiedener α-Resorcylsäurekonzentrationen erklärt. Bildungskonstanten der entsprechenden Komplexe wurden nach *DeFord/Hume* und nach *Mihailov* ermittelt. Die logarithmischen Werte der Gesamtbildungskonstanten β_1, β_2 und β_3 bei 298 K betragen nach der *De Ford/Hume*-Methode 7,47, 8,60 und 9,66, nach der *Mihailov*-Methode 7,44, 8,64 und 9,66. Die thermodynamischen Parameter der Komplexbildung werden angegeben.

Introduction

Palladium does not give a polarographic wave in aqueous medium. Well defined wave of Pd(II) has been reported in Pyridine + HCl medium[1]. *Magee* and *Douglas*[2] showed the reversible reduction of palladium in Pyridine medium with sodium sulphate as base elec-

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trolyte. We have obtained a well defined wave in 0.2M-Pyridine + 0.1N-HCl medium, and found that reduction of Pd(II) in this medium at d.m.e. is quasireversible.

Experimental

All chemicals used were of reagent grade purity. KNO_3 was used as supporting electrolyte to keep ionic strength constant at 1.0M. $5 \times 10^{-4}M$-Pd^{2+} ion concentration require 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 d.m.e. had the following characteristics: $m = 1.62$ mg/s and $t = 3.9$ s at the height of 70 cm of the mercury head. Purified nitrogen gas was passed through each solution for about 15 min. to expel dissolved oxygen Polarograms were taken manually.

Results and Discussion

Pd(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 log $(i/i_d\text{-}i)$ vs. $E_{\text{d.e.}}$ plots from 50–60 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 $(h_{\text{eff}}^{1/2})$ of mercury column.

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

From the shift in $E^r_{1/2}$ as a function of ligand concentration the *DeFord Hume*[3] 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 Tab. 1 and 2 at 298 K and 308 K respectively.

Table 1. *Polarographic measurements and $F_j(X)$ functions values of the* Pd^{2+} *(α-resorcyclic acid) system at 298 K ($\mu = 1.0\,M$)*

c_x (mol)	i_d (civ)	$E^r_{1/2}$ (— V vs. S.C.E.)	$F_0(X)$ $\times 10^{-7}$	$F_1(X)$ $\times 10^{-7}$	$F_2(X)$ $\times 10^{-8}$	$F_3(X)$ $\times 10^{-8}$
0.00	68	0.1685	—	—	—	—
0.02	67	0.3500	0.1139	5.6950	13.4750	—
0.04	66	0.3580	0.2135	5.3375	5.8437	46.09
0.06	65	0.3665	0.4164	6.9400	6.5666	42.77
0.08	63	0.3735	0.7350	9.1875	7.7344	46.67
0.10	62	0.3795	1.1840	11.8400	8.8400	48.40
0.12	61	0.3845	1.7670	14.7250	9.7788	48.15
0.15	60	0.3905	2.8450	18.9666	10.6440	44.20
0.20	59	0.3990	5.9500	29.7500	13.3772	46.80

Table 2. *Polarographic measurements and $F_j(X)$ function values of the* Pd^{2-}*(α-resorcyclic acid) system at 308 K* ($\mu = 1.0 M$)

c_X (mol)	i_d (div)	$E^r_{1/2}$ (— V vs. S.C.E.)	$F_0(X)$ × 10^{-7}	$F_1(X)$ × 10^{-7}	$F_2(X)$ × 10^{-7}	$F_3(X)$ × 10^{-8}
0.00	78	0.1650	—	—	—	—
0.02	78	0.3145	0.0096	0.4800	0.4000	—
0.04	78	0.3330	0.0397	0.9925	1.4812	24.53
0.06	77	0.3455	0.1049	1.7483	2.2472	29.12
0.08	75	0.3550	0.2233	2.7912	2.9890	31.11
0.10	74	0.3630	0.4181	4.1810	3.7810	32.81
0.12	72	0.3690	0.6808	5.6733	4.3944	32.45
0.15	71	0.3770	1.2630	8.4200	5.3466	32.31
0.20	70	0.3870	2.7870	13.9350	6.7675	31.34

Using $F_0(X)$ values corresponding to different ligand concentration the values of *Mihailov*[4] constant "A" and "a" are calculated and recorded in Tab. 3.

Using average values of "A" and "a" the stepwise formation constants of the complexes are calculated. Stability constants according to the methods of *DeFord* and *Hume* and *Mihailov* are summarized below:

	Method					
Temp.	*DeFord Hume*			*Mihailov*		
	log β_1	log β_2	log β_3	log β_1	log β_2	log β_3
298 K	7.47	8.60	9.66	7.44	8.64	9.66
308 K	6.60	7.70	9.48	—	—	—

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

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 $K_s = \Lambda D^{1/2}$, where D is the diffusion coefficient and is determined from the diffusion currents using the *Ilkovic* equation. Tab. 4 records the kinetic parameters of Pd^{2+} reduction calculated by *Gellings* method[5] in various concentration of α-resorcylic acid.

Table 3. *Mihailov constant "a" for various combinations of α-resorcyclic acid concentration (c_x) and "A" at various α-resorcyclic acid concentrations at 298 K*

c_x combinations	"a"	c_x	"A"
0.04 0.06	25.89	0.04 0.06	8.84×10^5 8.56×10^5
0.04 0.08	30.14	0.08 0.10	8.66×10^5 8.75×10^5
0.04 0.10	20.92	0.12 0.14	8.72×10^5 9.84×10^5
0.04 0.12	31.05	0.16	14.96×10^5
0.06 0.12	33.16	"Average" "a" = 31.73 "Average" "A" = 8.70×10^5	
0.08 0.12	32.59		

Table 4. *Kinetic parameters at 298 K*

c_x (mol)	$E^r_{1/2}$ (— V vs. S.C.E.)	α	Λ	$D^{1/2} \times 10^3$ cm^2 s^{-1}	$K_s \times 10^3$ cm s^{-1}
0.02	0.3500	0.65	0.5265	3.834	2.0184
0.04	0.3580	0.50	0.4278	3.777	1.6158
0.06	0.3665	0.50	0.4481	3.720	1.6668
0.08	0.3735	0.50	0.3992	3.606	1.4394
0.10	0.3795	0.40	0.3392	3.492	1.1865
0.12	0.3845	0.40	0.3557	3.549	1.2624
0.15	0.3905	0.45	0.3537	3.435	1.2219
0.20	0.3990	0.42	0.5640	3.375	1.9035

From the values of K_s (which are of the order of 10^{-3}) it 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 changes taking place when the solvent molecules already attached to the metal ions are replaced by the stronger complexing ligands. An increase in temperature generally increase 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 ligand decreases the value of rate constant. Probably in this concentration range the viscosity increase which offsets the effect of enthalpy change 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 the metal ion, the ligand field of the complexing species may excite the electrons of the metal ion to some higher energy state and may form an activated complex which reduces relatively fast.

Thermodynamic parameters were also calculated and are reported in Tab. 3.

Table 5. *Thermodynamic parameters of the* Pd(II) *α-resorcyclate system in aqueous medium*

Complex Species	Thermodynamic Parameters		
	ΔF^0 kcal deg^{-1} mol^{-1}	ΔH^0 kcal deg^{-1} mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}
[Pd(α-resorcylate)]	—10.26	—36.99	—89.60
$[\text{Pd}(\alpha\text{-resorcylate})_2]^{2-}$	—11.80	—38.18	—88.40
$[\text{Pd}(\alpha\text{-resorcylate})_3]^{4-}$	—13.26	—7.53	+ 19.20

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