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(Received, 16 July 1987

Revised form, 27 November 1987)

TEMPERATURE EFFECT ON POLAROGRAPHIC BEHAVIOUR OF Co(II) and Zn(II) 2:1 COMPLEXES WITH PALUDRINE

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SUMMARY

The polarographic reduction of Zn(II) and Co(II) complexes with paludrine has been studied in moderated acid media. The Zn(II) 2:1 complex shows two well defined waves. The Co(II) 2:1 complex shows only one wave. Arrhenius activation energies, obtained from diffusion currents of np, dp, ac₁, ac₂, K₁ and K₂ polarograms, show that all cathodic and anodic processes are controlled by diffusion. The mechanism of these processes is proposed.

INTRODUCTION

The first published studies on polarography of biguanides were related to their complexes^{1,2}. In order to reduce the biguanide group at the d.m.e., it is required that the nitrogen bridge between the biguanide plane is protonated at the electronic delocalization on the biguanide group thus lost, which makes them susceptible to saturation and reduction, producing the corresponding amino groups³⁻⁵.

In the present study, direct current (dc), normal(np) and differential pulse (dp), first (ac₁) and second (ac₂) harmonic superimposed alternating current polarography and methods based on the Kalousek commutator are employed to elucidate the behaviour of 2:1 biguanide complexes on the d.m.e. of paludrine-cobalt and paludrine-zinc buffer aqueous solutions.

EXPERIMENTAL

Polarographic measurements were made with a Polarecord E-506 (Methrom S.A.). A digital Radiometer pHmeter with a combined electrode enabled us to obtain a pH accuracy of +0.01 units. The temperature was kept constant to +0.1°C using a Heto O3T623 cryostat and a Heto O5E623 thermostat.

Table 3.- Temperature effect on the wave of paludrine 2:1 complex with Co(II).

(paludrine) = 8×10^{-4} M ; (Co(II)) = 3.6×10^{-4} M ; pH = 5.03 ;
 $t = 0.6$ s ; $\Delta E_{\text{pulse}} = -20$ mV ; $\Delta E_{\text{ac}} = 10$ mV ; $\phi = 0$ rad ;
 $E_{\text{pb}}(K_1) = -1320$ mV ; $E_{\text{pb}}(K_2) = -960$ mV ; $f_k = 75$ Hz .

T(°C)	dc	np	K ₁	K ₂	ac ₁	dp	ac ₂	
5.4	$i_{1,p}$ (μA)	5.8	8.0	5.4	10.4	0.75	1.53	0.090 $i_{1,p}$ (μA)
	n, n', n''	1.1	1.0	0.8	0.9	0.7	0.9	0.7 $n''P_1$ (mV)
	$-E_{1/2,p,i}$ (mV)	1260	1264	1326	1286	1344	1276	1306 E_{1,p_1} (mV)
9.8	$i_{1,p}$ (μA)	6.2	8.6	6.4	11.1	0.85	1.68	0.099 $i_{1,p}$ (μA)
	n, n', n''	1.2	1.2	0.8	0.9	0.6	0.9	0.7 $n''P_1$ (mV)
	$-E_{1/2,p,i}$ (mV)	1254	1258	1326	1284	1340	1274	1300 E_{1,p_1} (mV)
15.6	$i_{1,p}$ (μA)	7.2	9.6	6.9	12.4	0.95	1.93	0.111 $i_{1,p}$ (μA)
	n, n', n''	1.1	1.2	0.9	1.0	0.7	1.0	0.7 $n''P_1$ (mV)
	$-E_{1/2,p,i}$ (mV)	1254	1258	1324	1276	1336	1270	1296 E_{1,p_1} (mV)
20.6	$i_{1,p}$ (μA)	8.2	11.0	8.1	14.2	1.08	2.25	0.125 $i_{1,p}$ (μA)
	n, n', n''	1.0	1.1	0.9	1.0	0.7	1.0	0.7 $n''P_1$ (mV)
	$-E_{1/2,p,i}$ (mV)	1250	1252	1322	1274	1332	1266	1292 E_{1,p_1} (mV)
24.6	$i_{1,p}$ (μA)	8.9	12.1	9.1	15.2	1.20	2.50	0.137 $i_{1,p}$ (μA)
	n, n', n''	1.2	1.3	0.8	1.0	0.7	1.0	0.8 $n''P_1$ (mV)
	$-E_{1/2,p,i}$ (mV)	1248	1252	1320	1274	1328	1264	1292 E_{1,p_1} (mV)
30	$i_{1,p}$ (μA)	10.0	13.7	9.7	17.2	1.35	2.83	0.149 $i_{1,p}$ (μA)
	n, n', n''	1.2	1.2	0.9	1.0	0.7	1.0	0.8 $n''P_1$ (mV)
	$-E_{1/2,p,i}$ (mV)	1246	1252	1320	1276	1328	1264	1288 E_{1,p_1} (mV)
35.2	$i_{1,p}$ (μA)	11.9	15.1	10.6	18.5	1.53	3.15	0.164 $i_{1,p}$ (μA)
	n, n', n''	1.3	1.2	0.9	1.0	0.8	1.1	0.8 $n''P_1$ (mV)
	$-E_{1/2,p,i}$ (mV)	1248	1252	1316	1274	1324	1264	1288 E_{1,p_1} (mV)
40.4	$i_{1,p}$ (μA)	12.3	16.7	11.6	20.2	1.73	3.53	0.180 $i_{1,p}$ (μA)
	n, n', n''	1.3	1.3	0.9	1.1	0.8	1.1	0.8 $n''P_1$ (mV)
	$-E_{1/2,p,i}$ (mV)	1248	1252	1318	1276	1324	1264	1286 E_{1,p_1} (mV)
45.2	$i_{1,p}$ (μA)	14.1	18.7	12.4	21.6	1.93	3.90	0.197 $i_{1,p}$ (μA)
	n, n', n''	1.3	1.3	0.9	1.1	0.8	1.1	0.8 $n''P_1$ (mV)
	$-E_{1/2,p,i}$ (mV)	1250	1254	1318	1276	1322	1286	1283 E_{1,p_1} (mV)

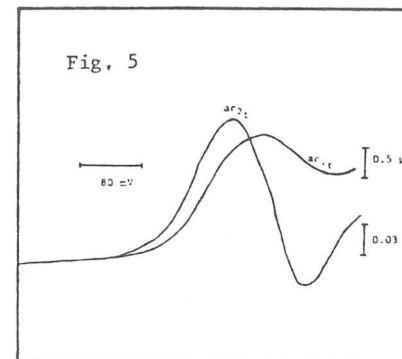
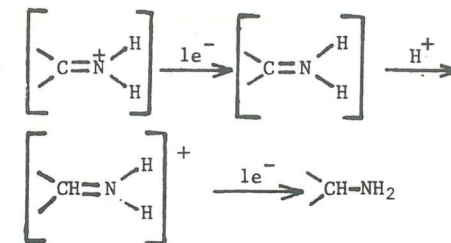
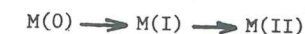


Fig. 5.- Alternating current polarography of Co(II) 2:1 complex. (paludrine) = 8×10^{-4} M ; (Co(II)) = 3.6×10^{-4} M ; T = 298 K ; pH = 5.03 ; $t = 0.6$ s ; $\Delta E = 10$ mV ; $\phi = 0$ rad .



The shape and heights of ac_1 , ac_2 and Kalousek's waves correspond to overlap of mono-electronic processes. The reoxidation process of ions:



occurs analogously for free or complexed divalent M(II) ions.

Theoretical separations of α_c and α_a obtained from equations¹⁰:

$$n'' \approx n' \approx n\alpha_c = j_c - 1/2 \quad (5)$$

and

$$n\alpha_a = n - j_a + 1/2 \quad (6)$$

respectively, for $j_c = 1$ and $j_a = 2$ differ from experimental values in the order of the double layer or Frumkin-Gierst effect¹¹ in the whole temperature interval.

On the other hand, when $j_c = 1$, for an $E, E^{1/2}$ mechanism, it is possible to use the following relation between the symmetry factor, β ,

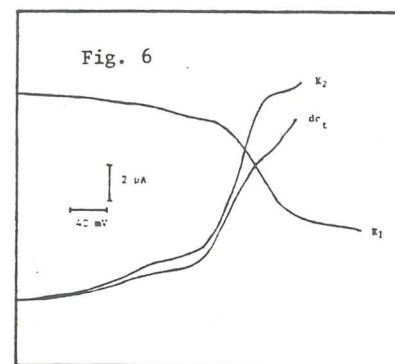


Fig. 6.- Kalousek and dc polarography of Co(II) 2:1 complex. (paludrine) = 8×10^{-4} M ; (Co(II)) = 3.6×10^{-4} M ; T = 298 K ; pH = 5.03 ; $t = 0.6$ s ; $E_{\text{pb}}(K_1) = -1320$ mV ; $E_{\text{pb}}(K_2) = -960$ mV ; $f_k = 75$ Hz .

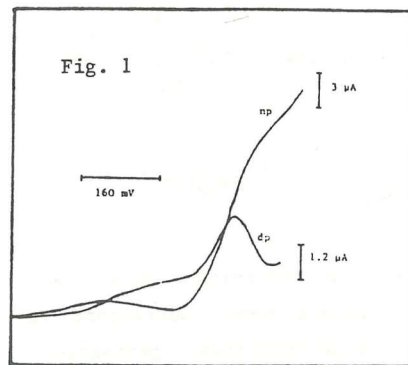


Fig. 1.- Pulse polarography of Zn(II) 2:1 complex. (paludrine) = 8×10^{-4} M ; (Zn(II)) = 3.7×10^{-4} M ; T = 298 K ; pH = 5.03 ; t = 0.6 s ; $\Delta E = -20$ mV .

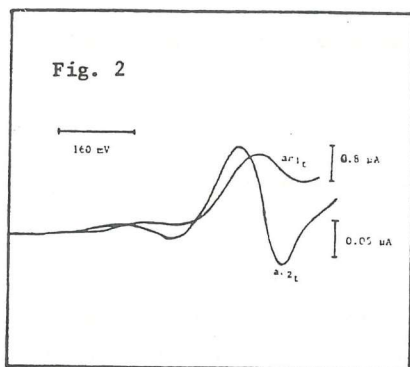


Fig. 2.- Alternating current polarography of Zn(II) 2:1 complex. (paludrine) = 8×10^{-4} M ; (Zn(II)) = 3.7×10^{-4} M ; T = 298 K ; t = 0.6 s ; pH = 5.03 ; $\Delta E = 10$ mV ; $\phi = 0$ rad.

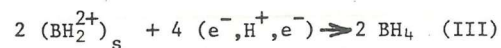
complexes of Zn(II), B_2M , the first wave would correspond to the reduction of the complexed cation, whereas the second wave would be associated to the biguanide group, B, on the electrode, such as it happens when only biguanide is in the medium. The fact that only one wave is recorded from Co(II) solutions, can be related to the fact that paludrine and Co(II) are reduced at the same zone of potentials⁷ (Table 1).

The change in diffusion currents (or peak currents) were studied as a function of temperature from 5° to 45°C, and it was found that it can be expressed by the following Arrhenius equation⁸ (Table 2 and Table 3):

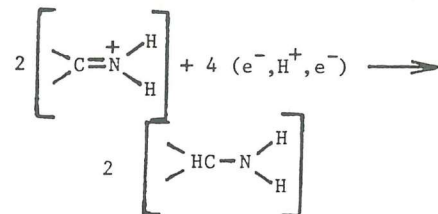
$$i_d = K \exp(-Q / RT) \quad (4)$$

MECHANISM

Therefore, the reduction mechanism of these complexes B_2M can be described in the following steps:



Also, the last step can be written in a more explicit form:



The paludrine (proguanil B.P.) was supplied by ICI Pharma S.A., the phenformine hydrochloride by Funk S.A.

The mercury flow was estimated to be $2.63 + 0.03 \text{ mg.s}^{-1}$.

Britton-Robinson acetate-phosphate-borate mixtures were prepared, adjusting the pH value with KOH. Ionic strength was adjusted to I = 0.5 M adding KCl_{10} .

Limiting currents, i_l , were measured correcting graphically the charging current. Peak potentials values, E_p , and peak intensities, i_p , were measured directly over the polarograms. $E_{1/2}$ values were obtained by semilogarithmic treatment of the waves. Also, the α_c cathodic values were obtained, corresponding to calculations based on dc polarograms under application of the expression⁹:

$$E = E_{1/2} - \frac{RT}{n\alpha_c F} \ln \frac{i}{i_l - i} \quad (1)$$

The α_a anodic values were obtained by the same semilogarithmic treatment from K₁ polarograms. At 25°C, the half-width of ac_1 and dp waves has a value close to

$$\omega_{1/2} = \frac{4RT}{n'F} \ln(\sqrt{2} + 1) \quad (2)$$

wherein the n' parameter has analogous significance as α_c . Also, the peak-to-peak separation of ac_2 waves are a value close to

$$E_{p2} - E_{p1} = \frac{2RT}{n''F} \ln(2 + \sqrt{3}) \quad (3)$$

wherein the n'' parameter has a theoretical similar significance as α_c . Measurement criteria are previously described for normal (np) and differential (dp) pulse waves³, ac_1 and ac_2 waves⁴ and Kalousek polarograms⁵.

RESULTS

The polarograms obtained by different techniques show two waves in the case of complexes with Zn(II), where as only one wave is recorded from complexes paludrine-Co(II) (Fig. 1 Fig. 6). In the case of

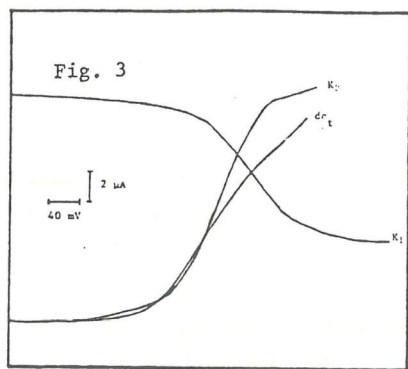


Fig. 3.- Kalousek and dc polarography of Zn(II) 2:1 complex. (paludrine) = 8×10^{-4} M ; (Zn(II)) = 3.7×10^{-4} M ; T = 298 K ; pH = 5.03 ; t = 0.6 s ; $E_{pb}(K_1) = -1320$ mV ; $E_{pb}(K_2) = -960$ mV ; $f_k = 75$ Hz .

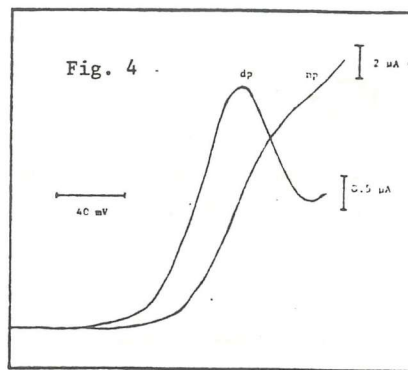


Fig. 4.- Pulse polarography of Co(II) 2:1 complex. (paludrine) = 8×10^{-4} M ; (Co(II)) = 3.6×10^{-4} M ; T = 298 K ; pH = 5.03 ; t = 0.6 s ; $\Delta E = -20$ mV .

All experimental results seem to agree with this mechanism:

a) It is observed that the E_p and $E_{1/2}$ potentials of the second wave of the Zn 2:1 complex are the same than the corresponding to the reduction of the paludrine (Table 1). Also, values of $n\alpha$ and morphology of quassi-diffusion waves are analogous.

b) The activation energy values, $3 < Q < 4$ kcal. mol^{-1} , which characterizes reduction processes associated with the second wave (Table 4).

c) The reduction wave's height of Zn(II) added to its ligands is of the same size of the one the Co(II) complex provides. In this case, electron transfers of the step (I) are produced at the same potentials of step (III).

The $E_{1/2}$ or E_p variation on the temperature of cathodic processes point out higher entropic variation in the case of Zn(II) reduction than the one corresponding to the paludrine.

SIGNIFICANCE OF THE TRANSFER COEFFICIENTS

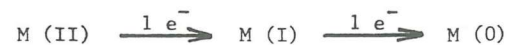
The $n\alpha$, n' or n'' values can be explained on the basis of a model of mono-electronic transfers coupled with chemical steps² or simply structural changes of interfaces¹⁰. Thus, the

Table 1.- Parameters of polarographic waves of paludrine and its 2:1 complex.

T = 25°C ; pH = 5.03 ; t = 0.6 s ; $\Delta E_{\text{pulse}} = -20$ mV ; $\Delta E_{ac} = 10$ mV ; $E_{pb}(K_1) = -1320$ mV ; $E_{pb}(K_2) = -960$ mV ; $f_k = 75$ Hz ; $\phi = 0$ rad ; (paludrine) = 8×10^{-4} M ; (Co(II)) = 3.6×10^{-4} M ; (Zn(II)) = 3.7×10^{-4} M .

		P	P ₂ Zn		P ₂ Co
		Paludrine	a)	b)	
dc	$-E_{1/2}$ (mV)	1232	984	1248	1248
	$n\alpha$	1.1	0.7	1.2	1.2
	i_1 (μA)	4.3	2.0	7.5	8.9
np	$-E_{1/2}$ (mV)	1236	996	1252	1252
	$n\alpha$	1.3	0.7	1.5	1.3
	i_1 (μA)	5.7	2.7	10.4	12.1
K ₁	$-E_{1/2}$ (mV)	1316	760	1312	1320
	$n\alpha$	0.8	1.1	0.9	0.8
	i_1 (μA)	4.6	3.7	8.6	9.1
K ₂	$-E_{1/2}$ (mV)	1250	1028	1276	1274
	$n\alpha$	1.1	0.9	1.1	1.0
	i_1 (μA)	7.6	2.7	12.9	15.2
ac ₁	$-E_p$ (mV)	1312	1088	1324	1328
	n'	0.7		0.8	0.7
	i_p (μA)	0.65	0.12	1.04	1.20
dp	$-E_p$ (mV)	1248	1024	1268	1264
	n'	1.0	0.8	1.1	1.0
	i_p (μA)	1.23	0.30	2.22	2.50
ac ₂	$-E_{1/2}$ (mV)	1342	1100	1348	1356
	n''	0.7	0.8	0.8	0.8
	i_p (μA)	0.065	0.010	0.115	0.137

reduction of divalent cations can be simplified:



and also each azomethinic double bond of the diprotonated biguanide group

Table 2.- Temperature effect on two waves of paludrine 2:1 complexes with Zn(II).

(paludrine) = 8×10^{-4} M ; (Zn(II)) = 3.7×10^{-4} M ; pH = 5.03 ;
 $t = 0.6$ s ; $\Delta E_{\text{pulse}} = -20$ mV ; $\Delta E_{\text{ac}} = 10$ mV ; $\phi = 0$ rad ;
 $E_{\text{pb}}(K_1) = -1320$ mV ; $E_{\text{pb}}(K_2) = -960$ mV ; $f_k = 75$ Hz .
 a) first wave ; b) second wave.

T(°C)	ac		np		K ₁		K ₂		ac ₁		dp		ac ₂		i _{p1} (μA)	i _{p2} (μA)	E _i (mV)			
	a)	b)	a)	b)	a)	b)	a)	b)	a)	b)	a)	b)	a)	b)						
5	1.5	5.3	2.0	7.2	5.6	2.3	9.3	0.12	0.64	0.36	1.48	0.008	0.029	0.005	0.029	i _{p1} (μA)	i _{p2} (μA)	E _i (mV)		
	0.7	1.0	1.0	1.0	0.8	0.8	0.9	0.8	0.7	0.9	1.0	0.9	0.7	0.8	0.7	n ₁ ^{ac}	n ₂ ^{ac}	E _i (mV)		
	1040	1260	1044	1264	1320	1068	1284	1120	1344	1064	1272	1144	1364							
9.5	1.5	0.6	1.8	7.8	6.8	2.0	9.9	0.08	0.72	0.42	2.82	0.012	0.033	0.005	0.028	i _{p1} (μA)	i _{p2} (μA)	E _i (mV)		
	0.9	1.1	1.1	1.1	0.7	1.2	1.1	0.8	0.7	1.1	1.0	0.8	0.7	0.8	0.7	n ₁ ^{ac}	n ₂ ^{ac}	E _i (mV)		
	1024	1256	1036	1260	1316	1060	1280	1112	1340	1052	1264	1176	1360							
15.4	1.7	6.8	2.4	8.9	3.5	7.1	2.4	11.6	0.12	0.84	0.30	1.92	0.010	0.109	0.008	0.035	i _{p1} (μA)	i _{p2} (μA)	E _i (mV)	
	0.9	1.2	0.8	1.2	1.1	0.8	1.1	1.0	0.8	0.7	0.9	1.0	0.8	0.8	0.8	0.8	0.8	n ₁ ^{ac}	n ₂ ^{ac}	E _i (mV)
	1016	1256	1024	1260	756	1316	1044	1280	1104	1340	1048	1272	1124	1356						
20.8	1.8	7.1	2.3	9.6	3.8	8.3	2.3	11.9	0.12	0.92	0.30	2.70	0.013	0.113	0.008	0.038	i _{p1} (μA)	i _{p2} (μA)	E _i (mV)	
	0.8	1.4	1.0	1.5	1.1	0.8	1.1	1.1	0.8	0.7	0.8	1.1	0.8	0.8	0.8	0.8	0.8	n ₁ ^{ac}	n ₂ ^{ac}	E _i (mV)
	1000	1256	1008	1256	756	1316	1028	1280	1096	1336	1040	1268	1120	1356						
25	2.0	7.5	2.7	10.4	3.7	8.6	2.7	12.9	0.12	1.04	0.30	2.22	0.010	0.115	0.010	0.050	i _{p1} (μA)	i _{p2} (μA)	E _i (mV)	
	0.7	1.2	0.7	1.5	1.1	0.9	0.9	1.1	0.8	0.8	0.8	1.1	0.8	0.8	0.8	0.8	0.8	n ₁ ^{ac}	n ₂ ^{ac}	E _i (mV)
	984	1248	996	1252	760	1312	1028	1276	1088	1324	1024	1268	1100	1348						
30.2	2.3	8.4	2.6	11.0	4.4	9.8	2.7	14.6	0.12	1.16	0.36	2.52	0.008	0.133	0.010	0.049	i _{p1} (μA)	i _{p2} (μA)	E _i (mV)	
	0.7	1.4	1.0	1.4	1.1	0.8	0.9	1.1	0.9	0.8	0.7	1.2	0.7	0.8	0.7	0.8	0.8	n ₁ ^{ac}	n ₂ ^{ac}	E _i (mV)
	958	1248	984	1252	768	1324	1016	1276	1089	1328	1012	1266	1096	1352						
35.4	2.3	9.8	3.2	12.8	4.4	10.2	2.9	15.8	0.16	1.28	0.42	2.82	0.008	0.143	0.013	0.043	i _{p1} (μA)	i _{p2} (μA)	E _i (mV)	
	0.9	1.1	0.8	1.3	1.1	0.8	0.9	1.1	0.8	0.8	0.6	1.1	0.7	0.8	0.7	0.8	0.8	n ₁ ^{ac}	n ₂ ^{ac}	E _i (mV)
	960	1252	968	1252	772	1320	1008	1276	1068	1324	988	1264	1084	1344						
41.2	2.6	10.7	3.5	14.4	4.4	10.5	2.9	17.0	0.16	1.52	0.48	3.18	0.008	0.163	0.010	0.043	i _{p1} (μA)	i _{p2} (μA)	E _i (mV)	
	0.8	1.2	0.8	1.5	1.0	1.3	0.9	0.9	0.7	0.8	0.6	1.3	0.7	0.8	0.7	0.8	0.8	n ₁ ^{ac}	n ₂ ^{ac}	E _i (mV)
	940	1248	952	1256	772	1320	1000	1276	1064	1340	960	1264	1072	1344						
45.6	2.7	12.0	3.0	15.8	3.1	11.7	2.4	18.5	0.16	1.60	0.48	3.48	0.008	0.165	0.010	0.063	i _{p1} (μA)	i _{p2} (μA)	E _i (mV)	
	0.8	1.4	0.9	1.5	1.1	1.2	1.2	0.9	0.6	0.8	0.6	1.2	0.7	0.8	0.7	0.8	0.8	n ₁ ^{ac}	n ₂ ^{ac}	E _i (mV)
	928	1240	944	1244	772	1316	992	1268	1016	1320	940	1256	1056	1340						

and the cathodic transfer coefficient, $\alpha_c^{1,2}$:

$$\alpha_c = \left(\frac{1}{n} \right) \left[z \left(\frac{\phi_x}{\eta} + 1 \right) + \beta - 0.14 m \right] \quad (7)$$

to determinate the number of water molecules displaced on the d.m.e. by each ion.

Replacing in equation (7) $\beta = 1/2$, $\phi_x/\eta = 0.1^{\circ}$ and $z=2$ for the complexed Zn(II), it is obtained $m \approx 14$ molecules of water for each reduced ion. Then the form of Zn(II) reduced is the complexed 2:1 π -electronic

Table 4.- Arrhenius activation energies of polarographic processes of paludrine and its

2:1 complexes. T = 25°C ; pH = 5.03 ; t = 0.6s ;
 $\Delta E_{\text{pulse}} = -20$ mV ; $\Delta E_{\text{ac}} = 10$ mV ; $f_k = 75$ Hz ;
 $E_{\text{pb}}(K_1) = -1320$ mV ; $E_{\text{pb}}(K_2) = -960$ mV ; $\phi = 0$ rad.

	P	P ₂ Zn	P ₂ Co	
dc	a	-5.60	-5.99	-5.11
	b	-2010.70	-1546.50	-1940.60
	r	-0.988	-0.992	-0.998
	Q(Kcal.mol ⁻¹)	4.00	3.40	3.90
np	a	-5.47	-5.80	-4.94
	b	-1967.90	-1686.80	-1899.10
	r	-0.991	-0.994	-0.999
	Q(Kcal.mol ⁻¹)	3.90	3.30	3.80
K ₁	a	-5.57	-6.59	-5.60
	b	-2029.60	-1515.90	-1802.80
	r	-0.986	-0.986	-0.993
	Q(Kcal.mol ⁻¹)	4.10	3.00	3.60
K ₂	a	-6.13	-6.20	-5.48
	b	-1692.60	-1499.60	-1671.10
	r	-0.995	-0.996	-0.998
	Q(Kcal.mol ⁻¹)	3.40	3.00	3.30
ac ₁	a	-7.39	-6.99	-6.69
	b	-2048.30	-2023.60	-2064.50
	r	-0.995	-0.999	-0.999
	Q(Kcal.mol ⁻¹)	4.10	4.00	4.10
dp	a	-7.23	-6.82	-5.86
	b	-1912.50	-1635.20	-2099.90
	r	-0.994	-0.998	-0.999
	Q(Kcal.mol ⁻¹)	3.80	3.70	4.20
ac ₂	a	-11.90	-10.58	-10.07
	b	-1608.50	-1597.50	-1713.10
	r	-0.992	-0.996	-0.999
	Q(Kcal.mol ⁻¹)	3.20	3.20	3.40

system, since it is bigger^{1,2} than the free Zn(II), which has $\alpha \approx 1.5^{10}$ and $m \approx 8$ in the same experimental conditions.

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(Received, 25 September 1987)

Revised form 16 March 1988)

THE EFFECT OF ADATOMS ON THE REVERSIBILITY OF SOME REDOX COUPLES

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Abstract

Cyclic voltammetric studies were performed for six redox couples at a Pt electrode, in the absence and in the presence of Bi, Pb and Cd adatoms. Standard rate constants were evaluated for all the systems in the absence and in the presence of adatoms.

Whenever a catalytic effect was obtained the effect of coverage was studied in a quantitative way. It was found that the rate constant increases initially rapidly and then passes through a maximum or reaches a constant value, at coverages of the order of a monolayer. For all the systems the influence of the adatoms decreases in the order Bi > Pb > Cd.

Introduction

Heavy metals electrodeposited at an under potential (UPD) onto a Pt surface have shown to catalyse a number of electrochemical reactions. The subject has been reviewed by Adzic [1]. One somewhat surprising observation is that such adatom modified surfaces catalyse "simple" electron transfer reactions, as it has been demonstrated earlier by Adzic et al. [2] and recently by Kokkinidis [3].

Adzic and Despic [2] have found that the heterogeneous rate constants for the reactions of Ti^{3+}/Ti^{4+} and Fe^{2+}/Fe^{3+} couples at Au/Cu_{ads} and Au/Ag_{ads} electrodes were increased by almost an order of magnitude. Recently Schultze et al. [4] have studied the kinetics of the $Ru(NH_3)_6^{2+} / Ru(NH_3)_6^{3+}$ couple at Pt/Tl_{ads} and Pt/Pb_{ads} . They found no effect on the exchange current densities due to the presence