

ELECTRODE KINETIC PARAMETERS FOR THE ANODIC DISSOLUTION
OF COBALT, COPPER, ZINC AND BISMUTH

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Electrode kinetic parameters, β and k , the charge transfer coefficient and the conditional charge transfer rate constant, respectively, for the anodic dissolution of copper, cobalt, zinc and bismuth have been calculated from voltammetric scans carried out in solutions containing a selected supporting electrolyte and the same supporting electrolyte plus EDTA, respectively. The values found for the parameters in both media showed that they are affected by the presence of the complexing agent. β was found to be related to the conditional formation constant, $K_{M,Y}$, of the metal-EDTA complex studied and the k_0/k_{0EDTA} ratios obtained evidenced adsorption of the metal-EDTA compound on the electrode surface for all the cases but bismuth; its extent being closely related to the metal transition character of the metal ion involved in the complex.

Keywords: Electrode kinetic parameters; anodic dissolution of pure metals; arbitrary current method.

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INTRODUCTION

The coulometric work carried out¹ was complemented by studies on the electrode kinetic parameters for the anodic dissolution of the ultra-pure metals utilized, namely cobalt, copper, zinc and bismuth into solutions containing an appropriate supporting electrolyte and the same supporting electrolyte plus EDTA, respectively, as to enable the parameters k , the conditional charge transfer rate constant, and β , the charge transfer coefficient, to be compared and also to establish whether or not these parameters are affected by the presence of the complexing agent.

As for the anodic dissolution of a metal the limiting current is not experimentally measurable, an appropriate method, referred to as "pattern theory" by its author², was employed. This method affords a simple means of calculating k and β for nearly any situation, according to the data available, including processes wherein the limiting current, I_L , is not known. The method applied to this particular situation is called the "arbitrary-current method" by the author and proved to yield reliable results during the course of the present investigation. Tafel lines³ were also plotted just for the sake of comparison.

The electrode kinetic parameters were extracted from voltammograms obtained using linear sweep voltammetry with a precise, interchangeable disc electrode.

The experimental values found for the parameters demonstrated that they are influenced by the presence of the complexing agent.

EXPERIMENTAL

CHEMICALS AND SOLUTIONS

All the chemicals employed throughout this work were Analar Grade, supplied by Hopkin and Williams Ltd. and were used as received, except EDTA that was thoroughly purified to exclude NTA¹. The distilled water was obtained from a special all-glass still⁴. The solutions were prepared in Grade A, calibrated glassware. White spot nitrogen was purified by bubbling the gas into a chromium(II) sulphate solution in sulphuric acid to eliminate vestiges of oxygen.

APPARATUS

A conventional three electrodes potentiostat was constructed using general purpose FET operational amplifiers.

The rotating electrode assembly used in the course of the present work has been described elsewhere⁵, however, considering that the electrode units employed in the assembly could not be dismantled to change the electrode material without serious damage of the disc surface, an electrode holder that takes short metal rods, that can be used as discs, was designed. This electrode holder is shown in Fig. 1. The rod j is pushed up through the two silicone washers g and i until its lower face is levelled with washer i lower plane, providing an exposed surface in the form of a disc of known area, and, at the same time, it will exert a small pressure against disc k , which in turn touches disc e giving the final electric contact with the potentiostat by means of wire l connected to the jack-plug b . Washer f is to avoid short-

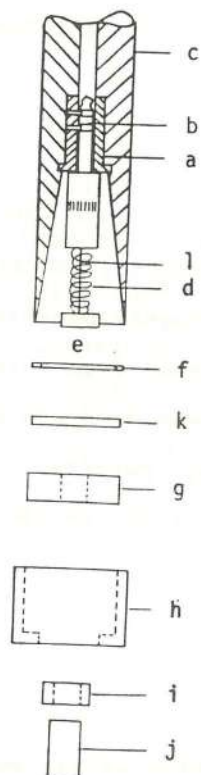
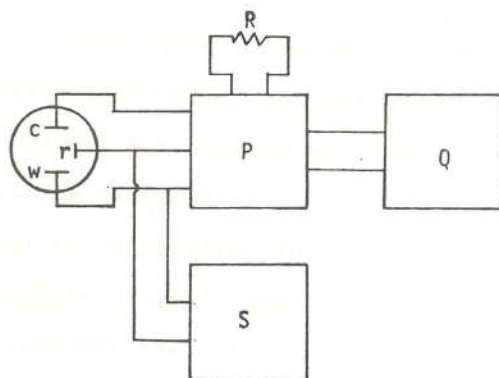


Fig. 1. ROTATING DISC ASSEMBLY FOR METAL RODS. a, three-contact jack socket; b, three-contact jack plug; c, shaft; d, spring; e and k, brass discs; f, PTFE washer; g and i, silicone rubber washers; h, screw cap; j, metal rod; l, tinned copper wire.

Fig. 2. BLOCK DIAGRAM. P, potentiostat; Q, X-Y recorder; S, voltmeter; R, standard resistor for current measurement; w, r and c, working, reference and counter electrodes, respectively.



circuit between disc k and the shaft c. The shaft is protected by a loose fitting PTFE cover, not shown in Fig. 1, which fits tightly into the cell lid.

Voltammograms were recorded on a Hewlett-Packard Moseley 7035 X-Y recorder.

A high capacity, large area saturated calomel electrode (SCE), with a working area of 20 cm², was used as reference electrode.

Rotation speed of the working electrode was measured on a S.E. Laboratories (Engineering) Ltd. crystal timer Model SM 200.

Disc electrodes were made out of 6N random crystal 8 mm width metal rods supplied by B.D.H. Chemicals Ltd., Johnson, Matthey & Co. Ltd. and Metal Research & Co. Ltd.

A coiled 22 S.W.G. platinum wire 5 cm long, sealed into soft glass, served as counted electrode

PROCEDURE

A conventional procedure was employed to record voltammograms using a jacketed cell maintained at 20⁰ C. Before each set of scans the electrode surface was conditioned by polishing with fine chromatography alumina to produce a bright, scratch-free surface, washing thoroughly with distilled water, dipping into 6 M nitric acid for a few seconds and, finally, rinsing with water. The apparent electrode area was 0.5 cm².

The working solution was allowed to reach the selected temperature while purified nitrogen was flushed through the cell and the input voltage offset of the operational amplifiers was checked and reset when needed. The rotation speed of the

working electrode was set at 26 Hz and then the first scan was run. The scan rate utilized throughout was 70 mV min^{-1} . Two voltammetric scans were run for each metal electrode for the anodic dissolution into (i) the given supporting electrolyte that prevent chemical attack; and (ii) the same electrolyte as in (i) but in addition containing 0.002 M of EDTA. A block diagram of the facilities employed is shown in Fig. 2.

RESULTS AND DISCUSSION

The voltammograms obtained for the anodic dissolution of cobalt, copper, zinc and bismuth are shown in Figs. 3 and 4. There are two curves for each element: one shows the anodic oxidation wave when the process was carried out in the specified supporting electrolyte, curves 1, 3, 5 and 7, and the other when the complexing agent was also present, curves 2, 4, 6 and 8. Curves in Figs. 3 and 4 are the expanded bottom region of the original i - E curves in the scale of 1:4 (the complete curves are not shown since they are irrelevant, as far as the extraction of the kinetic parameters is concerned). This was so to increase the precision of the current and potential readings required for the application of pattern theory and Tafel plots. The curves in Fig. 3 have been scaled down to the ratio 1:2 with respect to the original size. This is not so in Fig. 4.

Deduction of the equations employed for calculating the kinetic parameters by the arbitrary current method will not be presented here and readers are referred to the original paper².

The arbitrary current method provides the following equa-

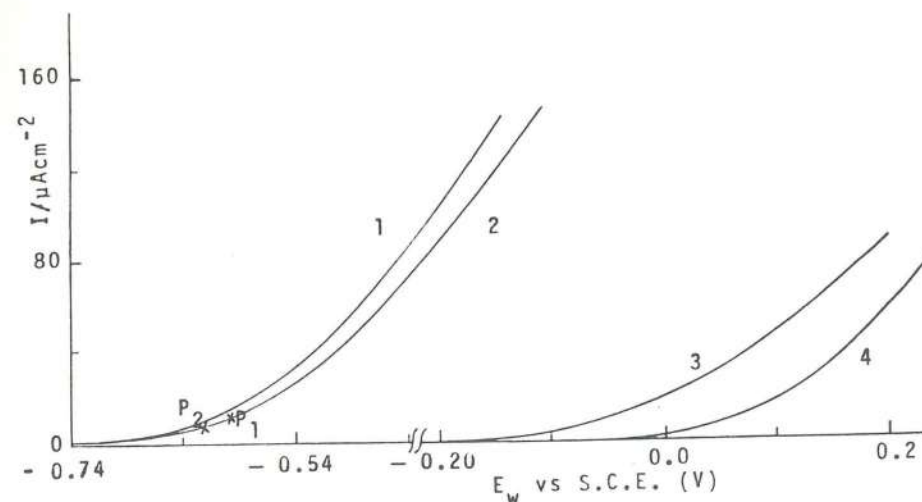


Fig. 3. VOLTAMMOGRAMS FOR THE ANODIC DISSOLUTION OF COBALT AND ZINC. Curves 1 and 3, dissolution of zinc and cobalt into a 10^{-2} M potassium sulphate solution, pH 5.6 for zinc and pH 6 for cobalt. Curves 2 and 4, as for curves 1 and 3, but the solution also $2 \times 10^{-3} \text{ M}$ in EDTA.

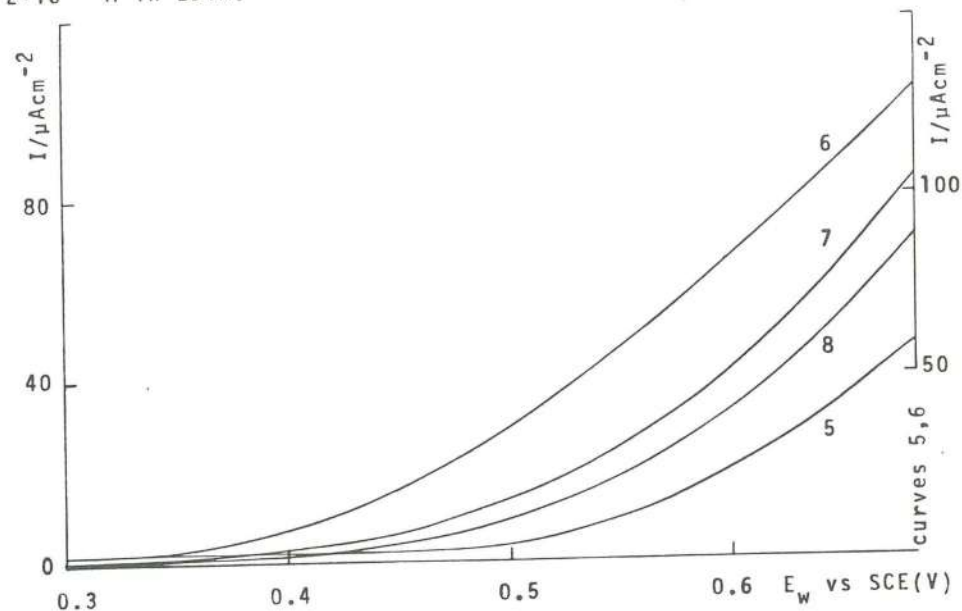


Fig. 4. VOLTAMMOGRAMS FOR THE ANODIC DISSOLUTION OF BISMUTH AND COPPER. Curve 5, bismuth in $3 \cdot 10^{-3} \text{ M HClO}_4$ of pH 2.5; curve 6, as for curve 5, but also $2 \cdot 10^{-2} \text{ M}$ in EDTA. Curve 7, copper in a 10^{-2} M KNO_3 of pH 5.5; curve 8, as for curve 7, but also $2 \cdot 10^{-2} \text{ M}$ in EDTA.

tions to calculate k and β :

$$\log k = \frac{-I_1}{nFA |\text{Red}|_B} - \frac{E_1 - E_0'}{E_1 - E_2} \log \frac{I_1}{I_2} \quad (1)$$

$$\beta = \frac{2.303 RT}{nF(E_1 - E_2)} \log \frac{I_1}{I_2} \quad (2)$$

wherein E_1 , I_1 and E_2 , I_2 are the potential and current values for points P_1 and P_2 , respectively, in Fig. 3; E_0' is the conditional potential taken as the reference potential in the present example; $|\text{Red}|_B$ is the concentration of Red in the bulk of the solution. The other symbols have their usual meaning. This method is valid when the chosen currents I_1 and I_2 are less than 5% of the estimated limiting current, I_L , i.e., $I_1 \ll I_L$ and $I_2 \ll I_L$. Moreover, as I_L is unknown, so is the potential at which solvent oxidation commences and that is the reason why the pair of points to be computed should be selected as close to the foot of the voltammetric curve as possible. Calculation of the kinetic parameters utilizing this method was carried out by taking two successive points at a time and the value of potential and current were substituted into Eqs. 1 and 2. The procedure was repeated for at least two more points. The average k and β so found are included in Table I. Faced to the impossibility of measuring E_0' experimentally, probably due to a minute chemical dissolution of the metals employed, the standard hydrogen electrode (SHE) was chosen as a convenient reference potential instead of E_0' . in expression 1, consequently values of k are reported as k_0 .

Kinetic parameters from Tafel plots were also obtained by taking points in the same region as for the arbitrary current method. The kinetic parameters were obtained from the slope, β , and from the intersection at $\log i_0$ when η_a is zero, k , using a least square program in conjunction with a Sobax ICC-2550E Electronic Calculator. Once again η_a , the charge transfer overpotential, has been expressed with respect to the SHE.

A summary of the values found for k_0 and β using the arbitrary current method and Tafel plots is presented in Table I. The close agreement between both methods can be appreciated thereof.

The values of β show a definite pattern: they are larger in the presence of EDTA. This effect has been ascribed to a decrease of the energy barrier for the anodic process, $nFBE$, due to adsorption of the complexing agent on the electrode surface. Since $nFBE$ is the amount by which this barrier is lowered then, for a given set of conditions, the larger the value of β the lower the energy barrier to pass over. In the present case the increase in β in the presence of the chelating agent has been interpreted as a result of the direct reaction between the anodically released metal ion and adsorbed EDTA. The complex formation at the metal/solution boundary thus enhances the electron transfer process. This assumption has been corroborated by comparing the values of $\Delta(n\beta)$, i.e., the difference between $(n\beta)$ in the presence and in the absence of the complexing agent, and the conditional formation constant, $K_{M,Y}^9$, of the metal complexes involved. This values are included in Table II, along with the working pH utilized. From there it can be inferred that $\Delta(n\beta)$ increases as $K_{M,Y}^9$ increases; moreover, $\Delta(n\beta)$ for copper(II) is significantly larger than for the rest of the metals studied

TABLE I. Electrode Kinetic Parameters

METAL	METHOD	MEDIUM	pH	β	$n\beta$	$-\log k_0$ (k_0 in cm s^{-1})
COBALT	ACM	K_2SO_4	6.0	0.23	0.46	10.6
		K_2SO_4 +EDTA	6.0	0.27	0.54	12.6
	TP	K_2SO_4	6.0	0.23	0.46	10.6
		K_2SO_4 +EDTA	6.0	0.27	0.54	12.6
COPPER	ACM	KNO_3	5.5	0.19	0.38	9.3
		KNO_3 +EDTA	5.5	0.26	0.52	10.5
	TP	KNO_3	5.5	0.19	0.38	9.3
		KNO_3 +EDTA	5.5	0.26	0.52	10.5
ZINC	ACM	K_2SO_4	5.6	0.26	0.52	10.4
		K_2SO_4 +EDTA	5.6	0.29	0.58	10.9
	TP	K_2SO_4	5.6	0.26	0.52	10.4
		K_2SO_4 +EDTA	5.6	0.29	0.58	10.9
BISMUTH	ACM	HClO_4	2.5	0.13	0.39	10.2
		HClO_4 +EDTA	2.5	0.16	0.48	9.7
	TP	HClO_4	2.5	0.14	0.42	10.2
		HClO_4 +EDTA	2.5	0.16	0.48	9.7

ACM: Arbitrary Current Method

TP : Tafel Plots

(roughly twice as much) and so is the $K_{\text{Cu},\gamma}$, (about two orders of magnitude). This correlation supports our assumption since for the other metals $K_{\text{M},\gamma}$'s are quite close to one another and so are the values of $\Delta(n\beta)$'s. In addition, the sequence of the $\Delta(n\beta)$'s is in close agreement with that of $K_{\text{M},\gamma}$ in Table II.

TABLE II. RELATIONSHIP BETWEEN $\Delta(n\beta)$ AND $\log K_{\text{M},\gamma}$ [§]

METAL	pH	$\Delta(n\beta)$	$\log K_{\text{M},\gamma}$
Copper	5.5	0.14	13.3
Cobalt	6.0	0.08	11.3
Bismuth	2.5	0.07	11.3
Zinc	5.6	0.06	11.0

$$^{\S} \log K_{\text{M},\gamma} = \log K_{\text{MY}} - \log \alpha_{\gamma(\text{H})} - \log \alpha_{\text{M}(\text{OH})}^9$$

If no electrode complications are assumed by the presence of the complexing agent the k_0 values found for the same metal in a solution containing just the selected supporting electrolyte and a solution that in addition to the supporting electrolyte contains also EDTA, respectively, should be essentially the same since the kinetics of the charge transfer process should not be disturbed: EDTA would react just chemically with the anodically released metal ion. But this is not so and k_0 decreases in the presence of EDTA for all metals, except for Bi(III) that increases. This fact is contradictory with

the previous interpretation, namely that the electron transfer is enhanced due to the direct formation of the complex on the electrode surface. A likely explanation to this discrepancy is to assume that the low value of k_0 obtained when EDTA is present has been brought about by a reduction of the effective area of the electrode surface owing to adsorption of the metal-EDTA complex formed on it. Consequently, the experimental value found for k_0 represents actually an apparent rate constant rather than a real one. Specific adsorption of some metal-EDTA complexes have been studied by Anson et al.^{6,7,8}, which showed that Co(II)- and Co(III)-EDTA are strongly adsorbed on mercury and platinum electrodes. From the ratio $k_0/k_{0\text{EDTA}}$, i.e., without and with EDTA, calculated (Table III) it can be inferred that Co(II)-EDTA is the most strongly adsorbed compound as well, if the values of the $k_0/k_{0\text{EDTA}}$ ratios are supposed to represent an estimate of the adsorbability of the substance on the electrode surface.

TABLE III. $k_0/k_{0\text{EDTA}}$ SEQUENCE[§].

METAL	Cobalt	Copper	Zinc	Bismuth
$k_0/k_{0\text{EDTA}}$	91.2	13.5	2.8	0.3

[§] values based upon the arbitrary current method in Table I.

From Table III the following sequence can be established

Co(II)-EDTA > Cu(II)-EDTA > Zn(II)-EDTA > Bi(III)-EDTA

The same sort of sequence exists for the transition metal

character of the metal ions under survey: Co(II) with a d^7 configuration is a typical transition metal ion; Cu(II) with a d^9 structure is the next typical transition metal ion; Zn(II) with three complete orbitals, d^{10} configuration, presents only few of the properties associated to a transition metal ion; and finally Bi(III) with a $6s^2$ configuration presents none of the properties of a transition metal ion. It seems therefore that a relationship between the transition metal character of the ion involved in the metal chelate and the extension of the adsorption of the complex on the electrode surface exists. It may be postulated thus that apparent inhibition of the charge transfer due to adsorption increases as the transition metal character of the metal-ion involved increases. The low value found for the ratio $k_0/k_{0\text{EDTA}}$ for Bi(III)-EDTA is consistent with the abovementioned interpretation. In fact, the figure 0.3 points to absence of adsorption and consequently apparent inhibition of the charge transfer process is totally prevented. Lack of adsorption yields a $k_{0\text{EDTA}}$ which is larger than k_0 without EDTA as expected, i.e., k_0 follows the increase in β , and the so obtained k_0 represents a real value for an electrode free of adsorbate.

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