JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 1035–1040

Dynamic behaviour of electrochemical reactors for a step change in the inlet concentration under galvanostatic or potentiostatic control

J. M. BISANG

Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química (UNL), Santiago del Estero 2829, 3000 Santa Fe, Argentina

Received 9 September 1997; accepted in revised form 10 December 1997

The dynamic modelling of a cascade of continuous stirred tank electrochemical reactors under galvanostatic and potentiostatic control is performed. The response of the system in outlet concentration and current (potentiostatic case) for a step change in the inlet concentration in terms of the number of reactors is analysed. The idealised models, stirred tank and plug flow, are also included as limiting cases. The time required to reach approximate steady-state values in terms of the number of reactors and electrochemical parameters is discussed.

List of symbols

a_e	specific surface area (m^{-1})
A	magnitude of step change in the inlet concentration (mol m^{-3})
C	concentration (mol m^{-3})
C_j	concentration of the jth reactor (mol m^{-3})
C_0^*	inlet concentration before perturbation (mol m^{-3})
C_j^*	concentration of the jth reactor before perturbation (mol m^{-3})
Da	Damköhler number
F	Faraday constant (A s mol^{-1})
G	transfer function
H	Heaviside shifting function
i	current density (A m^{-2})
I	total current (A)
I_j	current of the jth reactor (A)
k	kinetic constant (m s^{-1})
k_f	rate constant (m s^{-1})
K	constant defined by Equation 16 or 18
L	electrode length (m)
n	number of tanks in the cascade
s	Laplace transform operator
t	time (s)
t_s	time to reach 99% of the steady-state value (s)
T	time constant defined by Equation 17 or 19 (s)
v	superficial liquid flow velocity (m s^{-1})
V	volume of each reactor (m^3)
W	electrode width (m)
x	axial coordinate (m)
X	perturbation variable for inlet concentration (mol m^{-3})
Y	perturbation variable for outlet concentration (mol m^{-3})

Greek symbols

β	constant given by Equation 20
ε	porosity
ν_e	charge number of the electrode reaction
τ	cascade residence time (s)

1. Introduction

A convenient method of dynamic modelling of electrochemical reactors is to consider a cascade of continuous stirred tank reactors, from which the behaviour of the idealised models, stirred tank and plug flow, can be obtained as limiting cases.

Fahidy [1] has analysed the dynamics of the isothermal continuous stirred tank and plug flow models under galvanostatic control when perturbations in the feed concentration and current are produced. In [2] the transient response of a nonisothermal continuous stirred tank electrochemical reactor is presented. In [3] the case of nonisothermal plug flow reactors is treated. It was assumed that a single electrolytic process is carried out galvanostatically and that the axial distribution of current may be represented, at least in a first approximation, by means of an appropriate average value. Additionally, Scott [4, 5] examined the behaviour of a cascade of two tanks and the dynamic response for multiple reactions.

The aim of this work is to develop the dynamics of a cascade of n tanks under galvanostatic and potentiostatic control and to analyse the necessary time to achieve conditions close to the steady state.

0021-891X

2. Dynamics of the tank series model

2.1. *Concentration as a function of time*

The transfer function for a cascade of continuous stirred tank electrochemical reactors is given by [4]

$$\frac{Y_n(s)}{X_1(s)} = \prod_{j=1}^{n} G_j(s) \tag{1}$$

where G_j is the transfer function of each reactor, being

$$G_j(s) = \frac{K_j}{(T_j\, s + 1)} \tag{2}$$

The time constant T_j, and the constant K_j depend on the electrical control. Thus, for galvanostatic control:

$$K_j = 1 \tag{3}$$

$$T_j = \tau_j \tag{4}$$

Under potentiostatic operation the kinetics of a first-order reaction at high electrode potentials is given by [6]

$$i(t) = \nu_e\, F\, k\, C(t) \tag{5}$$

being

$$k = \frac{k_f}{(1 + \mathrm{Da})} \tag{6}$$

High values of the Damköhler number indicate an approach to mass transport controlled rates. T_j and K_j for potentiostatic control are given by

$$K_j = \frac{1}{\left(1 + \frac{k\, a_e\, \tau_j}{\varepsilon}\right)} \tag{7}$$

$$T_j = \frac{\tau_j}{\left(1 + \frac{k\, a_e\, \tau_j}{\varepsilon}\right)} \tag{8}$$

A cascade of electrochemical reactors is an attractive model to represent the behaviour of real reactors. Thus, an interesting alternative is to consider a cascade where all the tanks have the same residence time. Then

$$\tau_j = \frac{\tau}{n} \tag{9}$$

where τ is the cascade residence time. Therefore, the gain and the time constant are the same for all the reactors in the cascade. Introducing Equation 2 into Equation 1 yields

$$\frac{Y_n(s)}{X_1(s)} = \frac{K^n}{(Ts + 1)^n} \tag{10}$$

Assuming a step perturbation in the inlet concentration of magnitude A, Equation 10 is

$$Y_n(s) = \frac{A\, K^n}{s(Ts + 1)^n} \tag{11}$$

Equation 11 can be solved by Laplace transform inversion. Thus, for $n = 1$

$$Y_1(t) = A\, K\left[1 - \exp\left(-\frac{t}{T}\right)\right] \tag{12}$$

for $n = 2$

$$Y_2(t) = A\, K^2\left[1 - \left(1 + \frac{t}{T}\right)\exp\left(-\frac{t}{T}\right)\right] \tag{13}$$

and for $n = 3$

$$Y_3(t) = A\, K^3\left\{1 - \left[1 + \frac{t}{T} + \frac{1}{2}\left(\frac{t}{T}\right)^2\right]\exp\left(-\frac{t}{T}\right)\right\} \tag{14}$$

Equations 12 and 13 are also given by Scott [4, 5]. From Equations 12–14 the following general expression can be inferred

$$Y_n(t) = A\, K^n\left\{1 - \left[\sum_{j=1}^{n}\frac{1}{(j-1)!}\left(\frac{t}{T}\right)^{j-1}\right]\exp\left(-\frac{t}{T}\right)\right\} \tag{15}$$

where for the galvanostatic case

$$K = 1 \tag{16}$$

and

$$T = \frac{\tau}{n} \tag{17}$$

For the potentiostatic case

$$K = \frac{n}{n + \beta} \tag{18}$$

and

$$T = \frac{\tau}{n + \beta} \tag{19}$$

being

$$\beta = \frac{k\, a_e\, \tau}{\varepsilon} \tag{20}$$

Thus, β lumps the electrochemical kinetics, k, electrode properties a_e and ε, with the system residence time.

Evaluating Equation 15 at $t \to \infty$ yields

$$C_n(\infty) - C_n^* = A\, K^n \tag{21}$$

Likewise, for a cascade of tanks the outlet concentration is related to the inlet concentration by

$$C_n^* = C_0^*\, K^n \tag{22}$$

Combining Equations 21 and 22 yields

$$\frac{C_n(\infty) - C_n^*}{C_n^*} = \frac{A}{C_0^*} \tag{23}$$

For the galvanostatic case Equation 21 gives

$$C_n(\infty) = C_n^* + A \tag{24}$$

Thus when the current is constant the electrochemical reaction rate does not depend on the concentration and a change in the inlet concentration produces the same change in the outlet concentration. A similar situation corresponds to a mixer.

For the potentiostatic case introducing Equation 18 into 21 yields

$$C_n(\infty) - C_n^* = A\left(\frac{n}{n + \beta}\right)^n \tag{25}$$

For $n \to \infty$, according to Zucker [7] Equation 25 approaches

$$C_n(\infty) - C_n^* = A\ \exp(-\beta) \tag{26}$$

2.2. *Current as a function of time for the potentiostatic case*

The current drained by the *j*th reactor in the cascade is given by

$$I_j(t) = \nu_e\ F\ k\ a_e\ V\ C_j(t) \tag{27}$$

Introducing Equation 12 into Equation 27, and taking into account Equations 18–20, the current of the first reactor in the cascade is

$$\begin{aligned} I_1(t) - I_1(0) = {} & \nu_e\ F\ k\ a_e\ V\ A\frac{n}{n+\beta} \\ & \times \left\{1 - \exp\left(-\frac{t}{\tau}(n+\beta)\right)\right\} \end{aligned} \tag{28}$$

Analogously for the second and third reactors:

$$\begin{aligned} I_2(t) - I_2(0) = {} & \nu_e\ F\ k\ a_e\ V\ A\left(\frac{n}{n+\beta}\right)^2 \\ & \times \left\{1 - \left[1 + \frac{t}{\tau}(n+\beta)\right] \right. \\ & \left. \times \exp\left(-\frac{t}{\tau}(n+\beta)\right)\right\} \end{aligned} \tag{29}$$

$$\begin{aligned} I_3(t) - I_3(0) = {} & \nu_e\ F\ k\ a_e\ V\ A\left(\frac{n}{n+\beta}\right)^3 \\ & \times \left\{1 - \left[1 + \frac{t}{\tau}(n+\beta) + \frac{1}{2}\left(\frac{t}{\tau}(n+\beta)\right)^2\right] \right. \\ & \left. \times \exp\left(-\frac{t}{\tau}(n+\beta)\right)\right\} \end{aligned} \tag{30}$$

For the *j*th reactor

$$\begin{aligned} I_j(t) - I_j(0) = {} & \nu_e\ F\ k\ a_e\ V\ A\left(\frac{n}{n+\beta}\right)^j \\ & \times \left\{1 - \sum_{i=1}^{j}\left[1 + \frac{1}{(i-1)!}\left(\frac{t}{\tau}(n+\beta)\right)^{i-1}\right] \right. \\ & \left. \times \exp\left(-\frac{t}{\tau}(n+\beta)\right)\right\} \end{aligned} \tag{31}$$

The total current in the cascade is given by

$$I(t) = \sum_{j=1}^{n} I_j(t) \tag{32}$$

Introducing Equations 28–31 into Equation 32 gives

$$\begin{aligned} & I(t) - I(0) \\ & = \frac{\nu_e F k a_e V A}{C_0^*}\left\langle C_1^*\left\{1 - \exp\left(-\frac{t}{\tau}(n+\beta)\right)\right\} \right. \\ & + C_2^*\left\{1 - \left[1 + \frac{t}{\tau}(n+\beta)\right]\exp\left(-\frac{t}{\tau}(n+\beta)\right)\right\} \\ & + C_3^*\left\{1 - \left[1 + \frac{t}{\tau}(n+\beta) + \frac{1}{2}\left(\frac{t}{\tau}(n+\beta)\right)^2\right] \right. \\ & \left. \times \exp\left(-\frac{t}{\tau}(n+\beta)\right)\right\} \\ & + \cdots + C_n^*\left\{1 - \sum_{j=1}^{n}\left[1 + \frac{1}{(j-1)!}\left(\frac{t}{\tau}(n+\beta)\right)^{j-1}\right] \right. \\ & \left. \left. \times\ \exp\left(-\frac{t}{\tau}(n+\beta)\right)\right\}\right\rangle \end{aligned} \tag{33}$$

Evaluating Equation 32 at $t = 0$ results in

$$I(0) = \nu_e\ F\ k\ a_e\ V\sum_{j=1}^{n} C_j^* \tag{34}$$

Introducing Equation 34 into Equation 33 and rearranging yields

$$\begin{aligned} & \frac{I(t) - I(0)}{I(0)} \\ & = \frac{A}{C_0^*\sum_{j=1}^{n} C_j^*}\left\{\sum_{j=1}^{n} C_j^* - \left[\sum_{j=1}^{n} C_j^* + \left(\frac{t}{\tau}(n+\beta)\right)\right.\right. \\ & \times \sum_{j=2}^{n} C_j^* + \frac{1}{2}\left(\frac{t}{\tau}(n+\beta)\right)^2\sum_{j=3}^{n} C_j^* + \frac{1}{3!}\left(\frac{t}{\tau}(n+\beta)\right)^3 \\ & \left.\left. \times \sum_{j=4}^{n} C_j^* + \cdots + \frac{1}{(n-1)!}\left(\frac{t}{\tau}(n+\beta)\right)^{n-1} C_n^*\right]\right\} \\ & \times \exp\left(-\frac{t}{\tau}(n+\beta)\right) \end{aligned} \tag{35}$$

Likewise

$$\begin{aligned} \sum_{j=1}^{n} C_j^* = C_1^*\left[1 + \frac{n}{n+\beta} + \left(\frac{n}{n+\beta}\right)^2 + \left(\frac{n}{n+\beta}\right)^3\right. \\ \left. + \cdots + \left(\frac{n}{n+\beta}\right)^{n-1}\right] \end{aligned} \tag{36}$$

Equation 36 can be rearranged to

$$\sum_{j=1}^{n} C_j^* = C_1^*\frac{K^n - 1}{K - 1} \tag{37}$$

Then

$$\frac{\sum_{j=2}^{n} C_j^*}{\sum_{j=1}^{n} C_j^*} = \frac{K^n - K}{K^n - 1} \tag{38}$$

Analogously

$$\frac{\sum_{j=3}^{n} C_j^*}{\sum_{j=1}^{n} C_j^*} = \frac{K^n - K^2}{K^n - 1} \tag{39}$$

$$\frac{\sum_{j=4}^{n} C_j^*}{\sum_{j=1}^{n} C_j^*} = \frac{K^n - K^3}{K^n - 1} \tag{40}$$

$$\frac{C_n^*}{\sum_{j=1}^{n} C_j^*} = \frac{K^n - K^{n-1}}{K^n - 1} \tag{41}$$

Introducing Equations 38–41 into Equation 35 yields

$$\begin{aligned} & \frac{I(t) - I(0)}{I(0)} \\ & = \frac{A}{C_0^*}\left\{1 - \left[1 + \left(\frac{t}{\tau}(n+\beta)\right)\frac{K^n - K}{K^n - 1}\right.\right. \\ & + \frac{1}{2}\left(\frac{t}{\tau}(n+\beta)\right)^2\frac{K^n - K^2}{K^n - 1} \\ & + \frac{1}{3!}\left(\frac{t}{\tau}(n+\beta)\right)^3\frac{K^n - K^3}{K^n - 1} + \cdots + \frac{1}{(n-1)!} \\ & \left.\left. \times \left(\frac{t}{\tau}(n+\beta)\right)^{n-1}\frac{K^n - K^{n-1}}{K^n - 1}\right]\right\} \\ & \times \exp\left(-\frac{t}{\tau}(n+\beta)\right) \end{aligned} \tag{42}$$

or in general

$$\frac{I(t)-I(0)}{I(0)}=\frac{A}{C_0^*}\left\{1-\left[\sum_{j=1}^{n}\frac{1}{(j-1)!}\left[\frac{t}{\tau}(n+\beta)\right]^{j-1}\times\frac{K^n-K^{j-1}}{K^n-1}\right]\right\}\exp\left(-\frac{t}{\tau}(n+\beta)\right) \quad (43)$$

For high t values Equation 43 approaches

$$\frac{I(\infty)-I(0)}{I(0)}=\frac{A}{C_0^*} \quad (44)$$

3. Dynamics of the plug flow model

The dynamics of a plug flow reactor corresponds to a distributed parameter system. The mass balance gives

$$\varepsilon\frac{\partial C(x,t)}{\partial t}=-v\frac{\partial C(x,t)}{\partial x}-\frac{i(x,t)\ a_{\mathrm{e}}}{\nu_{\mathrm{e}}\ F} \quad (45)$$

Assuming that the electrolytic process is carried out galvanostatically and the current density distribution is not affected by a step perturbation in the inlet concentration, the solution of Equation 45 is

$$Y(x,t)=AH\left(t-\frac{x\varepsilon}{v}\right) \quad (46a)$$

with

$$H\left(t-\frac{x\varepsilon}{v}\right)=0 \qquad t<\frac{x\varepsilon}{v} \quad (46b)$$

$$H\left(t-\frac{x\varepsilon}{v}\right)=1 \qquad t\geq\frac{x\varepsilon}{v} \quad (46c)$$

Equation 46 was deduced and discussed by Fahidy [1] and Scott [4].

Likewise, introducing the following kinetic expression into Equation 45

$$i(x,t)=\nu_{\mathrm{e}}\ F\ k\ C(x,t) \quad (47)$$

and rearranging in terms of perturbation variables results in

$$\varepsilon\frac{\partial Y(x,t)}{\partial t}=-v\frac{\partial Y(x,t)}{\partial t}-k\ a_{\mathrm{e}}\ Y(x,t) \quad (48a)$$

with the following initial and boundary conditions:

$$Y(x,0)=0 \quad (48b)$$

and

$$Y(0,t)=A \qquad \text{for } t>0 \quad (48c)$$

In order to simplify the solution of Equation 48a, it is necessary to assume that k is independent of position along the reactor. This assumption is valid under potentiostatic control when the potential distribution along the electrode length does not alter the reaction rate, which is fulfilled by reactions under mass-transport control.

Using Laplace transforms the solution of Equation 48a is

$$Y(x,t)=AH\left(t-\frac{x\varepsilon}{v}\right)\ \exp\left(-k\ a_{\mathrm{e}}\ \frac{x}{v}\right) \quad (49)$$

Evaluating Equation 49 at $x=L$ for $t\geq\tau$ gives Equation 26, which corroborates the well known behaviour that a cascade of reactors approaches the plug flow model when $n\rightarrow\infty$ [8]. Fahidy [3] has deduced an equation of the same form as that of Equation 49 for the galvanostatic case assuming that the ratio between the current density and the electrolyte density along the reactor is a function of the concentration, which was approximated by a Taylor expansion truncated to the two first terms.

The total current, for the reactor, is given by

$$I(t)=W\int_0^L i(x,t)\ \mathrm{d}x \quad (50)$$

Combining Equations 47, 49 and 50 gives

$$I(t)-I(0)=W\nu_{\mathrm{e}}\ F\ k\ A\int_0^L H\left(t-\frac{x\varepsilon}{v}\right)\times\exp\left(-k\ a_{\mathrm{e}}\frac{x}{v}\right)\ \mathrm{d}x \quad (51)$$

Equation 51 can be rearranged to

$$I(t)-I(0)=W\nu_{\mathrm{e}}\ F\ k\ A\int_0^{tv/\varepsilon}\exp\left(-k\ a_{\mathrm{e}}\frac{x}{v}\right)\ \mathrm{d}x \quad (52)$$

Equation 52 is valid for

$$0\leq t\leq\frac{L\varepsilon}{v} \quad (53)$$

Solving Equation 52 and rearranging yields

$$\frac{I(t)-I(0)}{I(0)}=\frac{A}{C_0^*}\frac{1-\exp\left(-\frac{\beta t}{\tau}\right)}{1-\exp(-\beta)} \quad (54)$$

And for $t=\tau$ Equation 54 is reduced to

$$\frac{I(\tau)-I(0)}{I(0)}=\frac{A}{C_0^*} \quad (55)$$

4. Comparison of the dynamic behaviours and discussion

Figure 1 shows the response of electrochemical reactors according to the tank series model under gal-

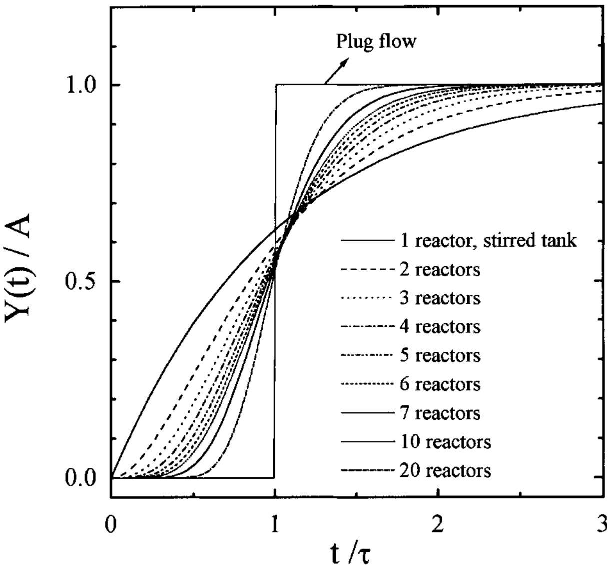

Fig. 1. Transient response in outlet concentration. Galvanostatic control.

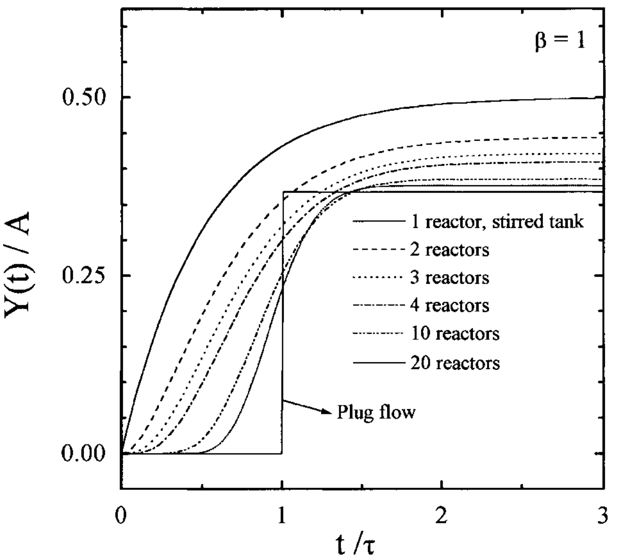

Fig. 2. Transient response in outlet concentration. Potentiostatic control ($\beta = 1$).

vanostatic control, Equations 15–17, for a step change of magnitude A in the inlet concentration. Thus, the difference between the outlet concentration at time t and the outlet concentration before the perturbation related to the magnitude of the step change in the inlet concentration as a function of the normalized time, t/τ, is plotted. The behaviour of the plug-flow model under the same conditions, Equation 46a evaluated at $x = L$, is also given. As expected, when the number of reactors increases the performance of the tank series model approaches the plug flow model. Likewise, for high t values the electrochemical system approaches unity independent of the number of reactors in the stack.

Figures 2 and 3 show typical responses of the tank series model, Equations 15, 18–20, and the plug-flow model, Equation 49 evaluated at $x = L$, under potentiostatic control. In this case the response depends on β, which was assumed unity in Fig. 2 and ten in Fig. 3. Again at high t values the tank series model approaches a constant, but the constant value decreases when the number of reactors in the stack increases and approaches a limiting value in accordance with the plug-flow model. This behaviour can be explained taking into account that under potentiostatic control the reaction rate depends on the concentration.

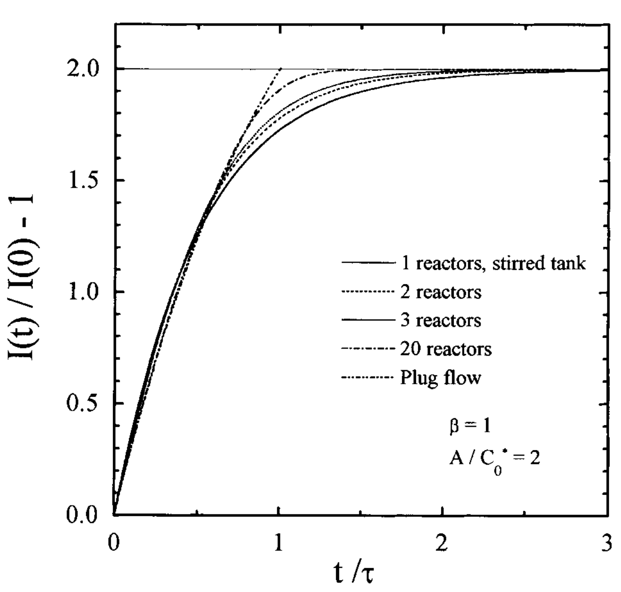

Fig. 4. Transient response in current. Potentiostatic control ($\beta = 1$).

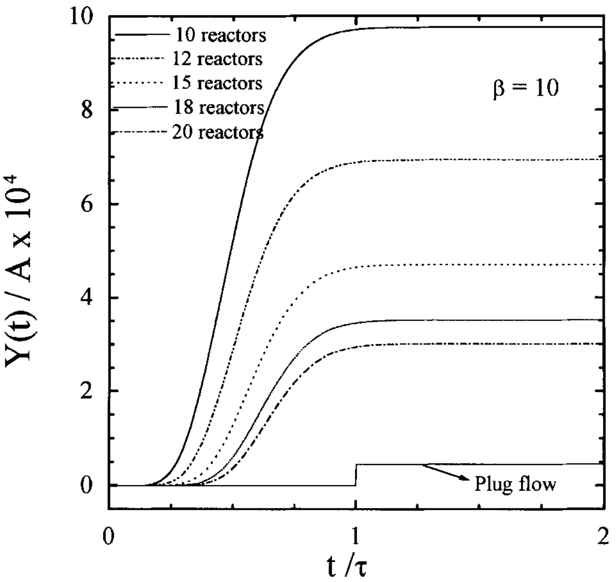

Fig. 3. Transient response in outlet concentration. Potentiostatic control ($\beta = 10$).

Figure 4 shows the response in current of the studied systems, under potentiostatic control, for a step change in the inlet concentration. At $t \rightarrow \infty$ the variation in the current related to the initial current approaches a constant value. The constant value is the same for the tank series model, Equation 44, and

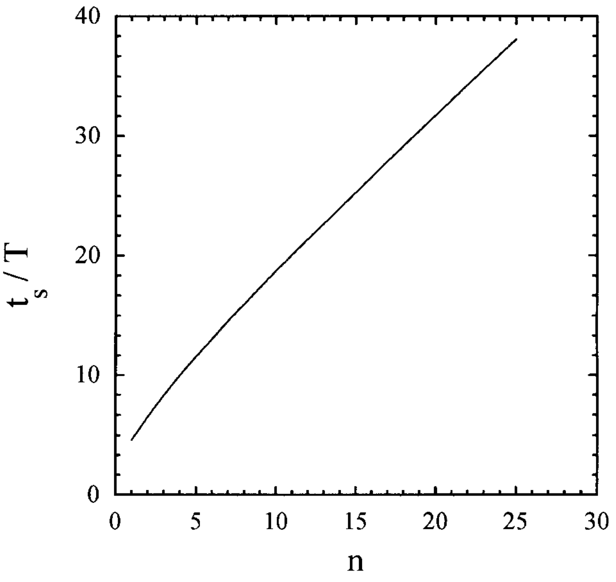

Fig. 5. Time to reach the 99% of the steady-state outlet concentration normalized by the time constant as a function of the number of reactors in the cascade.

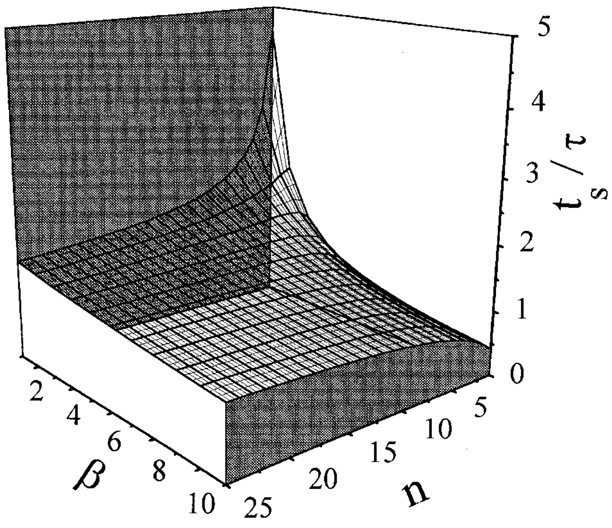

Fig. 6. Time to reach the 99% of the steady-state outlet concentration normalized by the cascade residence time as a function of β and the number of reactors in the cascade.

for the plug-flow model, Equation 55. This behaviour is a consequence of Equation 23, which states that the response in the outlet concentration, related to the outlet concentration before the perturbation, C_n^*, is constant independent of the reactors number in the cascade.

Figures 1–3 show that a cascade of electrochemical reactors achieves the steady state at $t \to \infty$. From a practical point of view it is interesting to know the necessary time to achieve conditions close to the steady state. Thus, a time t_s, termed the stabilization time, where the response of the system is the 99% of the steady-state value may be defined. Figure 5 shows the time t_s normalized by T as a function of the number of reactors. t_s/T increases with n and at high n values the relation is approximately linear, which allows determination of t_s. However, T is a function of n, β and τ (according to Equation 19). The results of Fig. 5 are re-plotted in three-dimensional form in Fig. 6, where the effect of changes in n and β on t_s/τ is elucidated. The galvanostatic case is taken into account in Fig. 6 for $\beta = 0$. For a given value of n the stabilization time normalized with respect to τ always decreases as β increases. However, for a given β value t_s/τ decreases with n for low β values and increases with n for high β values. Likewise, for high values of n or β the stabilization time approaches the reactor residence time.

Acknowledgements

This work was supported by the Universidad Nacional del Litoral (CAI+D 94-0858-007-058), and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, Argentina).

References

[1] T. Z. Fahidy, 'Principles of Electrochemical Reactor Analysis', Elsevier, Amsterdam (1985), Ch. **10**, p. 244.
[2] T. Z. Fahidy, *J. Appl. Electrochem.* **14** (1984) 231.
[3] T. Z. Fahidy, *Electrochim. Acta* **29** (1984) 1321.
[4] K. Scott, 'Electrochemical Reaction Engineering', Academic Press, London (1991) Ch. **5**, p. 315.
[5] K. Scott, *J. Appl. Electrochem.* **21** (1991) 945.
[6] K. Scott, 'Electrochemical Reaction Engineering', Academic Press, London (1991), Ch. **2**, p. 54.
[7] R. Zucker, in 'Handbook of Mathematical Functions' (edited by M. Abramowitz and I. A. Stegun), Dover Publications, New York (1972), Ch. **4**, p. 70.
[8] O. Levenspiel, 'Chemical Reaction Engineering' 2nd edn, J. Wiley & Sons, New York (1972), Ch. **6**, p. 134.