

KALOUSEK POLAROGRAPHIC STUDY OF Co(II) IN BRITTON-ROBINSON MEDIA

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ABSTRACT

The polarographic behaviour of Co(II) in Britton-Robinson media is studied by Kalousek's polarographic methods. The experimental contribution at the study of the reduction of Co(II) and re-oxidation of Co(0), mechanism which takes place on the d.m.e. , is discussed. The α_c and α_a values correspond to processes where monoelectronic transfer steps are coupled with chemical-physical steps.

INTRODUCTION

The polarographic reduction of Co(II) has been taken as a pattern of an irreversible process¹⁻⁶. In the present work, we show results obtained by Kalousek polarography⁷⁻¹¹ in the study of cation Co(II) in Britton-Robinson buffer media. The objective is verify if the pattern that explains electrochemical oxidations and reductions of some organic substances, in base to a sucession of monoelectronic transfer steps coupled with quick chemical-physical steps, also is valid for processes that involve the cation Co(II).

EXPERIMENTAL

A Polarecord E-506 (Metrohm S.A.) polarograph was used for dc, K₁, K₂, K₃ and K₄ techniques of controlled drop time. Potentials were measured with respect to the following reference electrode : Ag/AgCl(s), KCl(sat.). An auxiliary Ag/AgCl(s),KCl(sat.) electrode was used also. The pH value was measured with a grade of accuracy of ± 0.01 units, with the aid of a Radiometer PHM-62 pH-meter.

Solutions were thermostated at 298 ± 0.2 K. All solutions were prepared with reagents grade Merck and distillate water. The stock of the depolarizer was prepared dissolving CoCl₂ (reagent grade Merck).

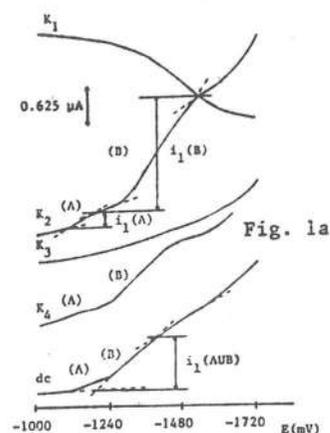


Fig. 1a

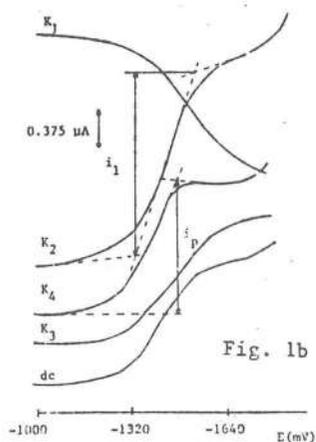


Fig. 1b

Morphology of Co(II) waves and measure criteria.

- a) 0.01% of gelatine.
 - b) 0.01% of Triton-X.
- $T=303\text{ K}$, $c=4.10^{-4}\text{ M}$, $\text{pH}=7.3$, $I=0.5\text{ M}$, $t=0.4\text{ s}$, $m=0.88\text{ mg}\cdot\text{s}^{-1}$, $f_k=150\text{ Hz}$
 $U_{pb}(K_1) = -1.500\text{ mV}$,
 $U_{pb}(K_2) = -1.200\text{ mV}$.

Gelatine and Triton-X, used for these studies, had a concentration of 0.01% in the final solution. Britton-Robinson buffer solutions^{12,13} have been prepared like it has already been described previously¹⁴.

The amplitude of Kalousek polarography is determined by the initial and final voltage (U_{start} , $U_{\text{start}} + \Delta U$) of the step. For K_1 (anodic recorder) and K_2 (cathodic recorder) methods, the pulse base voltage is adjusted. In the base of K_3 (anodic recorder) and K_4 (cathodic recorder) methods, the pulse amplitude superposed to dc sweep is fixed at 50 mV.

The cathodic ($n\alpha_c$) and anodic ($n\alpha_a$) parameters were obtained from the semilogarithmic treatment of K_1 and K_2 waves, respectively, according to the following equations:

$$\ln(i/i_1 - i) = \frac{n\alpha_c F}{RT} (E - E_{1/2}^r) \quad (1)$$

$$\ln(i/i_1 - i) = \frac{n\alpha_a F}{RT} (E - E_{1/2}^r) \quad (2)$$

similarly to the treatment of dc waves^{15,16}.

Measure criteria are shown in Fig. 1a and 1b.

RESULTS AND DISCUSSION

In the presence of gelatine as suppressor of polarographic maxima, the same pre-wave observed in dc polarography¹⁻⁴ can be recorded by Kalousek cathodic polarography (K_2 and K_4). However, using Triton-X that pre-wave can be eliminated and

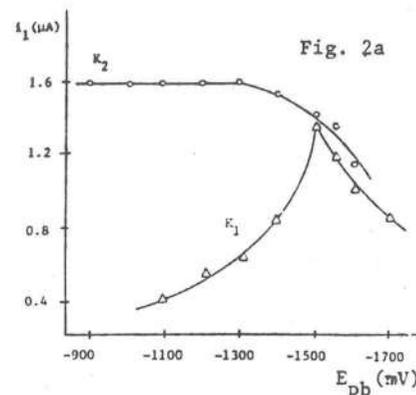


Fig. 2a

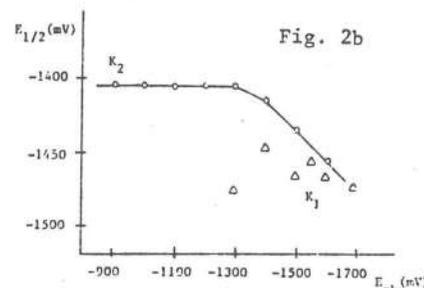


Fig. 2b

Effect of the selected pulse base on (a) $i_{1,p}$ and (b) $E_{1/2,p}$ of Co(II) waves. $T=298\text{ K}$, $\text{pH}=7.02$, $c=4.10^{-4}\text{ M}$ (0.01% Triton-X), $I=0.5\text{ M}$, $m=0.88\text{ mg}\cdot\text{s}^{-1}$, $t=0.6\text{ s}$, $f_k=75\text{ Hz}$.

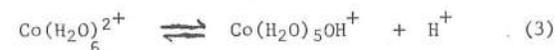
a single wave is recorded corresponding to the reduction process of Co(II).

In Britton-Robinson buffer media, the existence of Co(II) can be admitted in the form of hexahydrated complex⁶ $\text{Co}(\text{H}_2\text{O})_6^{2+}$, since none of present components in the solution (PO_4^{3-} , CH_3COO^- , BO_3^{3-} , Cl^-) form stable complexes with Co(II).

While these solutions were studied by Kalousek polarography (K_1 and K_2 with variable pulses, K_3 and K_4 with constant pulses), it was observed that neutral or slightly basic pH and in the presence of gelatine as suppressor of polarographic maxima, a small pre-wave (A) observed by Brdicka in dc polarography was recorded displaced +0.2 V from that corresponding to the reduction wave of Co(II), wave (B). This pre-wave is recorded by K_2 reduction technique in the range $5^\circ\text{C} < T < 50^\circ\text{C}$, while in K_4 and dc reduction techniques this wave is recorded at temperatures higher than 30°C . With oxidation techniques, only one wave (K_1) is recorded or else the dc component of the overall process (K_3) (fig. 4).

According to Brdicka's studies^{1,2}, this pre-wave (A) is due to a partial dehydration of the complex $\text{Co}(\text{H}_2\text{O})_6^{2+}$.

The following equilibrium:



is established slowly.

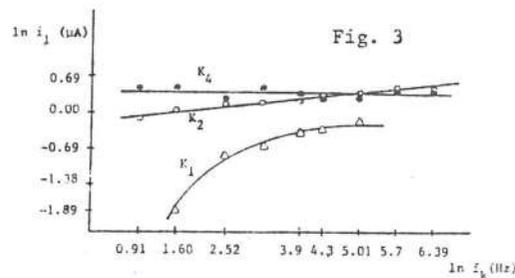


Fig. 3

Effect of the pulse frequency on $i_{1,p}$ of Co(II) waves. $T=298\text{ K}$, $c=4.10^{-4}\text{ M}$ (0.01% gelatine), $\text{pH}=7.02$, $I=0.5\text{ M}$, $m=0.88\text{ mg}\cdot\text{s}^{-1}$, $t=0.4\text{ s}$, $U_{pb}(K_1)=-1500\text{ mV}$, $U_{pb}(K_2)=-1200\text{ mV}$.

The amplitude of applied pulses to the K_1 and K_2 recorders has influence not only on the current intensities (fig. 2a), but also on half-wave potentials (fig. 2b). We have worked with values of pulse base (U_{pb}) previously fixed to obtain well defined and reproduced waves.

A quantitative relation between $i_1(K_1)$ and the pulse frequency (f_k) could not be established (fig. 3). The current intensity of K_2 waves fulfills the following experimental equation :

$$i_1(K_2) = a + b f_k^{1/6} \quad (4)$$

The K_4 waves are not dependent of the frequency.

We have studied the effect of drop time from $t=0.4\text{ s}$ to $t=2\text{ s}$, on Kalousek's polarographic waves of Co(II) :

a) In the presence of Triton-X, $i_1(K_1)$ and $i_1(K_2)$ values depend on $t^{1/3}$ being this dependence lower than the one established by Ruzic's expression¹¹ for a reversible process, while $i_1(K_4)$ depends approximately on $t^{1/6}$, in accordance with Ilkovic's expression (Table 1a).

b) When gelatine is used as suppressor of maxima, the influence of drop time is similar to the previous results (Table 1b).

Nevertheless, it has been proved that in the presence of small traces of Triton-X the pre-wave (A) is not detected, and only the wave (B), characteristic of the cation Co(II) (fig. 1b), is recorded. The K_3 waves present only dc component such as it is corresponding to an irreversible process¹⁷. For this reason, we will abstain to study K_3 waves since they do not provide information about re-oxidation processes of the depolarizer.

Table 1a.- Effect of drop time on Kalousek waves of Co(II).

$T=298\text{ K}$, $c=4.5.10^{-4}\text{ M}$ (0.01% Triton-X), $\text{pH}=7$, $I=0.5\text{ M}$, $m=0.88\text{ mg}\cdot\text{s}^{-1}$, $f_k=75\text{ Hz}$, $U_{pb}(K_1)=-1500\text{ mV}$, $U_{pb}(K_2)=-1200\text{ mV}$, $0.4 < t < 2\text{ s}$.

	$\ln i_{1,p}(\mu\text{A}) = a + b \ln t(\text{s})$			$E_{i/2,p}(\text{mV}) = a' + b' \ln t(\text{s})$		
	a	b	c	a'	b'	c'
K_1	0.07	0.34	0.99	-1470	14.2	0.99
K_2	0.69	0.32	0.99	-1427	20.3	0.99
K_4	0.26	0.23	0.99	-1518	19.3	0.99

Table 1b.- Effect of drop time on Kalousek waves of Co(II).

$T=298\text{ K}$, $c=4.10^{-4}\text{ M}$ (0.01% gelatine), $\text{pH}=7$, $I=0.05\text{ M}$, $m=0.88\text{ mg}\cdot\text{s}^{-1}$, $f_k=75\text{ Hz}$, $U_{pb}(K_1)=-1500\text{ mV}$, $U_{pb}(K_2)=-1200\text{ mV}$.

	$\ln i_1(\mu\text{A}) = a + b \ln t(\text{s})$			$E_{i/2}(\text{mV}) = a' + b' \ln t(\text{s})$		
	a	b	c	a'	b'	c'
K_1	1.500	0.38	0.99	-1457	29.3	0.99
$i_{1/2}(A)$	0.620	0.22	0.99	-1183	17.0	0.99
$E_{1/2}(E)$	2.200	0.33	0.99	-1393	27.1	0.99
K_4	1.057	0.15	0.99	-1323	34.2	0.99

In all techniques, values of current intensities are proportional to $h_{\text{curr}}^{2/3}$, namely to the surface of the mercury drop; and the small deviation observed is attributed to the effect of the charging current¹⁸.

In despite of the irreversibility of the electrodic process, K_1 , K_2 and K_4 polarographic waves of Co(II) can be used analytically in the range of concentrations from 10^{-5} M to 4.10^{-4} M . In this inter-

val, the half-wave potential or peak potentials are not dependent with the concentration of Co(II) (Table 2).

Table 2.- Effect of the concentration of Co(II) on $i_{1,p}$.
 T=298 K, 0.01% Triton-X, pH=6.98, I=0.5 M,
 m=0.88 mg.s⁻¹, $f_k=75$ Hz, $U_{pb}(K_1)=-1500$ mV,
 $U_{pb}(K_2)=-1200$ mV.

	$\ln i_{1,p} (\mu A) = a + b \ln c (M)$			$E_{1/2,p} (mV)$
	a	b	c	
dc	6.1	1.00	0.99	-1435
K ₁	4.8	0.95	0.98	-1485
K ₂	5.9	0.96	0.99	-1445
K ₄	6.3	1.10	0.99	-1535

The influence of the temperature on waves in a solution of Co(II) has been studied, using gelatine as suppressor of maxima, in order to analyse the evolution of pre-wave (A) and wave (B) recorded in cathodic processes. It was observed (fig. 4) that pre-wave (A) is detected by K₂ polarography during all the studied interval (5°C < T < 50°C), while it begins to become discernible by dc and K₄ techniques at temperatures higher than 30°C approximately. Relations between $\ln i_{1,p}$ vs. 1/T and $E_{1/2,p}$ vs. T were analysed and calcula of activation energies (Q) were made in processes associated with recorded waves of Co(II) by dc and Kalousek polarography in accordance with the following Arrhenius expressions¹⁹ :

$$i_1 = A \cdot \exp (-Q/RT) \quad (5)$$

$$i_p = A \cdot \exp (-Q/RT) \quad (6)$$

Table 3.- Effect of the temperature on $i_{1,p}$ of Co(II) waves and activation energy values.
 c=4.10⁻⁴ M (0.01% gelatine), pH=7, I=0.5 M,
 m=0.88 mg.s⁻¹, t=0.4 s, $f_k=75$ Hz,
 $U_{pb}(K_1)=-1500$ mV, $U_{pb}(K_2)=-1200$ mV.

		$\ln i_{1,p} (\mu A) = a + b.1/T (K)$			Q (Kcal/mol)
		a	b	c	
dc (AUB)	5°C<T<50°C	4.08	-1280	0.99	2.5
dc (A)	T>30°C	23.23	-7701	0.99	14.2
dc (B)	T>30°C	-4.30	1125	0.99	-2.2
K ₁	T>30°C	5.20	-1631	0.99	3.0
	T<30°C	9.58	-2929	0.98	5.4
K ₂ (AUB)	T>30°C	1.35	-219	0.99	0.4
	T<30°C	3.60	-904	0.99	1.8
K ₂ (A)	5°C<T<50°C	9.94	-3250	0.98	5.9
	T>30°C	-4.18	1371	0.99	-2.5
K ₂ (B)	T<30°C	3.13	-813	0.99	1.5
K ₄ (AUB)	5°C<T<50°C	4.24	-1264	0.98	2.3
K ₄ (A)	T>30°C	25.68	-8415	0.99	15.5
K ₄ (B)	T>30°C	-0.87	246	0.99	-0.5

According to the Q obtained values, it is evident that the pre-wave (A) is controlled by a chemical step, probably due to the dehydration reaction (3) of the complex $Co(H_2O)_6^{2+}$ which is favoured by the presence of gelatine (Table 3). The disimintion in the intensity value of wave (B) with the increase of the temperature is due to the progressive increase experimented by the pre-wave (A) (fig. 4). As for the complete process (wave A U B), calculated activation energies show that the process is controlled by diffusion (Table 3). The re-oxi-

dation process associated with the anodic wave (K_1) is controlled by diffusion (Table 3).

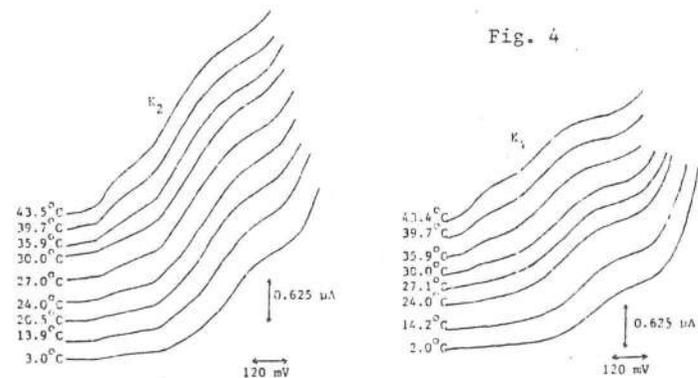
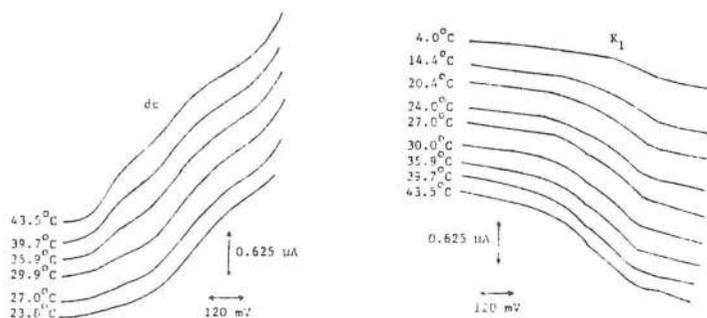


Fig. 4

Fig. 4.- Effect of the temperature on the morphology of Kalousek and dc waves of Co(II). $c=4.10^{-4}$ M (0.01% gelatine) , $I=0.5$ M , $pH=7.02$, $m=0.88$ $mg \cdot s^{-1}$, $f_k=150$ Hz , $t=0.4$ s , $U_{pb}(K_1)=-1500$ mV , $U_{pb}(K_2)=-1200$ mV.

Applying equations (1) and (2) to K_1 and K_2 waves, the $n\alpha_c = n\alpha_a = 0.5$ values are obtained and taking into account that the electrodic process of Co(II) involves two moles of electrons per mole of depolarizer, this behaviour corresponds to a totally irreversible process.

The presence of gelatine favours the electrodic process associated to the pre-wave (A), due this substance possesses amino groups which act as active centers capable of interacting with Co(II) present on the electrode, so that the reaction (3) is favoured.

Both pre-wave (A) and wave (B) appear to involve two moles of electrons per mole of depolarizer, although it is admitted that they are processes with mono-electronic transfer steps where chemical and physical steps are inserted.

Devanathan's expression²⁰ :

$$j_c = n\alpha_c + 1/2 \quad (7)$$

is satisfied by K_2 cathodic waves of Co(II). The determinant step of reduction process is the first mono-electronic transfer, $j_c = 1$, in the experimental conditions tried. By means of anodic Devanathan's expression :

$$j_a = n - n\alpha_a + 1/2 \quad (8)$$

values of the determinant mono-electronic transfer step, $j_a = 2$, are calculated from K_1 waves. This shows that the determinant step of re-oxidation process is the second mono-electronic transfer. As reduction process of Co(II) as oxidation of Co(0) can be explained by mono-electronic transfers coupled with chemical-physical process.

The $n\alpha_a$ values have been corroborated also by Voltammetry on Kemula electrode. Also, The $n\alpha_c = 0.5$ values have been obtained by this method and "dc", "np", "dp", "ac 1" and "ac 2" polarography.

The $n\alpha$ values obtained for another divalent cations²¹ in different media, can be proved in the base of a model in which mono-electronic transfer steps and chemical-physical steps are coupled, like structural changes at the interface, transport, solvation changes and others.

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POSSIBILITIES OF VOLTAMMETRIC METHODS
FOR SPECIATION IN THE PRESENCE OF PARTICLES

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ABSTRACT

Differential pulse polarography and anodic stripping voltammetry can be used directly in suspensions without pre-filtration; heavy metals like copper(II) and lead(II) adsorbed on hydrous oxides such as silica and α -goethite are not being released during the time scale of the techniques and are thus not sensed by these techniques.

In samples with colloids and organics such as EDTA and NTA in the presence of heavy metals, when the complexes are non-labile but electrochemically reducible at a more negative potential, one can determine the ligand concentration and the binding capacity of the colloid from the voltammetric measurements of individual batches with different amounts of cations like copper(II) and lead(II).

From the differential pulse measurements of solutions with heavy metals and the organic ligands EDTA and NTA, it is possible to know directly the amount of metal bound to each one of the ligands and the free cation. This can also be determined by anodic stripping voltammetry at different deposition potentials.