CROATICA CHEMICA ACTA CCACAA 49 (4) 751—756 (1977)

YU ISSN 0011-1643
CCA-1048 541.138
Original Scientific Paper

Chronopotentiometric Studies of a Preceding Chemical Reaction of Second Order: Ti(IV) in SCN$^-$ Solution

M. Vuković and V. Pravdić

Laboratory of Electrochemistry and Surface Phenomena, Center for Marine Research, »Ruđer Bošković« Institute, 41001 Zagreb, Croatia, Yugoslavia

Received May 18, 1977

The case of a preceding chemical reaction in a chronopotentiometric experiment under second order conditions was studied by digital simulation and experimental verification. Chronopotentiometry is sensitive enough to distinguish second from pseudo-first order preceding chemical reaction, only when the ligand ion concentration is less than five times higher than the electroactive metal ion concentration. These findings are based on experiments of reduction of Ti(IV) in thiocyanate solutions.

INTRODUCTION

The aim of the present paper is to study how a preceding chemical reaction is seen in a chronopotentiometric experiment. The case is described when the concentration of the complex forming ligand is comparable with the electroactive metal ion concentration, i. e. when the reaction proceeds under second order kinetic conditions. It is also the aim of this work to determine the limits of sensitivity for the range of ligand concentrations of 2 to 100 times that of the electroactive metal ion.

The complexation equilibrium is defined as

$$\mathrm{M} + \mathrm{X} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{MX} + e \rightarrow \mathrm{P} \tag{1}$$

where M is the free metal ion, X is the ligand, MX is the electroactive metal complex, and P the product. The solution of Delahay and Berzins[1] for the conditions of a galvanostatic experiment in the case of the pseudo-first order preceding chemical reaction (X in excess) is:

$$i_0 \tau^{1/2} = \frac{nF(\pi D)^{1/2} C^*_{\mathrm{CM}}}{2} - \frac{\pi^{1/2} i_0}{2K C^*_{\mathrm{X}} (k_1 C^*_{\mathrm{X}} + k_2)^{1/2}} \operatorname{erf}[(k_1 C^*_{\mathrm{X}} + k_2)^{1/2} \tau^{1/2}] \tag{2}$$

where τ is the transition time, i_0 the current density; C^*_{X} is the ligand concentration, C^*_{CM} is total (analytical) concentration of the metal ion, and $K = k_1/k_2$.

Plot of the chronopotentiometric parameters $i_0\tau^{1/2}$ vs. i_0, gives a straight line, when the argument of the error function is greater than 2 (the error function becomes unity). From the slope the value of $(k_1 C^*_{\mathrm{X}} + k_2)$ can be calculated. Independent knowledge of the equilibrium constant K is necessary to calculate the rate coefficients k_1 and k_2. At high current densities the chronopotentiometric parameter becomes constant again[2] and if this condition can be achieved experimentally, K can be determined. However, this is often not the case, as double layer charging becomes a limiting factor in the millisecond range of transition times.

Koutecky and Čižek[3], and Fischer, Dračka, and Fischerova[4] solved the problem of preceding monomerization reaction of the type $B \rightleftharpoons 2A + e \rightarrow C$ in a galvanostatic experiment. It was assumed that the chemical reaction was fast and the equilibrium was shifted towards dimer formation. A solution was obtained where the plot of $i_0\tau^{1/2}$ vs. $i_0^{4/3}$ gives a straight line, from which the quotient k_1/K can be obtained. In this case, also, independent knowledge of K is necessary to calculate the rate coefficient.

EXPERIMENTAL

Instrumentation used in present chronopotentiometric experiments was described earlier[5,6]. Chronopotentiograms were recorded on a Hewlett-Packard 7100 strip chart recorder, or for short transition times, on the screen of a Tektronix 564B storage oscilloscope. Transition times were corrected for double layer charging by recording chronopotentiograms for the supporting electrolyte solutions including the complex forming agent.

The cell with mercury pool electrode, saturated calomel, and platinum counter electrode was of conventional design[7]. Sodium thiocyanate (Kemika, Zagreb) was recrystallized once from aqueous solution, perchloric acid (Merck, Darmstadt) and $TiCl_4$ (Johnson, Matthey and Co., London) were used without further purification. Ti(IV) thiocyanate solutions were prepared immediatelly prior to the experiment from corresponding stock solutions. Mercury was cleaned chemically and twice distilled in vacuo. Extra pure nitrogen for deoxygenation of solutions was passed through a BTS copper catalyst. All experiments were done at (25 ± 0.1) °C.

Computational Methodology

The partial differential equations, describing changes of concentrations of all species in eq 1, as function of time and distance from the electrode, are:

$$\frac{\partial C_{MX}(x, t)}{\partial t} = D_{MX}\frac{\partial^2 C_{MX}(x, t)}{\partial x^2} + k_1 C_M C_X - k_2 C_{MX} \tag{3}$$

$$\frac{\partial C_M(x, t)}{\partial t} = D_M\frac{\partial^2 C_M(x, t)}{\partial x^2} - k_1 C_M C_X + k_2 C_{MX} \tag{4}$$

$$\frac{\partial C_X(x, t)}{\partial t} = D_X\frac{\partial^2 C_X(x, t)}{\partial x^2} - k_1 C_M C_X + k_2 C_X \tag{5}$$

The boundary conditions for a chronopotentiometric experiment (constant current flux) in the case of a one-electron electrode reaction are:

$$t > 0 \quad x = 0 \quad D_{MX}\left(\frac{\partial C_{MX}}{\partial x}\right)_{x=0} = -D_M\left(\frac{\partial C_M}{\partial x}\right)_{x=0} = \frac{i_0}{nF}$$

$$t = 0 \quad x \geqslant 0 \quad C_{MX} = C_{MX}^* \quad C_M = C_M^* \quad C_X = C_X^*$$

Bulk concentration values C_{MX}^*, C_M^* and C_X^* for the case of 1 : 1 complex are defined by:

$$C_M^* + C_{MX}^* = C_{CM}^* \tag{8}$$

$$C_X^* + C_{MX}^* = C_{CM}^* \tag{7}$$

and can be calculated, provided the concentration of metal ion, C_{CM}^*, and the analytical concentration of ligand, C_{CX}^*, are known.

The equilibrium constant, K, is defined as:

$$K = \frac{[MX]}{[M]\,[X]} \tag{9}$$

The second term on the right hand side of eqs 3 to 5 the product $C_M\,C_X$, does not allow rigorous analytical solutions. By Feldberg's digital simulation method[8], numerical solutions of equations like these are possible. In this method differentials are replaced by finite dirrerences, and, e. g., eq 3 can be rewritten as:

$$\frac{\Delta\, C_{MX}}{\Delta\, t} = D_{MX}\,\frac{\Delta^2\, C_{MX}}{(\Delta\, x^2)} + k_1 C_M C_X - k_2 C_{MX} \tag{10}$$

Input data in the case of a preceding chemical reaction (1) include model values for C_{CM}, C_{CX}, k_1, k_2, (i. e. K), diffusion coefficients and current densities, MX, M and K are calculated from eqs 7—9.

The procedure is as follows:

The distance from the electrode toward the bulk of solution is divided into a number of compartments, where the changes of concentrations due to the respective chemical reaction are calculated by computer iterations. The number of iterations, necessary for the concentration of the electroactive species to reach zero at the electrode surface, is equated with the model value of the transition time. The reasonably achievable precision of this method is of the order of 0.1%.

RESULTS AND DISCUSSION

Digital simulation of the chronopotentiometric experiment, in the case of a 1 : 1 complex formation preceding chemical reaction, was done for model C^*_X concentration from 2 to 100, keeping the total metal ion concentration constant and equal to one. Two sets of calculations for second order conditions are presented in Figure 1. Model chronopotentimoetric parameter values $i_0\tau^{1/2}$ and ploted vs. model current density i_0. Points in Figure 1 show these results

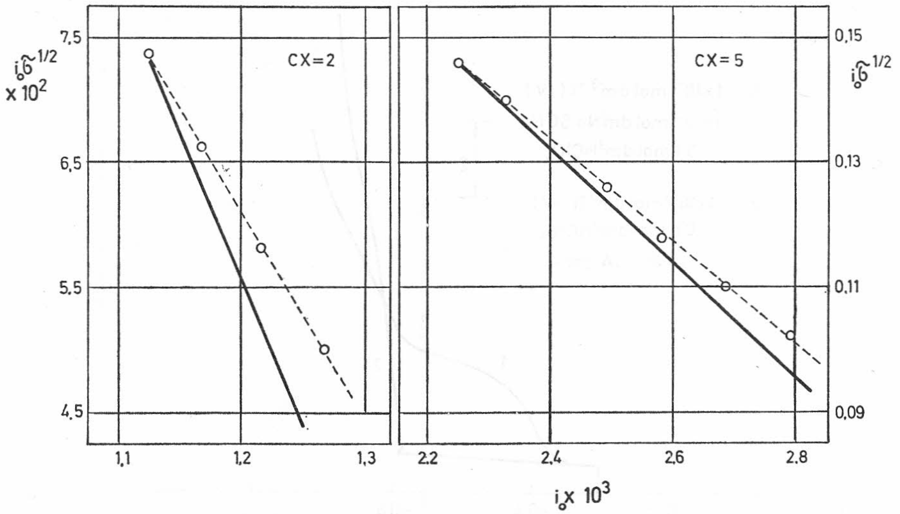

Figure 1. The chronopotentiometric parameter, $i_0\tau^{1/2}$ vs. current density, i_0, calculated by digital simulation of a preceding chemical reaction. Input data: $C^*_{CM} = 1$, $C^*_{CX} = 2$ (left), $C^*_{CX} = 5$ (right), $k_1 = 1 \times 10^{-4}$, $k_2 = 3 \times 10^{-3}$. Points indicate calculated values. Dashed lines are the best fit regression calculations. Full straight lines were drawn through the highest $i_0\tau^{1/2}$ values using slopes calculated by eq 2.

for $C^*_X = 2$ and $C^*_{CX} = 5$, respectively. Straight full lines were drawn through the highest points at these diagrams with the slopes calculated from (2), i. e. assuming pseudo-first order chemical kinetics. Regression line calculations are shown by dashed lines. There is a 28% difference in the slopes of the two straight lines for $C^*_{CX} = 2$, and 9% for $C^*_{CX} = 5$. The difference is smaller for higher ligand concentration, as expected. Both straight lines had the same slope for 30 and 100 C^*_{CX} concentration, showing only 2% difference for $C^*_{CX} = 10$. Error function terms in all the calculations were greater than two, avoiding thus the influence of this term in the results.

From these calculations it follows that in the chronopotentimetric experiment we can detect the influence of second order conditions in preceding chemical reaction when the concentration of ligand is $C^*_{CX} \leqslant 5$. Blount, Winograd, and Kuwana[9] have determined the sensitivity of the double potential step spectroelectrochemical method for distinguishing second order behavior in a catalytic electrochemical reaction. They found that second order behaviour appears at $C^*_{CX} \leqslant 10$. The same resolution in chronopotentiometry would require determination of transition times to ± 1%. This is difficult to achieve experimentally[10], and represents a disadvantage of the chronopotentiometric method in comparison with the former.

The complexation reaction of Ti(IV) with thiocyanate was chosen to test these calculations. Figure 2 shows two chronopotentiograms, one in presence of complexing agent (SCN^-) the other in its absence. Free Ti(IV) is reduced at the mercury electrode at — 800 mV vs. SCE (curve 1), while in SCN^- solution the Ti(IV) complex is reduced at — 300 mV (curve 2). It is known from literature data[11–13] that Ti(IV) forms a 1 : 1 complex with SCN^- ions and that the species undergoing reduction at the electrode is $Ti(OH)SCN^{2+}$.

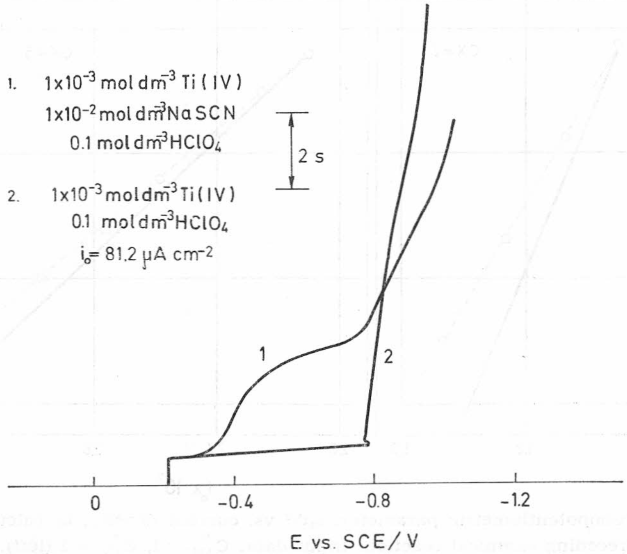

Figure 2. Chronopotentiogram of Ti(IV) in a thiocyanate solution (1), and in a noncomplexing perchloric acid solution (2) at a mercury pool electrode.

Dependence of the chronopotentiometric parameter $i_0\tau^{1/2}$ on current density is shown in Figure 3 for 10^{-3} mol dm^{-3} Ti(IV) solution in different concentration of thiocyanate in 0.2 mol dm^{-3} perchloric acid. The concentration of SCN^- was varied from 5×10^{-3} mol dm^{-3} to 3×10^{-2} mol dm^{-3} covering conditions from second order to pseudo-first order. Chronopotentiometric theory predicts that the plot of $i_0\tau^{1/2}$ vs. i_0 should be a straight line both for first and pseudo-first order preceding chemical reaction. This was obtained experimentally with Ti(IV)SCN complex for SCN^- concentrations 10 times the metal ion concentration and higher. For a 5 to 1 ratio of concentrations, there is a deviation from the straight line, closely following that obtained by digital simulation of a preceding chemical reaction of second order in Figure 1. It is evident that only below 10 : 1 SCN^- : Ti(IV) ratios second order conditions can be detected in this experimental system. For other systems this will depend not only on the ratio of ligand to metal ion concentrations, but also upon the equilibrium constant and the kinetics of complexation.

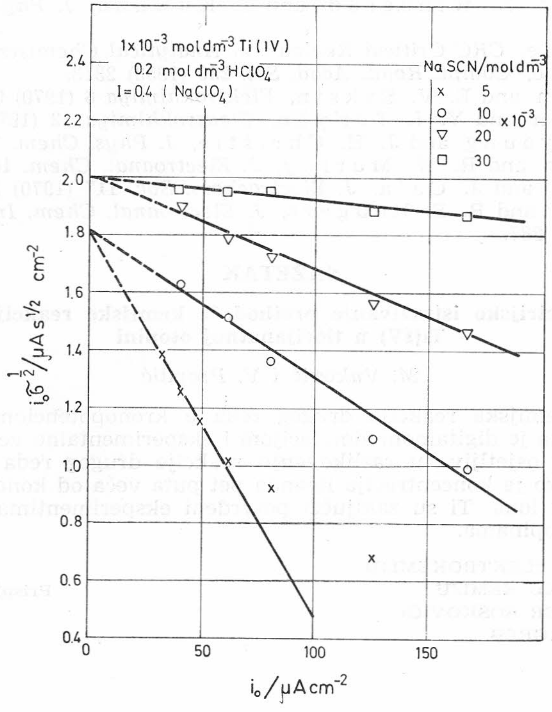

Figure 3. Chronopotentiometric parameter $i_0\tau^{1/2}$ vs. current density for reduction of Ti(IV) in thiocyanate solutions at the mercury pool electrode.

Extrapolation of $i_0\tau^{1/2}$ to zero current density gave a higher intercept for 2×10^{-2} and 3×10^{-2} mol dm^{-3} SCN^-, than that obtained for a 10^{-2} mol dm^{-3} SCN^- solution. Adsorption of electroactive species might influence the transition time and consequently the chronopotentiometric parameter. It is known that some metal ions are strongly adsorbed at the mercury electrode (Zn, In, Cr)[14–17].

However, there is no evidence of any significant adsorption of Ti(IV)SCN as reported in the literature[12].

Acknowledgment. This work was financially supported by the Self-managing Authority for Scientific Research of the SR of Croatia.

REFERENCES

1. P. Delahay and T. Berzins, *J. Amer. Chem. Soc.* **75** (1953) 2486.
2. P. Delahay, *New Instrumental Methods in Electrochemistry,* Interscience Publ., New York 1954.
3. J. Koutecky and J. Čižek, *Collect. Czech. Chem. Commun.* **22** (1957) 914.
4. O. Fischer, O. Dračka, and E. Fischerova, *Collect. Czech. Chem. Commun.* **25** (1960) 323.
5. T. Rabuzin, G. Smiljanić, and F. Jović, *J. Electroanal. Chem. Interfacial Electrochem.* **27** (1970) 397.
6. F. Jović and I. Kontušić, *J. Electroanal. Chem. Interfacial Electrochem.* **50** (1974) 269.
7. J. Čaja, *Dissertation,* Zagreb, 1967.
8. S. Feldberg, in: A. J. Bard (Ed.), *Electroanalytical Chemistry,* Vol. 3, Marcel Dekker Inc., New York 1969.
9. H. N. Blount, N. Winograd, and T. Kuwana, *J. Phys. Chem.* **74** (1970) 3231.
10. P. J. Lingane, *CRC Critical Reviews in Analytical Chemistry* **1971,** p. 587.
11. D. Delafosse, *Compt. Rend. Acad. Sci.* **236** (1953) 2313.
12. Y. I. Tur'yan and E. V. Saksin, *Elektrokhimiya* **6** (1970) 961.
13. V. N. Gnusin and Y. I. Tur'yan, *Elektrokhimiya* **13** (1977) 303.
14. R. A. Osteryoung and J. H. Christie, *J. Phys. Chem.* **71** (1967) 1348.
15. G. W. O'Dom and R. W. Murray, *J. Electroanal. Chem.* **16** (1968) 327.
16. F. C. Anson and J. Čaja, *J. Electrochem. Soc.* **117** (1970) 306.
17. F. C. Anson and R. S. Rodgers, *J. Electroanal. Chem. Interfacial Electrochem.* **47** (1973) 287.

SAŽETAK

Kronopotenciometrijsko istraživanje prethodeće kemijske reakcije drugog reda: Ti(IV) u tiocijanatnoj otopini

M. Vuković i V. Pravdić

Prethodeća kemijska reakcija drugog reda u kronopotenciometrijskom eksperimentu proučavana je digitalnom simulacijom i eksperimentalno verificirana. Kronopotenciometrija je osjetljiva u razlikovanju reakcije drugog reda od reakcije pseudo-prvog reda, ako je koncentracija liganda pet puta veća od koncentracije elektroaktivnog metalnog iona. Ti su zaključci potvrđeni eksperimentima redukcije Ti(IV) u tiocijanatnim otopinama.

LABORATORIJ ZA ELEKTROKEMIJU
I POVRŠINSKU KEMIJU
INSTITUT »RUĐER BOŠKOVIĆ«
41001 ZAGREB

Prispjelo, 18 svibnja 1977.