CHRONOPOTENTIOMETRIC STUDIES OF COMPLEXES IN THE ABSENCE OF LARGE LIGAND EXCESS.

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This communication is the Part II of another one reported to the "X Reunión del Grupo de Electroquímica de la R.S.E.Q."(1).In that report the following equations for the E-t curves and the free ligand concentration at interface were presented: $[C_X(0,t)/C_X]^{q-p}\exp(\Psi)+\sqrt{(t/\tau)}[C_X(0,t)/C_X]^{q}\exp(\theta)=1-\sqrt{(t/\tau)}$; $C_X(0,t)=C_X-qC_M[1-\sqrt{(t/\tau)}]$; $\Psi=[\alpha nF/RT][E-(E_1^p)']$; $\theta=\exp[nF/RT][E-(E_{e_c}^o)]$ for coordinated systems which fulfill the conditions: i) $C_X>qC_M$, ii) $\beta_q C_X^q(0,t)>>1$ and iii) $(E_s^o-E_{\frac{1}{2}})>(118/\alpha n)$mV.The experimental verification of these equations is the subject of this report.

The Bi(III)-NTA coordinated system has been choosen for it and, it has been studied in the same conditions corresponding to the polarographic study that N.G.Elenkova and T.K.Nedelcheva carried out(2).Likewise, this system fulfills the above conditions.The measurements were performed with a HMDE($A=0.032cm^2$) and at 25^oC.Three solutions were prepared using 0.1M $HClO_4$ as solvent.They were 0.1 mM Bi(III) with the following NTA concentrations:0.2;0.5 and 1.0mM.The pH of the three solutions were:0.95;0.92 and 0.93,respectively.

Several E-t curves were recorded for each solution for varying applied current intensity from 0.6 to 2.7 μA in order to verify the diffusion character of the reduction process. It was confirmed on obtaining the following $i\sqrt{\tau}$ values:2.37; 2.35 and 2.64 $\mu As^{\frac{1}{2}}$, regardless of applied current intensity.

The nature of the discharge was investigated by the logarithmic analysis - $\log[1-\sqrt{(t/\tau)}]$ vs E - of the recorded E-t curves corresponding to an applied current value of 2.1 μA.The Figure 1 shows this analysis for the solution corresponding to 0.1 mM Bi(III) and 0.5 mM NTA.The good linearity

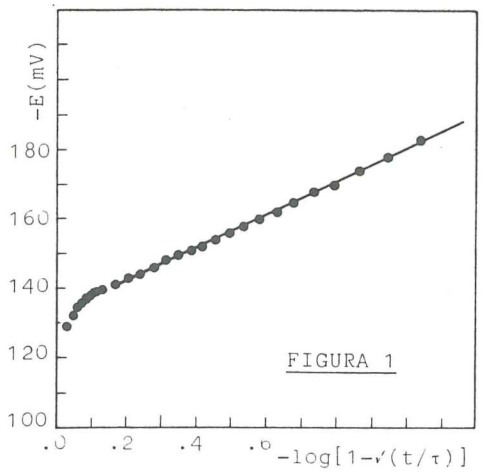

FIGURA 1

observed at the more cathodic potentials is indicating the charge transfer control in this potential region.As the potential shifts in anodic direction the quasi-reversible character increases.We have obtained from the slope of linear region the following values for the cathodic transfer coefficient corresponding to the three different concentrations:0.421;0.413 and 0.422, which are in a good agreement to that obtained by N.G.Elenkova and T.K.Nedelcheva (2).

According the notation used by R.Bennes (3) the value of $(E_i^p)'$ is given by:$[k_s/0.886][\sqrt{(\tau/D)}][\beta_p^{1-\alpha}/\beta_q]C_X^{p-q}\exp[\alpha nFE_s^o/RT]=\exp[\alpha nF(E_i^p)'/RT]$.The interceptions obtained from the logarithmic analysis led to the following values for $(E_i^p)'$:-136.2;-132.5 and -127.2 mV vs SSCE.This is indicating the no dependence of that parameter to the ligand concentration within the magnitude of experimental error of measurements; hence, according to the above equation it is obtained that the reduction occurs from the complex species.This result is the same than that found by N.G.Elenkova-T.K.Nedelcheva(2).

In order to determine the conditional stability constant, experimental data corresponding to the anodic region of the E-t curves have been used, according to the following equation: $\ln\beta_q=\ln[1-\sqrt{(t/\tau)}]-\exp[[\alpha nF/RT][E-(E_i^p)']]]-\ln C_X^q(0,t)-\ln\sqrt{(t/\tau)}-(nF/RT)(E-E_s^o)$.The employed E_s^o value was -80 mV vs SSCE(2).The obtained values for the conditional and overall stability constants and those for the standard rate constant

TABLE 1.Bi(III)-NTA system. k_s[cm/s].$\beta'(\beta)$[liter/mol].

[NTA] mM	logβ'	logβ	-logk_s
0.2	5.54	17.06	1.60
	5.88	17.40	1.46
	5.07	16.59	1.80
	6.16	17.68	1.34
	5.28	16.80	1.71
0.5	4.85	16.47	1.81
	5.77	17.39	1.43
	5.15	16.78	1.68
	5.54	17.16	1.52
	5.42	17.04	1.58
1.0	4.85	16.44	1.73
	4.21	15.80	1.99
	4.14	15.73	2.03
	4.78	16.36	1.76
	4.66	16.25	1.81

are collected in Table 1.

The data of Table 1 are in agree to those found in the literature (2,4).It shows the validity and usefulness of the presented equations.

At present, an enlargement of this study respect to the experimental conditions is carrying out.It will allow us to perform the statistical analysis which is necessary due to the low concentrations used in this study.

REFERENCES.

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