



Dynamic behaviour of electrochemical reactors for a step change in flow rate

J.M. BISANG

Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química (UNL), Santiago del Estero 2829, 3000 Santa Fe, Argentina
(e-mail: jbisang@fiqus.unl.edu.ar)

Received 26 October 1998; accepted in revised form 18 February 1999

Key words: dynamic behaviour, electrochemical engineering, flow rate perturbation, stability analysis

Abstract

Studies of the effect of a step change in flow rate on the dynamic behaviour of a cascade of continuous stirred tank electrochemical reactors under galvanostatic and potentiostatic control are reported. The idealized models, stirred tank and plug flow, are also included as limiting cases. The response of the system in outlet concentration and current and the time required to reach approximate steady-state values in terms of the number of reactors and electrochemical parameters are discussed.

List of symbols

a_e specific surface area (m^{-1})
 A magnitude of step change in flow rate ($\text{m}^3 \text{s}^{-1}$)
 C concentration (mol m^{-3})
 C_j concentration of the j th reactor (mol m^{-3})
 C_0 inlet concentration (mol m^{-3})
 C_j^* concentration of the j th reactor before perturbation (mol m^{-3})
 Da Damköhler number
 F Faraday constant (A s mol^{-1})
 H Heaviside shifting function
 i current density (A m^{-2})
 I total current (A)
 I^* total current before perturbation (A)
 I_j current of the j th reactor (A)
 I_j^* current of the j th reactor before perturbation (A)
 k kinetic constant (m s^{-1})
 k_f electrochemical rate constant (m s^{-1})
 K constant defined by Equation 17
 L electrode length (m)
 n number of tanks in the cascade
 Q volumetric flow rate ($\text{m}^3 \text{s}^{-1}$)
 Q^* volumetric flow rate before perturbation ($\text{m}^3 \text{s}^{-1}$)
 s Laplace transform operator

S cross-sectional area of the reactor (m^2)
 t time (s)
 t_s time to reach 99% of the steady-state value (s)
 T time constant defined by Equation 13 (s)
 v superficial liquid flow velocity (m s^{-1})
 v^* superficial liquid flow velocity before perturbation (m s^{-1})
 V volume of the cascade (m^3)
 x axial coordinate (m)
 $Y_{j,n}$ normalized perturbation variable for outlet concentration of the j th reactor in a cascade of n reactors defined by Equation 3
 Y normalized perturbation variable for outlet concentration

Greek characters

β constant given by Equation 9
 ΔC concentration change in the electrochemical reactor after perturbation (mol m^{-3})
 ΔC^* concentration change in the electrochemical reactor before perturbation (mol m^{-3})
 γ_j parameter defined by Equation 14
 ε porosity
 ν_e charge number of the electrode reaction
 τ cascade residence time (s)
 τ^* cascade residence time before perturbation (s)

1. Introduction

The dynamics of electrochemical reactors for changes in flow rate has been scarcely treated in the literature. Fahidy [1] analysed the effect of flow rate and current perturbations on the dynamics of tank flow electrolyzers

for the cases of single flow electrolyser, the batch electrolyser with recycle and the electrolyser cascade. The continuous stirred tank electrochemical reactor model under galvanostatic operation was adopted and the control of the current in order to minimize the concentration variation produced by the flow rate

perturbation was also discussed. Scott [2] examined the linearization of the perturbation equations for an isothermal continuous stirred tank reactor with input variations in flow rate, concentrations and current density. Unbehauen and Alatiqi [3] discussed control of temperature, flow rate, electrode position, voltage and current and Fleet and Small [4] analysed control strategies. Work dealing with the dynamic behaviour of electrochemical systems were summarised in previous papers from this laboratory, where the modelling of the startup of a continuous parallel plate electrochemical reactor [5] was analysed and the dynamic behaviour of electrochemical reactors for a step change in the inlet concentration [6] was reported.

In the model reported here the dynamics of a cascade of n tanks under galvanostatic and potentiostatic control for a step change in flow rate is analysed. The aim of this work is to obtain the necessary time to achieve conditions close to the steady state taking into account the effect of the kinetics of the electrochemical reaction and the number of reactors in the cascade.

2. Dynamic behaviour of the tank series model

2.1. Concentration as a function of time

The mass-balance for the j th reactor of a cascade of n equally sized reactors for all time after the input step change in flow rate is

$$\frac{V}{n} \varepsilon \frac{dC_j(t)}{dt} = QC_{j-1}(t) - QC_j(t) - \frac{I_j(t)}{v_e F} \quad (1)$$

where the output of the $j - 1$ th reactor flows into the j th reactor and so forth.

For $t = 0^-$ is

$$Q^* C_{j-1}^* - Q^* C_j^* - \frac{I_j^*}{v_e F} = 0 \quad (2)$$

$t = 0^-$ indicates that the respective values of C^* , Q^* and I_j^* apply to points very close to, but not at zero [7].

Defining the perturbation variable

$$Y_{j,n}(t) = \frac{C_j(t) - C_j^*}{\Delta C^*} \quad (3)$$

and combining Equations 1 to 3 gives:

$$\frac{\tau}{n} \frac{dY_{j,n}(t)}{dt} + Y_{j,n}(t) = Y_{j-1,n}(t) - \frac{1}{v_e F \Delta C^*} \left(\frac{I_j(t)}{Q} - \frac{I_j^*}{Q^*} \right) \quad (4)$$

where

$$\tau = \frac{V \varepsilon}{Q} \quad (5)$$

the cascade residence time. Equation 4 is valid for galvanostatic and potentiostatic control.

2.1.1. Potentiostatic control

Assuming that the reactors operate at identical electrode potentials and considering a first order reaction, the current drained by the j th reactor in the cascade is given by

$$I_j(t) = a_e \frac{V}{n} v_e F k C_j(t) \quad (6)$$

where

$$k = \frac{k_f}{1 + Da} \quad (7)$$

k_f is the electrochemical rate constant which is a function of potential and temperature and Da is the Damköhler number [8]. When $Da = 0$ the kinetic expression is truncated to a Tafel equation for a first order reaction and high values of the Damköhler number indicate an approach to mass transport controlled rates. It is assumed that the kinetic constant k is not a function of the flow rate in order to neglect its variation with time, due to the fact that a change in flow rate produces a change in the diffusion layer thickness. Therefore, the predictions of the model are valid when the electrochemical reaction is charge transfer kinetic controlled or is under combined diffusion and charge transfer kinetic control for rotating electrodes, where the effect of the volumetric flow rate on the mass-transfer coefficient can be neglected. For static electrodes and reactions under mass-transfer control the model is valid when the perturbation in flow rate is small.

Introducing Equation 6, evaluated at t and at $t = 0^-$, into Equation 4 and rearranging yields

$$\frac{\tau}{n} \frac{dY_{j,n}(t)}{dt} + \left(1 + \frac{\beta}{n} \right) Y_{j,n}(t) = Y_{j-1,n}(t) + \frac{\beta}{n} \frac{A C_j^*}{Q^* \Delta C^*} \quad (8)$$

where

$$\beta = \frac{k a_e \tau}{\varepsilon} \quad (9)$$

and

$$A = Q - Q^* \quad (10)$$

Taking into account Equation 2 and Equation 6, evaluated at $t = 0^-$, for each reactor of the stack and adding results

$$\Delta C^* = \frac{k a_e V}{n Q^*} \sum_{i=1}^n C_i^* \quad (11)$$

Likewise

$$C_j^* = \frac{C_0}{\left(1 + \frac{\beta\tau^*}{n\tau}\right)^j} \quad (12)$$

Defining

$$T = \frac{\tau}{n + \beta} \quad (13)$$

and

$$\gamma_j = \frac{1}{\sum_{i=1}^n \left(1 + \frac{\beta\tau^*}{n\tau}\right)^{j-i}} \quad (14)$$

Introducing Equations 11 and 12 into Equation 8 and rearranging yields

$$\frac{dY_{j,n}(t)}{dt} + \frac{Y_{j,n}(t)}{T} = \frac{n}{\tau} Y_{j-1,n}(t) + \frac{nA}{\tau Q} \gamma_j \quad (15)$$

Laplace transformation of Equation 15 gives

$$Y_{j,n}(s) = \frac{K}{1 + Ts} Y_{j-1,n}(s) + \frac{K}{1 + Ts} \frac{A \gamma_j}{s Q} \quad (16)$$

where

$$K = \frac{n}{n + \beta} \quad (17)$$

Equation 16 can be solved by Laplace transform inversion for different n and j values. Thus, for $j = 1$ it is simplified to

$$Y_{1,n}(s) = \frac{K}{1 + Ts} \frac{A \gamma_1}{s Q} \quad (18)$$

Solving Equation 18 by Laplace transform inversion gives

$$Y_{1,n}(t) = \frac{A}{Q} K \gamma_1 \left[1 - \exp\left(-\frac{t}{T}\right)\right] \quad (19)$$

For $j = 2$ Equation 16 gives

$$Y_{2,n}(s) = \frac{K}{1 + Ts} Y_{1,n}(s) + \frac{K}{1 + Ts} \frac{A \gamma_2}{s Q} \quad (20)$$

Introducing Equation 18 into Equation 20 and rearranging yields

$$Y_{2,n}(s) = \left(\frac{K}{1 + Ts}\right)^2 \frac{A \gamma_1}{s Q} + \frac{K}{1 + Ts} \frac{A \gamma_2}{s Q} \quad (21)$$

Solving Equation 21 by Laplace transform inversion gives

$$Y_{2,n}(t) = \frac{A}{Q} K^2 \left(\gamma_1 + \frac{\gamma_2}{K}\right) \times \left\{1 - \left[1 + \frac{K \gamma_1}{K \gamma_1 + \gamma_2} \frac{t}{T}\right] \exp\left(-\frac{t}{T}\right)\right\} \quad (22)$$

Performing the same procedure for $j = 3$ gives

$$Y_{3,n}(t) = \frac{A}{Q} K^3 \left(\gamma_1 + \frac{\gamma_2}{K} + \frac{\gamma_3}{K^2}\right) \times \left\{1 - \left[1 + \frac{K^2 \gamma_1 + K \gamma_2}{K^2 \gamma_1 + K \gamma_2 + \gamma_3} \frac{t}{T} + \frac{K^2 \gamma_1}{K^2 \gamma_1 + K \gamma_2 + \gamma_3} \left(\frac{t}{T}\right)^2\right] \exp\left(-\frac{t}{T}\right)\right\} \quad (23)$$

From Equations 19, 22 and 23 and solving for other j values the following general expression can be inferred

$$Y_{j,n}(t) = \frac{A}{Q} K^j \sum_{k=1}^j \frac{\gamma_k}{K^{k-1}} \times \left\{1 - \left[\frac{\sum_{h=k+1}^j \gamma_{j+1-h} K^{h-1}}{\sum_{h=1}^j \gamma_h K^{j-h}} \frac{(t/T)^k}{k!}\right] \exp\left(-\frac{t}{T}\right)\right\} \quad (24)$$

2.1.2. Galvanostatic control

From Equation 2 and assuming that the reactors are electrically connected in series gives

$$nI_j^* = v_e F Q^* \Delta C^* \quad (25)$$

Introducing Equation 25 into Equation 4 yields

$$\frac{dY_{j,n}(t)}{dt} + \frac{n}{\tau} Y_{j,n}(t) = \frac{n}{\tau} Y_{j-1,n}(t) + \frac{A}{\tau Q} \quad (26)$$

Comparing Equation 15, valid for the potentiostatic case, with Equation 26, valid for the galvanostatic case, it is concluded that Equation 15 is simplified to Equation 26 when $\beta = 0$. Therefore, the galvanostatic control can be considered as a singular case of the potentiostatic control. Thus, for $\beta = 0$ and $j = n$ Equation 24 yields

$$Y_{n,n}(t) = \frac{A}{Q} \left\{1 - \left[\sum_{k=0}^{n-1} \frac{n-k}{nk!} \left(\frac{t}{\tau/n}\right)^k\right] \exp\left(-\frac{t}{\tau/n}\right)\right\} \quad (27)$$

Equation 27, rearranged in a different manner, was also given by Fahidy [1].

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

Combining Equations 3 and 6 gives

$$I_j(t) - I_j^* = v_e F k a_e \frac{V}{n} \Delta C^* Y_{j,n}(t) \quad (28)$$

The total current in the cascade is given by

$$I(t) = \sum_{j=1}^n I_j(t) \quad (29)$$

Furthermore, the total mass-balance at $t = 0^-$ yields

$$I^* = v_e F Q^* \Delta C^* \quad (30)$$

Introducing Equation 28 into Equation 29, taking into account Equation 30 gives

$$\frac{I(t) - I^*}{I^*} = \frac{\beta \tau^*}{n \tau} \sum_{j=1}^n Y_{j,n}(t) \quad (31)$$

Evaluating Equation 31 at $\beta = 0$ yields

$$I(t) = I^* \quad \text{for all } t \quad (32)$$

Therefore, it is demonstrated that all the equations deduced for the potentiostatic control are valid for the galvanostatic case when $\beta = 0$.

3. Dynamic behaviour of the plug flow model

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

$$\varepsilon \frac{\partial C(x,t)}{\partial t} = -v \frac{\partial C(x,t)}{\partial x} - \frac{i(x,t) a_e}{v_e F} \quad (33)$$

at $t = 0^-$ is

$$v^* \frac{dC^*(x)}{dx} = -\frac{i^*(x) a_e}{v_e F} \quad (34)$$

Defining

$$Y(x,t) = \frac{C(x,t) - C^*(x)}{\Delta C^*} \quad (35)$$

Combining Equations 33 to 35 gives

$$\tau \frac{\partial Y(x,t)}{\partial t} = -L \frac{\partial Y(x,t)}{\partial x} + \frac{a_e L}{\Delta C^* v_e F} \left(\frac{i^*(x)}{v^*} - \frac{i(x,t)}{v} \right) \quad (36)$$

Adopting the following expression for the kinetics

$$i(x,t) = v_e F k C(x,t) \quad (37)$$

and introducing Equation 37 evaluated at t and at $t = 0^-$ into Equation 36 yields

$$\tau \frac{\partial Y(x,t)}{\partial t} = -L \frac{\partial Y(x,t)}{\partial x} - \beta Y(x,t) + \beta \frac{A}{Q^*} \frac{C^*(x)}{\Delta C^*} \quad (38)$$

Solving Equation 34 taking into account Equation 37 evaluated at $t = 0^-$ yields

$$C^*(x) = C_0 \exp\left(-\frac{\beta \tau^* x}{\tau L}\right) \quad (39)$$

Evaluating Equation 39 at $x = L$ and rearranging yields

$$\Delta C^* = C_0 \left(1 - \exp\left(-\frac{\beta \tau^*}{\tau}\right) \right) \quad (40)$$

Introducing Equations 39 and 40 into Equation 38 gives

$$\begin{aligned} \tau \frac{\partial Y(x,t)}{\partial t} = & -L \frac{\partial Y(x,t)}{\partial x} - \beta Y(x,t) \\ & + \beta \frac{A}{Q^*} \frac{\exp\left(-\frac{\beta \tau^* x}{\tau L}\right)}{1 - \exp\left(-\frac{\beta \tau^*}{\tau}\right)} \end{aligned} \quad (41)$$

with the following initial and boundary conditions

$$t = 0 \quad Y(x,t) = 0 \quad \text{for all } x \quad (41a)$$

$$x = 0 \quad Y(x,t) = 0 \quad \text{for all } t \quad (41b)$$

Laplace transformation of Equation 41 gives

$$L \frac{dY(x,s)}{dx} + (\tau s + \beta) Y(x,s) = \frac{\beta A}{s Q^*} \frac{\exp\left(-\frac{\beta \tau^* x}{\tau L}\right)}{1 - \exp\left(-\frac{\beta \tau^*}{\tau}\right)} \quad (42)$$

Solving Equation 42 by Laplace transform inversion gives

$$\begin{aligned} Y(x,t) = & \frac{\exp\left(-\frac{\beta \tau^* x}{\tau L}\right) \left\{ \exp\left[-\beta \left(1 - \frac{\tau^*}{\tau}\right) \frac{t}{\tau}\right] - 1 \right\}}{1 - \exp\left(-\frac{\beta \tau^*}{\tau}\right)} \\ & + \frac{\exp\left(-\frac{\beta x}{L}\right) \left\{ 1 - \exp\left[-\frac{\beta}{\tau} \left(1 - \frac{\tau^*}{\tau}\right) \left(t - \frac{x\varepsilon}{v}\right)\right] \right\}}{1 - \exp\left(-\frac{\beta \tau^*}{\tau}\right)} \\ & \times H\left(t - \frac{x\varepsilon}{v}\right) \end{aligned} \quad (43)$$

with

$$H\left(t - \frac{x\varepsilon}{v}\right) = 0 \quad t < \frac{x\varepsilon}{v} \quad (43a)$$

$$H\left(t - \frac{x\varepsilon}{v}\right) = 1 \quad t \geq \frac{x\varepsilon}{v} \quad (43b)$$

Evaluating Equation 43 at $x = L$ for $t < \tau$ yields

$$Y(L, t) = \frac{\exp\left(-\frac{\beta\tau^*}{\tau}\right) \left\{ \exp\left[-\beta\left(1 - \frac{\tau^*}{\tau}\right) \frac{t}{\tau}\right] - 1 \right\}}{1 - \exp\left(-\frac{\beta\tau^*}{\tau}\right)} \quad (44)$$

Evaluating Equation 43 at $x = L$ and $t \geq \tau$ gives

$$Y(L, t) = \frac{\exp(-\beta) - \exp\left(-\frac{\beta\tau^*}{\tau}\right)}{1 - \exp\left(-\frac{\beta\tau^*}{\tau}\right)} \quad (45)$$

For $\beta = 0$ Equation 44 is simplified to

$$Y(L, t) = \frac{A t}{Q \tau} \quad (46)$$

Analogously, for $\beta = 0$ Equation 45 yields

$$Y(L, t) = \frac{A}{Q} \quad (47)$$

The total current is given by

$$I(t) = a_e S \int_0^L i(x, t) dx \quad (48)$$

Combining Equations 35, 37 and 48 gives

$$I(t) - I^* = v_e F k a_e S \Delta C^* \int_0^L Y(x, t) dx \quad (49)$$

Introducing the total mass-balance at $t = 0^-$, Equation 30, into Equation 49 and rearranging produces

$$\frac{I(t) - I^*}{I^*} = \frac{\beta\tau^*}{L\tau} \int_0^L Y(x, t) dx \quad (50)$$

Introducing Equation 43 into Equation 50 and integrating yields

$$\begin{aligned} \frac{I(t) - I^*}{I^*} &= \frac{\tau^*}{\tau} \frac{1 - \exp\left(-\beta \frac{L}{\tau}\right)}{1 - \exp\left(-\beta \frac{\tau^*}{\tau}\right)} + \frac{\exp\left(-\beta \frac{L}{\tau}\right)}{1 - \exp\left(-\beta \frac{\tau^*}{\tau}\right)} \\ &\times \left\{ 1 - \exp\left[\beta \frac{\tau^*}{\tau} \left(\frac{t}{\tau} - 1\right)\right] \right\} - 1 \end{aligned} \quad (51)$$

For $t = \tau$ Equation 51 is reduced to

$$\frac{I(\tau) - I^*}{I^*} = \frac{\tau^*}{\tau} \frac{1 - \exp(-\beta)}{1 - \exp\left(-\beta \frac{\tau^*}{\tau}\right)} - 1 \quad (52)$$

For $\beta \rightarrow 0$ Equation 51 approaches Equation 32.

4. Results and discussion

Figure 1 shows the response of electrochemical reactors according to the tank series model under galvanostatic control, Equation 27, for a step change in the flow rate. Thus, the difference between the outlet concentration at time t and the outlet concentration before the perturbation related to the change of concentration between inlet and outlet before the perturbation as a function of the normalized time, t/τ , is plotted. The behaviour of the plug-flow model under the same conditions, Equations 46 and 47, 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 a constant independent of the number of reactors in the stack.

Figures 2 and 3 show typical responses of the tank series model, Equation 24 for $j = n$, taking into account Equations 13 and 17, and the plug-flow model, Equations 44 and 45, under potentiostatic control for different β values. Again, at high t values the tank series model approaches a limiting value, but the limiting value depends on the reactor number in the stack. This behaviour can be explained taking into account that under potentiostatic control the reaction rate depends on the concentration.

Taking into account Equation 3 for $j = n$ or Equation 35 evaluated at $x = L$, Y can be rearranged to give

$$Y = 1 - \frac{\Delta C}{\Delta C^*} \quad (53)$$

when $A > 0$ Figures 1 to 3 show that Y is lower than one and ΔC is lower than ΔC^* because the residence time in

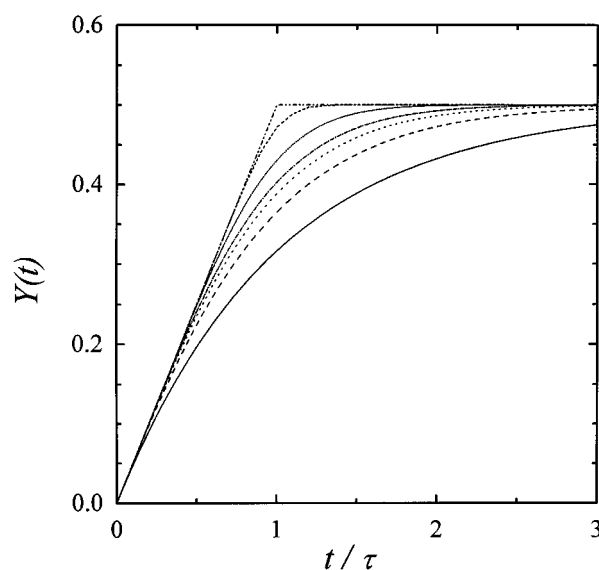


Fig. 1. Transient response in outlet concentration. Galvanostatic control. $A/Q = 0.5$. Key (lower to upper curve): (—) 1, (---) 2, (- - - -) 3, (- · - · - ·) 4, (· · · · ·) 8 and (- - - - -) 50 reactors; (· · · · ·) plug flow.

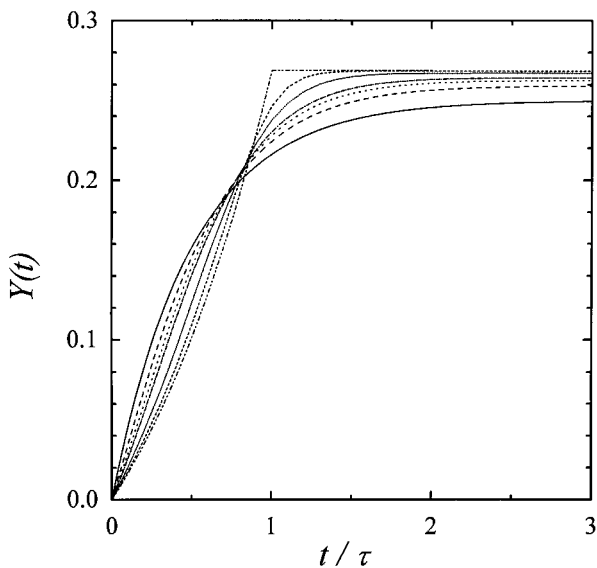


Fig. 2. Transient response in outlet concentration. Potentiostatic control. $\beta = 1$. $A/Q = 0.5$. Key: (—) 1, (---) 2, (.....) 3, (.....) 4, (.....) 10 and (.....) 30 reactors; (.....) plug flow.

the cascade is decreased. Likewise, when β increases Y decreases and a step change in flow rate has a less significant influence on the dynamic behaviour.

Figures 4 and 5 show the response in current of the studied systems, (Equations 31 and 51) for different β values. The transient behaviour in current takes place for $t/\tau < 2$, depending on the β value. At $t \rightarrow \infty$ the variation in the current related to the initial current approaches a constant value. But, unlike the case of a step change in the inlet concentration [6], the constant value depends on both n and β .

Figures 1–5 show that a cascade of electrochemical reactors achieves steady state at $t \rightarrow \infty$. From a practical point of view it is interesting to know the necessary time to achieve conditions close to steady state. Thus, a time t_s , termed the stabilization time,

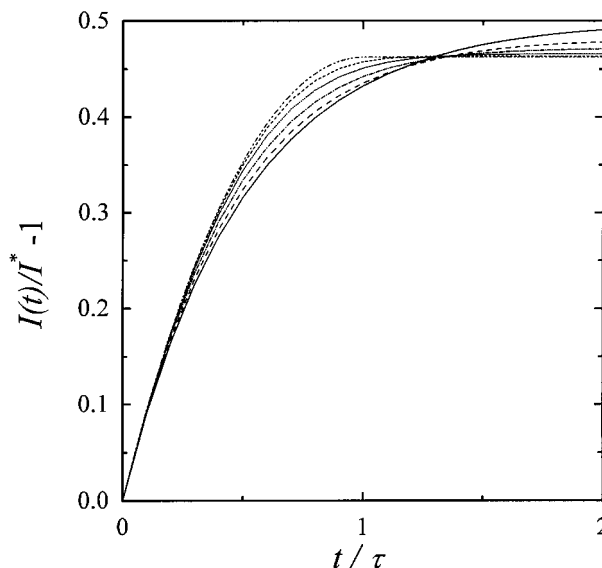


Fig. 4. Transient response in current. Potentiostatic control. $\beta = 1$. $A/Q = 0.5$. Key: (—) 1, (---) 2, (.....) 4, (.....) 10 and (.....) 30 reactors; (.....) plug flow.

where the response of the system is 99% of the steady state value may be defined. Figure 6 shows the time t_s normalized with respect to τ as a function of n and β . The results shown in Figure 6 are similar to those obtained for a step change in inlet concentration [6]. For a given value of n the normalized stabilization time always decreases when β increases. For high values of n and β the stabilization time approaches the reactor residence time. However, for a given β value t_s/τ decreases with n when β is small and increases with n for high β values. The results of Figure 6 are re-plotted in Figure 7 by using a contour plotting routine to produce iso- t_s/τ profiles. Figure 7 allows a simple estimation of the stabilization time of a cascade of electrochemical reactors.

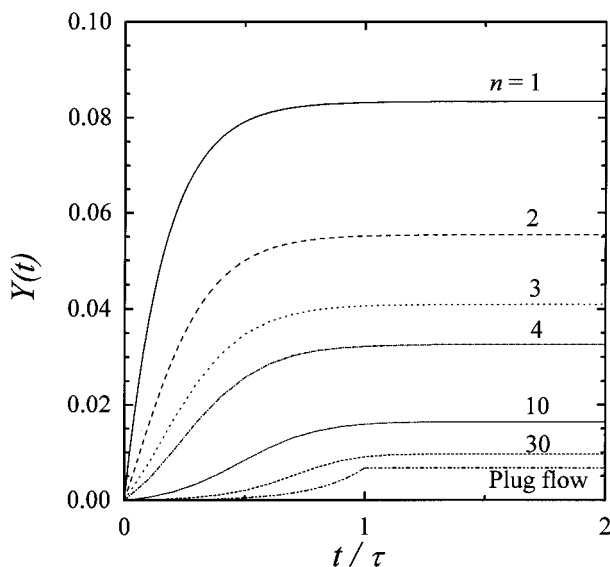


Fig. 3. Transient response in outlet concentration. Potentiostatic control. $\beta = 5$. $A/Q = 0.5$.

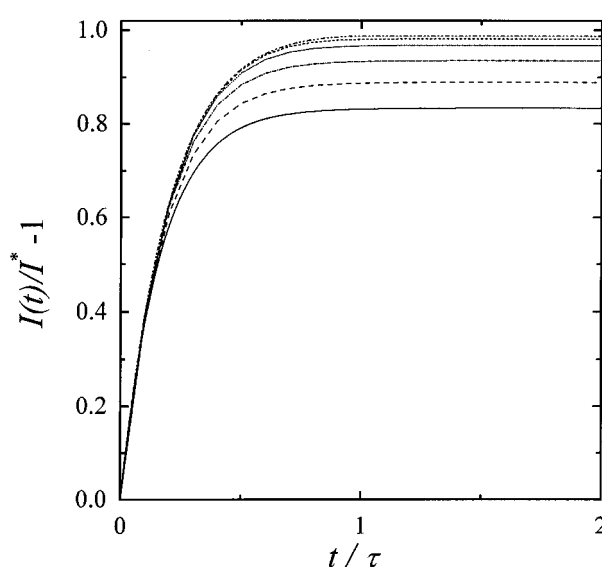


Fig. 5. Transient response in current. Potentiostatic control. $\beta = 5$. $A/Q = 0.5$. Key: as for Figure 4.

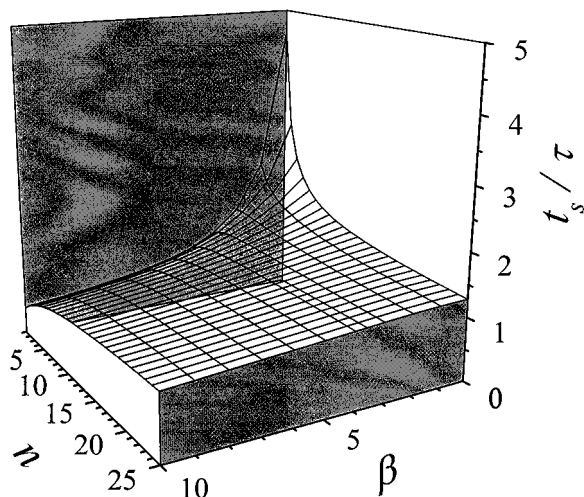


Fig. 6. Time to reach the 99% of the steady state outlet concentration normalized by the cascade residence time as a function of β and the number of reactors in the cascade.

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, *J. Electrochem. Soc.* **136** (1989) 2552.
2. K. Scott, 'Electrochemical Reaction Engineering' (Academic Press, London, 1991), chapter 5, p. 318.

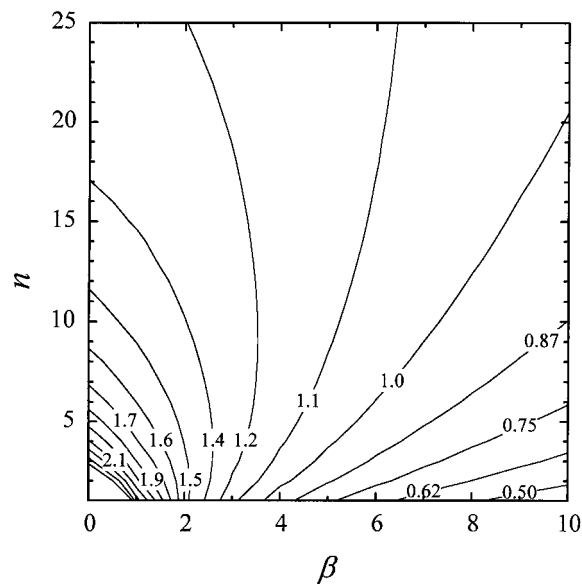


Fig. 7. Contour plots of the time to reach the 99% of the steady state outlet concentration normalized by the cascade residence time. Contour height numbers are t_s/τ values.

3. H. Unbehauen and I. Alatiqi, in 'Electrochemical Reactors: Their Science and Technology Part A' (edited by M.I. Ismail), (Elsevier Science, Amsterdam, 1989), chapter 12, p. 356.
4. B. Fleet and C.E. Small, in 'Electrochemical Reactors: Their Science and Technology Part A' (edited by M.I. Ismail), (Elsevier Science, Amsterdam, 1989), chapter 13, p. 365.
5. J.M. Bisang, *J. Appl. Electrochem.* **27** (1997) 379.
6. J.M. Bisang, *J. Appl. Electrochem.* **28** (1998) 1035.
7. D.D. Perlmutter, in 'Introduction to Chemical Process Control' (J. Wiley & Sons, New York, 1965), chapter 1, p. 3.
8. K. Scott, 'Electrochemical Reaction Engineering' (Academic Press, London, 1991), chapter 2, p. 54.