Electrosynthesis of cobalt (III) ions in concentrated H_3PO_4 medium

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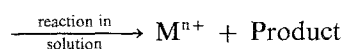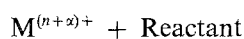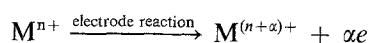
The electrosynthesis of cobalt(III) ions from cobalt(II) ions has been studied in 29, 57 and 85 wt % H_3PO_4 solutions. It has been shown that the conversion of Co(II) to Co(III) is limited by the chemical reaction between Co(III) ions and water. A kinetic study demonstrated that this reaction becomes more rapid as the Co(III) ion concentration increases. In order to find the best conditions for the electrolysis, the effect of some experimental parameters on the current yield and the chemical efficiency has been examined. A comparison between gold and platinum anodes has also been made. The following conditions were found to be the best: anode material, gold; initial Co(II) ion concentration, 5×10^{-3} M; solvent, 85 wt % H_3PO_4 solution; current density, 1 mA cm^{-2}; temperature, 20–30°C. Under these conditions the maximum value of current yield, and chemical efficiency are 66% and 48% respectively.

L'electrosynthèse des ions cobalt(III) à partir des ions cobalt(II) a été étudiée dans les solutions H_3PO_4 29, 57, et 85% en masse. Il a été montré que la conversion de Co(II) en Co(III) est limitée par la réaction chimique entre les ions Co(III) et l'eau. Une étude cinétique a montré que cette réaction devient plus rapide au fur et à mesure que la concentration de l'ion Co(III) augmente. Dans le but de trouver les conditions favorables pour l'electrolyse, l'effet de certains paramètres expérimentaux, sur les rendements électrique et chimique, a été examiné. Les résultats obtenus avec une anode en or et une anode en platine ont été comparés. Les conditions d'électrolyse suivantes ont été retenues: le matériau de l'anode, Au; concentration initiale de l'ion Co(II), 5×10^{-3} M; solvant, solution H_3PO_4 85% en masse; densité de courant, 1 mA cm^{-2}; température, 20–30°C. Dans ces conditions, les valeurs des rendements faradique et chimique maximum sont respectivement de 66% et 48%.

1. Introduction

There is considerable industrial interest in the electrochemical generation of powerful ionic oxidants such as silver(II), thallium(III), cerium(IV), manganese(IV) and lead(IV) from their stable lower oxidation states, and the subsequent reaction of these species with compounds not directly oxidized by electrolysis [1]. The subsequent reaction may be carried out either *in situ* in the electrochemical cell or in a separate reactor. In the latter case, the electroactive ion should be recycled after the chemical reaction so that, in each case, the overall reaction sequence is:

$$M^{n+} \xrightarrow{\text{electrode reaction}} M^{(n+\alpha)+} + \alpha e$$

$$M^{(n+\alpha)+} + \text{Reactant}$$

$$\xrightarrow[\text{solution}]{\text{reaction in}} M^{n+} + \text{Product}$$

Because of the high value of the equilibrium potential of the Ag(II)/Ag(I) system ($E_0 = 1.98$ V vs NHE), silver(II) is successfully used to oxidize organic compounds of pharmaceutical interest [1, 2]. Ag(II) is also used in the titration of mineral ions in their high oxidation state [3–7]. However, its use proves to be limited because of the high price of silver. The equilibrium potential of the Co(III)/Co(II) system is 1.82 V vs NHE [8]. Consequently, cobalt(III) can be used as a powerful oxidant instead of silver(II). Thus, several authors have investigated the kinetics of the reaction between Co(III) ions and organic compounds such as aldehydes, olefines, acids and alcohols [10–14].

In previous work [15] it was shown, using voltamperometry and chronopotentiometry, that in phosphoric acid medium, Co(II) can be oxidized to Co(III) in a fast reaction at a gold electrode. The oxidation potential of Co(II) in 96.5 wt % H_3PO_4 was

reported to be about 1.662 V vs SCE and this high value indicates the possibility of the use of Co(III) as a powerful oxidant in phosphoric acid medium.

The subject of the present paper is to establish the best experimental conditions to convert Co(II) to Co(III) by electrolysis in H_3PO_4 solutions.

2. Experimental details

The electrogeneration of Co(III) from Co(II) was achieved using a PRT 20-2X Tacussel potentiostat. The electrical charge was measured with the aid of a IG5 Tacussel integrator coulometer. The cells had an anodic compartment and cathodic compartment separated by a porous glass separator. The pore diameter was less than $10 \mu m$ in order to minimize diffusion of cobalt ions into the cathodic compartment. The gold and platinum anodes had an area of 25 and $40 cm^2$ respectively. The cathode was a platinum foil $(S = 10 cm^2)$.

The concentration of Co(III) ions in the solution was determined by direct potentiometric titration using gold foil as Co(III) indicator electrode and a standard Fe(II) solution. For dilute solutions, Co(III) ion concentration was determined by back titration with a standard Fe(II) solution. Excess Fe(II) was determined by polarography. The polarograph used was a PRG 5 Tacussel.

The conversion factor, R, was defined as the ratio of the amount of Co(II) converted to Co(III), to the initial amount of Co(II) in the anolyte.

$$R = \frac{[Co(III)]_t}{[Co(II)]_{t_0}} \times 100$$

The faradaic yield, E, was defined as the ratio between the electrical charge, Q, corresponding to the amount of Co(III) produced by electrolysis (calculated from Faraday's law) and the effective charge, Q_{eff}, passed through the cell (given directly by the coulometer).

$$E = \frac{Q}{Q_{eff}} \times 100$$

3. Results and discussion

Cobalt(III) ions are known to be unstable in aqueous solution since they are reduced by water according to the following reaction:

$$4Co(III) + 2H_2O \longrightarrow 4Co(II) + 4H^+ + O_2 \quad (1)$$

The detailed mechanism of this reaction has been the subject of previous research [9, 16, 17]. In the particular case of Co(III) in H_3PO_4/H_2O mixtures, an earlier investigation [15] has shown that the stability of the Co(III) ion increases with increasing H_3PO_4 concentration. In this paper the effect of H_3PO_4 concentration on the kinetics of Co(III) decomposition is examined (Fig. 1). The results show the advantage of 85 wt % H_3PO_4 medium in which the rate of Co(III) reduction is less than the reduction rate in 57 wt % and
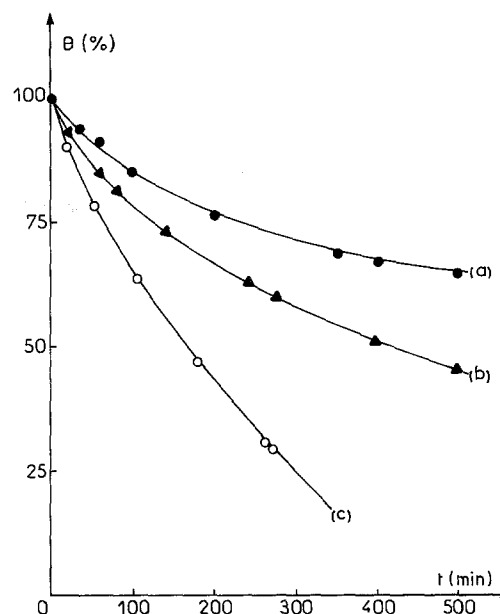

Fig. 1. Influence of H_3PO_4 concentration on θ versus time curves. (a) 85 wt % H_3PO_4; (b) 57 wt % H_3PO_4; (c) 29 wt % H_3PO_4. $[Co(III)] = 1.75 \times 10^{-3} M$ at $t = 0$; $T = 20°C$.

29 wt % H_3PO_4. The use of H_3PO solutions more concentrated than 85 wt % as solvent for the electrogeneration of Co(III) from Co(II) leads to lower values of R and E because of their high viscosity, which limits the diffusion of Co(II) to the anode surface.

The electrolytic oxidation of Co(II) to Co(III) in H_3PO_4 solutions is counteracted by the chemical reduction of Co(III) to Co(II). Consequently, it is not possible to obtain the complete conversion of Co(II) to Co(III) by electrolysis. In an attempt to explain the R and E versus time behaviour of the electrolysis curves, the spontaneous variation of Co(III) concentration with time was plotted (Fig. 2). A decrease in the rate of Co(III) chemical decomposition is observed. When Co(III) concentration is higher than $1.5 \times 10^{-3} M$, the decomposition kinetics are second order with respect to Co(III) ion. In fact, the curve $[Co(III)]^{-1} = f(t)$ is linear (Fig. 3). The kinetic constant value is $K_{II} = (1.4 \pm 0.2) M^{-1} m$: n^{-1}. When the concentration of Co(III) ion is lower than
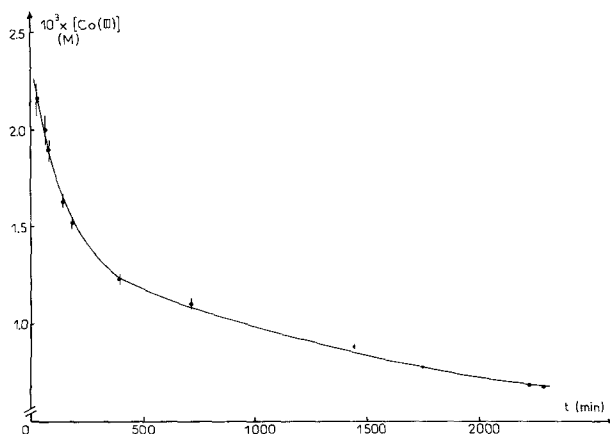

Fig. 2. Variation of Co(III) ion concentration with time in 85 wt % H_3PO_4; $[Co(III)] = 2.5 \times 10^{-3} M$ at $t = 0$; $T = 20°C$.
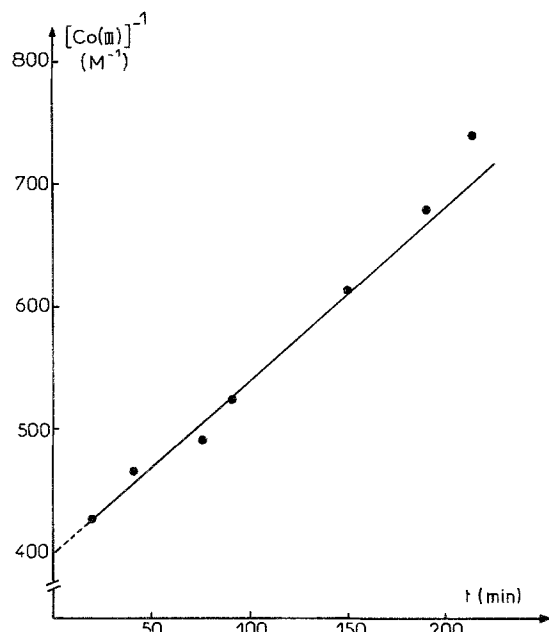
Fig. 3. Variation of Co(III) ion concentration reverse with time in 85 wt % H_3PO_4; [Co(III)] = 1.5 × 10^{-3} M at t = 0; T = 20° C.

Fig. 5. Influence of temperature on the kinetics of Co(III) ion reduction by water. 85 wt % H_3PO_4; [Co(III)] = 1.45 × 10^{-3} M at t = 0. (a) T = 3° C; (b) T = 20° C; (c) T = 30° C; (d) T = 40° C.

1.2 × 10^{-3} M, the curve log [Co(III)] = f(t) is linear (Fig. 4), so the kinetics become first order with respect to the Co(III) ion. The kinetic constant value is K_1 = (3.3 ± 0.3)10^{-4} m: n^{-1}. In the concentration range 1.5 × 10^{-3} M to 1.2 × 10^{-3} M, the kinetics deviate from both first and second order. Similar results were obtained with H_2SO_4 medium [16] and Na_2SO_4/H_2SO_4 mixtures [17].

The kinetic curve, θ = f(t), of the spontaneous decomposition of Co(III) in 85 wt % H_3PO_4 was plotted at 3, 20, 30 and 40° C (Fig. 5). (θ is defined as the ratio $[Co(III)]_t/[Co(III)]_{t_0}$, where $[Co(III)]_t$ is the effective concentration of Co(III) ion in the solution at time t, and $[Co(III)]_{t_0}$ is the initial Co(III) ion concentration (fixed at 1.45 × 10^{-3} M.) Fig. 5 shows that the stability of the Co(III) ion increases as temperature decreases, so the activation energy of the spontaneous reduction of Co(III) by water is positive. At 3° C, Co(III) is completely stable in 85 wt % H_3PO_4 (Fig. 5a).
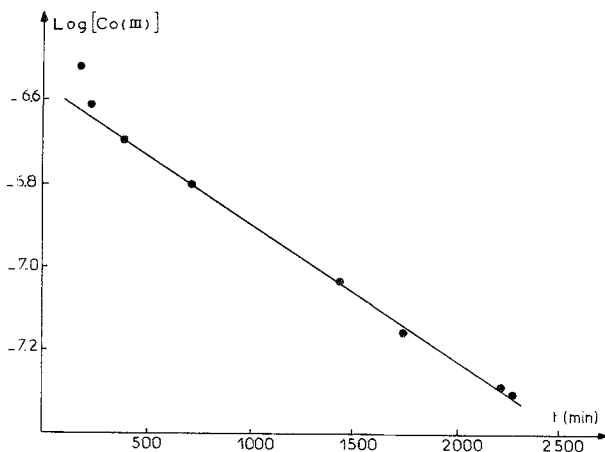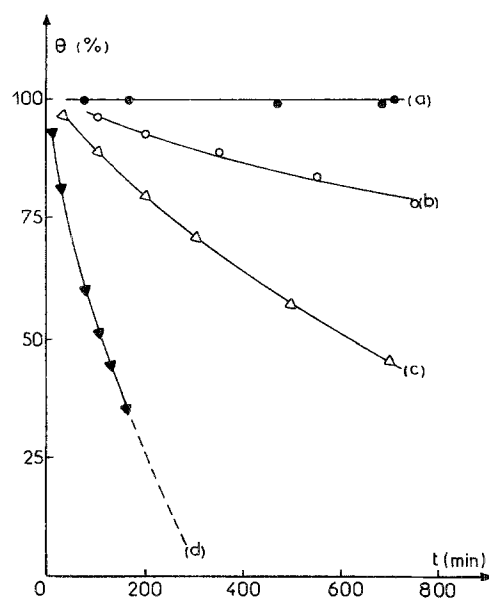
In order to find the best experimental conditions for

the electrosynthesis of Co(III) from Co(II) in 85 wt % H_3PO_4, the effect of some parameters on E and R were studied.

3.1. Effect of temperature

The electrosynthesis of Co(III) ions performed in the temperature range between 0 and 60° C shows that R and E are lower at both high and low temperatures (Fig. 6). Their maximum values obtained were in the range 20 to 30° C. This behaviour may be explained by a more important decrease of the rate of electrochemical oxidation of Co(II) than the rate of chemical reduction of Co(III) when temperature decreases. Therefore, it would be preferable to produce Co(III) ions by electrolysis at temperatures between 20 and 30° C and to decrease immediately the temperature of
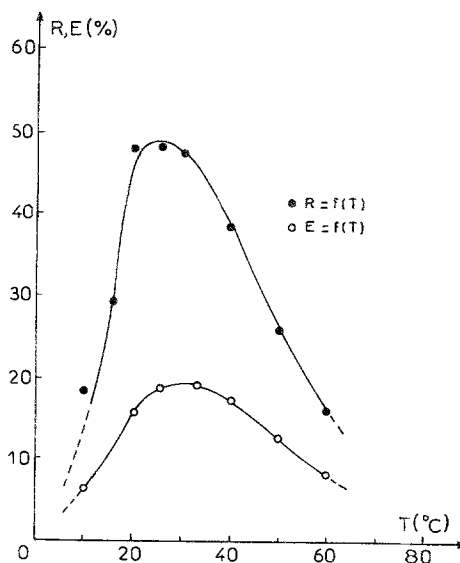

Fig. 4. Variation of log[Co(III)] with time in 85 wt % H_3PO_4; [Co(III)] = 1.2 × 10^{-3} M at t = 0; T = 20° C.

Fig. 6. Variation of conversion factor, R, and faradaic yield, E, with temperature in 85 wt % H_3PO_4.
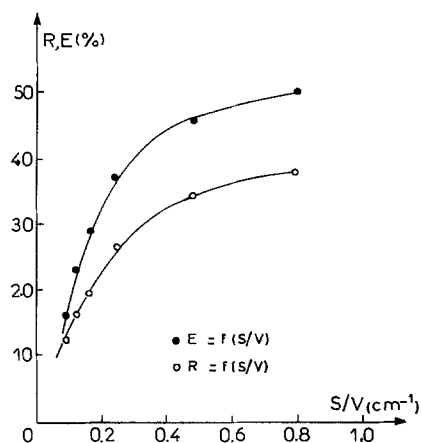
Fig. 7. Variation of conversion factor, R, and faradaic yield, R, with cell ratio, S/V in 85 wt % H_3PO_4; $I = 20\,mA$; $T = 20°C$; initial Co(II) concentration, 2×10^{-2} M.

the solution to $3°C$ in order to stabilize the Co(III) ions in phosphoric acid medium.

3.2. Effect of S/V cell ratio

Fig. 7 shows a plot of the maximum values of R and E versus the cell ratio, S/V (where S is the electrode area in cm^2 and V the volume of the anolyte in cm^3). The initial concentration of Co(II) was 2×10^{-2} M, the anodic current imposed was $20\,mA$ and the temperature was $20°C$.

The efficiency of the electrolysis is enhanced by an increase in the S/V ratio. The best values of R and E were obtained with an S/V ratio of $0.8\,cm^{-1}$ and all the electrolysis were performed with this value of S/V ratio, whereas an industrial electrosynthesis of Co(III) would require a greater S/V ratio.

3.3. Effect of current density

Tests using potentiostatic polarization have shown that although the faradaic yields are good ($E \approx 70\%$), the conversion factors are very low ($R \approx 15\%$)
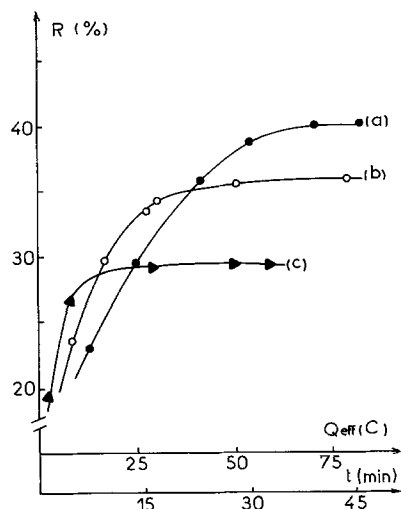

Fig. 8. Variation of faradaic yield, E, with electrolysis duration or total electrical quantity. 85 wt % H_3PO_4; $T = 20°C$; galvanostatic experiment (a) $I = 30\,mA$; (b) $I = 20\,mA$; (c) $I = 10\,mA$.

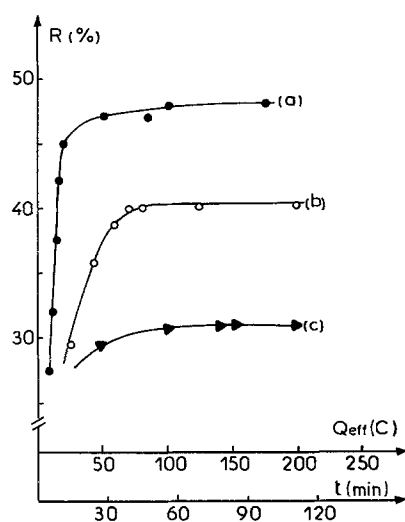Fig. 9. Influence of the initial Co(II) ion concentration on the R versus time curves. 85 wt % H_3PO_4; $i = 1.25\,mA\,cm^{-2}$. Initial Co(II) concentration (M): (a) 5×10^{-3}, (b) 10^{-2}, (c) 2×10^{-2}.

because of the decreasing current density during the electrolysis. In view of the above, the galvanostatic mode was adopted. The experiments were carried out with currents in the range 5–200 mA. The anolyte was a solution of Co(II) ions in 85 wt % H_3PO_4. The initial concentrations of Co(II) were choosen between 10^{-3} and 10^{-1} M. High E values were obtained with lower current densities (Fig. 8). This behaviour can be explained by the fact that the diminution of anodic current density causes a decrease in the anode potential and consequently leads to less evolved oxygen on the anode surface.

The maximum value of R increases as the current density is increased from 5 to 30 mA and stays constant and close to 40%. After long duration electrolysis ($t > 6\,h$), a slight decrease of R is observed and may be attributed to the formation of an increasingly thick oxide layer on the gold electrode during anodic polarization [18, 19].

3.4. Effect of initial Co(II) concentration

The influence of the initial concentration of Co(II) ions on the variation of R and E with the duration, t, of the electrolysis is presented in Fig. 9. Higher values of R are obtained with a lower initial Co(II) concentration. At the same time, the maximal value of E seems not to be modified by the variation of this parameter. A concentration of 5×10^{-3} M appears to be a good value; lower concentration leads to amounts of Co(III) which are too low to have any application in macroanalysis.

3.5. Use of platinum anode

In order to compare with a gold electrode, a platinum anode of $40\,cm^2$ surface area was tested. The volume of the anolyte was $50\,cm^3$ in order to keep the S/V ratio unchanged. The value of the current density was $i = 1\,mA\,cm^{-2}$, slightly lower than the value deter-
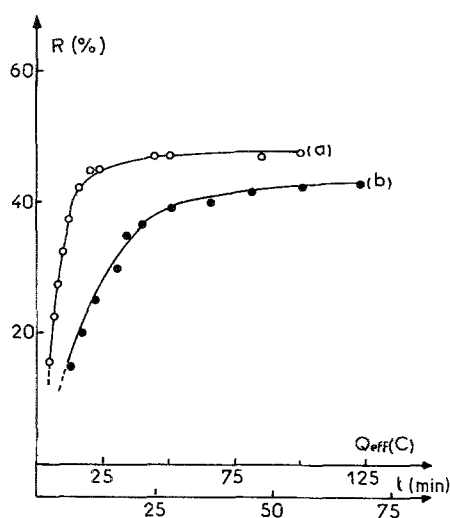
Fig. 10. Influence of anode metal on curves R versus time. 85 wt % H_3PO_4; $T = 20°C$; $S/V = 0.8\,cm^{-1}$; initial Co(II) concentration, 5×10^{-3} M. (a) Gold; (b) platinum.

Table 1. Comparative efficiencies of gold and platinum anodes

H_3PO_4 (wt %)	$E(\%)$ ($Q_{eff} = 10\,C$)		$R(\%)$ ($Q_{eff} = 180\,C$)	
	Au	Pt	Au	Pt
29	16	—	36	32
57	29	9	41.8	39
85	59	31	47.8	46

mined for the gold anode (i.e. $i = 1.25\,mA\,cm^{-2}$). Maximum values of R and E were in the temperature range of 20–30°C and the variation of the initial Co(II) concentration in the anolyte produced the same effects on R and E as those observed with the gold electrode.

In Table I the values of R and E are reported for gold and platinum anodes. Values of E were determined after a short duration electrolysis ($Q_{eff} = 10\,C$) while R values were determined after long duration electrolysis ($Q_{eff} = 180\,C$). For a given H_3PO_4 concentration, the values of R obtained with the two electrodes are close to one another while the E values are clearly lower with platinum. This behaviour is due essentially to the evolved oxygen which appears on platinum at lower potentials than those required with gold. This leads to a more significant energetic loss when a platinum anode is used.

On the $R = f(Q_{eff})$ curve (Fig. 10), it is observed that an electrical quantity, $Q = 110\,C$, is required to obtain an R value equal to 43%, whereas only 45 C are required with gold. This observation leads to the conclusion that the use of a gold anode leads to higher faradaic yields and faster kinetics of Co(II) oxidation.

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