NONLINEAR-EXPONENTIAL NUMERICAL MODELLING AND SIMULATION OF THE KINETIC RAPID REDOX REACTION Cu^{2+} WITH $S_2O_3^{2-}$

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Abstract: For a no periodically, rapid damped, evolution of reaction between Cu^{2+} and $S_2O_3^{2-}$, the paper proposes a variant of numerical modelling and simulation, based on two exponential functions. The method assures a good approximation of the experimental solution, with a remarkable flexibility for analyses and synthesis elaborated in the paper.

Keywords: kinetic of rapid reactions in solutions, nonlinear-exponential functions, systems of nonlinear equations, numerical simulation.

1. INTRODUCTION

Reactions between thiosulfate and ions of metallic elements in solution have been repeatedly studied, several papers being published, for instance (Bâldea I. *et al.,* 1968, 1970), (Niac G. *et al.,* 1962, 1971), (Cădariu I. *et al.,*1962).

The kinetics of the redox reaction between copper and thiosulfate ions as well as the formation of an uncharged intermediate complex, CuS_2O_3, was investigated. The reaction order, with respect to the intermediate complex in equilibrium with the reactants, depends upon the concentrations of the reactants.

The kinetics of fading away of the color of this complex has been traced spectrophotometrically with a stopped-flow apparatus (Ungureşan M.L., 2003, 2005).

The experiments realized with mixing chamber for a pomp's time < 0,5 s have allowed recording on the oscilloscope of the curves transmitted light intensity at the apparition of reaction intermediate as well as of its disappearance, for different reactant's concentrations. (fig. 1)

2. ANALOGICAL MODELLING

The qualitative form of the signal experimentally increased $y = y(t)$ in fig. 1 contains two extremes, in the moments (t_α) and (t_γ) , and then it is followed by an a decreasing asymptotic evolution towards the value (y_{00}) that corresponds also to the starting value $y_{00} = y(o)$, as well as to the value $y_{00} = y(t_\beta) = y_\beta$ (Ungureşan M.L., *et all.,* 2005).

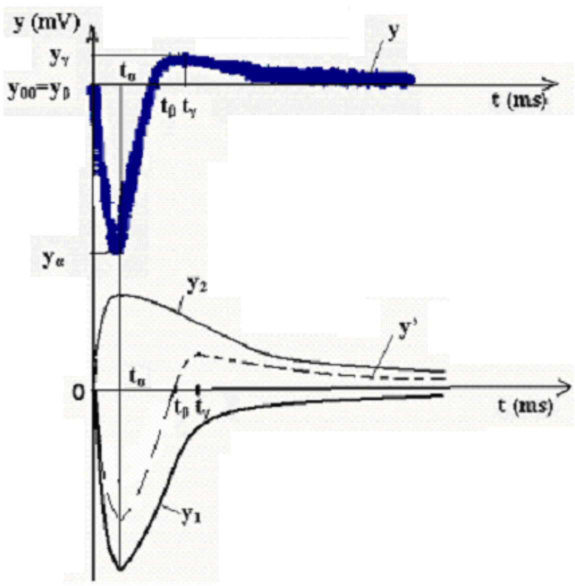

Fig. 1. Transmitted light intensity y(mV) as a function of time t(ms) at $[(S_2O_3)^{2-}]$ =0,005M and $[Cu^{2+}]$=0,005M

The paper tries to approximate the experimental signal y(t) through:

$$y(t) \approx y_{00} + y'(t) \quad (1)$$

where

$$y'(t) = y_1(t)+y_2(t) \quad (2)$$

It is considered that:

$$y_1(t) = -A_1 t^{\tau_1} \cdot \varepsilon^{-\frac{t}{T_1}} \quad (3)$$

and

$$y_2(t) = A_2 t^{\tau_2} \cdot \varepsilon^{-\frac{t}{T_2}} \quad (4)$$

which includes the parameters (t^{τ_1}) and (t^{τ_2}), less usual for exponential functions, by forcing behaviors more nonlinear (Bellomo N. *et al.,*1995).

As a result, in order to be able to approximate the experimental signal (1), respectively:

$$y(t) = y_{00} - A_1 t^{\tau_1} \cdot \varepsilon^{-\frac{t}{T_1}} + A_2 t^{\tau_2} \cdot \varepsilon^{-\frac{t}{T_2}} \quad (5)$$

the unknowns A_1, A_2, T_1, T_2, τ_1, τ_2 we will calculate and approximate from the following equations system (Bronstein I.N. , *et all.,* 1974):

$$y_\alpha = y_{00} - A_1 t_\alpha^{\tau_1} \cdot \varepsilon^{-\frac{t_\alpha}{T_1}} + A_2 t_\alpha^{\tau_2} \cdot \varepsilon^{-\frac{t_\alpha}{T_2}} \quad (6)$$

$$\left(\frac{dy}{dt}\right)_\alpha = -A_1 \cdot t_\alpha^{\tau_1} \cdot (\tau_1 - \frac{t_\alpha}{T_1}) \cdot \varepsilon^{-t_\alpha/T_1} +$$

$$+ A_2 \cdot t_\alpha^{\tau_2} \cdot (\tau_2 - \frac{t_\alpha}{T_2}) \cdot \varepsilon^{-t_\alpha/T_2} = 0 \quad (7)$$

$$y_\beta = y_{00} - A_1 t_\beta^{\tau_1} \cdot \varepsilon^{-\frac{t_\beta}{T_1}} + A_2 t_\beta^{\tau_2} \cdot \varepsilon^{-\frac{t_\beta}{T_2}} = y_{00} \quad (8)$$

$$y_\gamma = y_{00} - A_1 t_\gamma^{\tau_1} \cdot \varepsilon^{-\frac{t_\gamma}{T_1}} + A_2 t_\gamma^{\tau_2} \cdot \varepsilon^{-\frac{t_\gamma}{T_2}} \quad (9)$$

$$\left(\frac{dy}{dt}\right)_\gamma = -A_1 \cdot t_\gamma^{\tau_1} \cdot (\tau_1 - \frac{t_\gamma}{T_1}) \cdot \varepsilon^{-t_\gamma/T_1} +$$

$$+ A_2 \cdot t_\gamma^{\tau_2} \cdot (\tau_2 - \frac{t_\gamma}{T_2}) \cdot \varepsilon^{-t_\gamma/T_2} = 0 \quad (10)$$

In order to insure that $y_{1\alpha} = y_1(t_\alpha)$ and $y_{2\alpha} = y_2(t_\alpha)$ present the two extremes in the same moment $(t_\alpha)_1$ from (7) we have the conditions:

$$\tau_1 = \frac{t_\alpha}{T_1} \quad (11)$$

$$\tau_2 = \frac{t_\alpha}{T_2} \quad (12)$$

where the time constants (T_1) and (T_2) characterize the inertial-evolution of the curves $y_1(t)$ and $y_2(t)$. To insure at $t>t_\beta$ the condition $y'(t) > 0$, it is imposed that the decreasing speed for $y_2(t)$ to be less then the one for $y_1(t)$, that is $T_2 > T_1$.

The initial conditions (IC) known from the experimental measurements are: $t_0 = 0$ms, $y(t_0) = y_{00} = 1493.5$ mV, $t_\alpha = 50$ms, $y(t_\alpha) = y_\alpha = 1303$ mV, $t_\beta = 155$ms, $y(t_\beta) = y_{00}$, $t_\gamma = 215$ms, $y(t_\gamma) = y_\gamma = 1523$ mV, after that $y(t)$ decreases asymptotically towards y_{00}.

Introducing these IC in (6) and (9) we have:

$$A_1 = \frac{y_\gamma - y_{00}}{E_3} - \frac{E_4}{E_3} \quad (13)$$

and

$$A_2 = \frac{y_\gamma - y_{00}}{E_1} + \frac{E_2}{E_1} \cdot A_1 \quad (14)$$

where the intermediary expressions of calculus are:

$$E_1 = t_\alpha^{\tau_2} \cdot \varepsilon^{-t_\alpha/T_2} \quad (15)$$

$$E_2 = t_\alpha^{\tau_1} \cdot \varepsilon^{-t_\alpha/T_1} \quad (16)$$

$$E_3 = -t_\gamma^{\tau_1} \cdot \varepsilon^{-t_\gamma/T_1} + t_\gamma^{\tau_2} \cdot \varepsilon^{-t_\gamma/T_2} \cdot \frac{E_1}{E_2} \quad (17)$$

$$E_4 = t_\gamma^{\tau_2} \cdot \varepsilon^{-t_\gamma/T_2} \cdot \frac{y_\alpha - y_{00}}{E_1} \quad (18)$$

Introducing the results (A_1) and (A_2) in (6), (7) and (9) we have the three conditions that are necessary for $y(t)$ to go through the points (y_α), for $\left(\frac{dy}{dt}\right)_\alpha = 0$ and (y_γ).

In order to fulfill the other two conditions, that is $y_\beta = y_{00}$ and $\left(\frac{dy}{dt}\right)_\gamma = 0$ solving the transcendent equations (8) and (10) with respect to the unknowns (T_1) and (T_2) is necessary. For this, the great volume of calculus has been avoided by using a procedure of iterative and successive incrementation of the time constants (T_1) and (T_2) in the usual limits (0÷1000)ms, with the increment ΔT=1ms. We have obtained a good compromise for T_1=30ms and T_2=190ms, resulting: $\tau_1 = 1.666667$; $\tau_2 = 0.2631579$; $A_1 = 2.011715$; $A_2 = 31.2965$; $y_\alpha = 1303$; $\left(\frac{dy}{dt}\right)_\alpha = 0$; $y_\beta = 1494.375$; $y_\gamma = 1523$; $\left(\frac{dy}{dt}\right)_\gamma = 0.1389582$.

3. NUMERICAL SIMULATION (Coloşi T., *et all.,* 2002)

3.1. The program YREDOX 3(4)

It insures the semi iterative calculus of the time constants (T_1) and (T_2) for known the initial conditions (IC): (y_{00}), (y_α), (t_β), $y_\beta = y_{00}$, (t_γ) and (y_γ). (T_1) is predetermined, then (T_2) is being incremented, until the results become almost identical with the IC.

10 $t_0 = 0$; $t_k = t_0$; $\Delta t = 1$; $t_f = 1000$;

20 y_{00} =1493.5; t_α = 50; y_α = 1303; t_β = 155; $y(t_\beta)$= y_{00}, t_γ = 215ms, y_γ = 1523 mV; T_1 = 1; T_2 = 1; T_{1max}= 100; T_{2max}= 300; ΔT= 1.

30 $\tau_1 = \frac{t_\alpha}{T_1}$; $\tau_2 = \frac{t_\alpha}{T_2}$;

40 $E_1 = t_\alpha^{\tau_2} \cdot \varepsilon^{-t_\alpha/T_2}$; $E_2 = t_\alpha^{\tau_1} \cdot \varepsilon^{-t_\alpha/T_1}$;

$E_3 = -t_\gamma^{\tau_1} \cdot \varepsilon^{-t_\gamma/T_1} + t_\gamma^{\tau_2} \cdot \varepsilon^{-t_\gamma/T_2} \cdot \frac{E_1}{E_2}$;

$E_4 = t_\gamma^{\tau_2} \cdot \varepsilon^{-t_\gamma / T_2} \cdot \frac{y_\alpha - y_{00}}{E_1}$;

50 $A_1 = \frac{y_\gamma - y_{00}}{E_3} - \frac{E_4}{E_3}$; $A_2 = \frac{y_\gamma - y_{00}}{E_1} + \frac{E_2}{E_1} \cdot A_1$

60 $y_\alpha = y_{00} - A_1 t_\alpha^{\tau_1} \cdot \varepsilon^{-\frac{t_\alpha}{T_1}} + A_2 t_\alpha^{\tau_2} \cdot \varepsilon^{-\frac{t_\alpha}{T_2}}$;

70 $\left(\frac{dy}{dt}\right)_\alpha = -A_1 \cdot t_\alpha^{\tau_1} \cdot (\tau_1 - \frac{t_\alpha}{T_1}) \cdot \varepsilon^{-t_\alpha / T_1} +$

$+ A_2 \cdot t_\alpha^{\tau_2} \cdot (\tau_2 - \frac{t_\alpha}{T_2}) \cdot \varepsilon^{-t_\alpha / T_2}$;

80 $y_\beta = y_{00} - A_1 t_\beta^{\tau_1} \cdot \varepsilon^{-\frac{t_\beta}{T_1}} + A_2 t_\beta^{\tau_2} \cdot \varepsilon^{-\frac{t_\beta}{T_2}}$;

90 $y_\gamma = y_{00} - A_1 t_\gamma^{\tau_1} \cdot \varepsilon^{-\frac{t_\gamma}{T_1}} + A_2 t_\gamma^{\tau_2} \cdot \varepsilon^{-\frac{t_\gamma}{T_2}}$;

100 $\left(\frac{dy}{dt}\right)_\gamma = -A_1 \cdot t_\gamma^{\tau_1} \cdot (\tau_1 - \frac{t_\gamma}{T_1}) \cdot \varepsilon^{-t_\gamma / T_1} +$

$+ A_2 \cdot t_\gamma^{\tau_2} \cdot (\tau_2 - \frac{t_\gamma}{T_2}) \cdot \varepsilon^{-t_\gamma / T_2}$;

110 Print: T_1; T_2; A_1; A_2; τ_1; τ_2;

120 Print: y_α; $\left(\frac{dy}{dt}\right)_\alpha$; y_β; y_γ; $\left(\frac{dy}{dt}\right)_\gamma$; STOP;

130 IF $T_2 \geq T_{2max}$ go to 160;

140 $T_2 = T_2 + \Delta T$;

150 go to 30;

160 IF $T_1 \geq T_{1max}$ go to 190;

170 $T_2 = 1$; $T_1 = T_1 + \Delta T$;

180 go to 30;

190 STOP;

200 END.

The results obtained at the program's line 110 represents the primary data for solving (6), (7), (8), (9), and (10), and the results obtained at the program's line 120 have to approximate as well as possible the initial conditions (IC).

3.2. The program YREDOX 5(6)

With the results obtained in the previous program we raise y=y(t), which needs to approximate the experimental measurements as well as possible.

10 $t_0 = 0$; $t_k = t_0$; $\Delta t = 1$; $t_f = 1000$;

20 $y_{00} = 1493.5$; $t_\alpha = 50$; $y_\alpha = 1303$; $t_\beta = 155$; $y(t_\beta) = y_{00}$, $t_\gamma = 215$ms, $y_\gamma = 1523$ mV;

30 $T_1 = 30$; $T_2 = 190$; $\tau_1 = \frac{t_\alpha}{T_1}$; $\tau_2 = \frac{t_\alpha}{T_2}$; $A_1 = 2.011715$; $A_2 = 31.2965$;

40 $y = y_{00} - A_1 t_k^{\tau_1} \cdot \varepsilon^{-\frac{t_k}{T_1}} + A_2 t_k^{\tau_2} \cdot \varepsilon^{-\frac{t_k}{T_2}}$;

50 Print t_k; y; STOP;

60 IF $t_k \geq t_f$ go to 90;

70 $t_k = t_k + \Delta t$;

80 go to 40;

90 STOP;

100 END.

3.3. The results of the simulation

With the data obtained in the program's line 50 we complete the following comparative table.

Table 1: The experimental measurements and the measurements numerically simulated results

Nr.	t(ms)	Y_{exp}^{mV}	y_{sim}^{mV}
1.	0	1493.5	1493.5
2.	10	1460.938	1481
3.	20	1409.375	1403
4.	30	1354.687	1344
5.	40	1317.187	1312
6.	50	1303.125	1303
7.	60	1304.687	1310
8.	70	1325	1328
9.	80	1354.687	1351
10.	90	1376.562	1376
11.	100	1403.125	1401
12.	110	1421.875	1424
13.	120	1435.938	1444
14.	130	1454.688	1462
15.	140	1473.438	1477
16.	150	1492.188	1489
17.	160	1507.81	1499
18.	170	1517.188	1506
19.	180	1517.188	1512
20.	190	1520.313	1517
21.	200	1521.875	1520
22.	210	1523.538	1522
23.	220	1523.321	1526
23.	250	1520.313	1524.6
24.	300	-	1521
25.	400	-	1512
26.	500	-	1505
27.	600	-	1500
28.	700	-	1498
29.	800	-	1496
30.	900	-	1495
26	1000	-	1494.5

It can be observed the rigorous correspondence of the numerically simulated signal y(t), , with the signal $y_{exp}(t)$ experimentally raised to t_α=50ms, respectively y_α = 1303 mV with $\left(\frac{dy}{dt}\right)_\alpha = 0$ and at t_γ = 215 ms, for witch y_γ = 1523 mV. At t_β=155 ms we have y_β = 1494 mV, different from the experimental signal y = y_{00} = 1493,5 mV. Between those time intervals, the differences between y(t) and $y_{exp}(t)$ remain negligible, and for t > t_γ, the evolution of y(t) is asymptotically reaching y_{00}=1493,5 mV.

4. CONCLUSIONS

4.1. Analogical modelling and numerical simulation in report to time, for study the kinetic rapid redox reaction Cu^{2+} and $S_2O_3^{2-}$, proposed in the relation (5) contains two opposed nonlinear exponential functions, that approximate quite well large categories of chemical processes.

4.2. The six degrees of freedom from the relation (5) that is (A_1), (A_2), (T_1), (T_2), (τ_1) and (τ_2) can assure a good flexibility for its adaptation in a quite large diversification of applications in this domain.

4.3. Rigorously respecting the conditions (6), (7) and (9) leads to exact values for (y_α), $\left(\frac{dy}{dt}\right)_\alpha$ and (y_γ) the semi iterative procedure of approximation of the time constants (T_1) and (T_2) assures a good interpolation of (5), besides the reference intervals (t_α), (t_β) and (t_γ), including for $t >> t_\gamma$.

4.4. The program YREDOX 3(4), after declaring the initial conditions from the program's lines 10 and 20, calculates the amplitudes (A_1) and (A_2) and approximates through a semi iterative procedure the time constants (T_1) and (T_2) . The program also assures a checking of the references in (5), through (y_α), $\left(\frac{dy}{dt}\right)_\alpha$, (y_β), (y_γ) and $\left(\frac{dy}{dt}\right)_\gamma$.

4.5. The program YREDOX 5(6), after declaring the initial conditions from the program's lines 10 and 20, and the calculus results (T_1), (T_2), (τ_1), (τ_2), (A_1) and (A_2), taken from YREDOX 3(4), declared in line 30, calculates the chronogram y(t), with an extraction step Δt = 1msec (that can be arbitrarily chosen).

4.6. The two programs from above are easy to be initialized and adopted for an even larger diversity, belonging to those categories of processes.

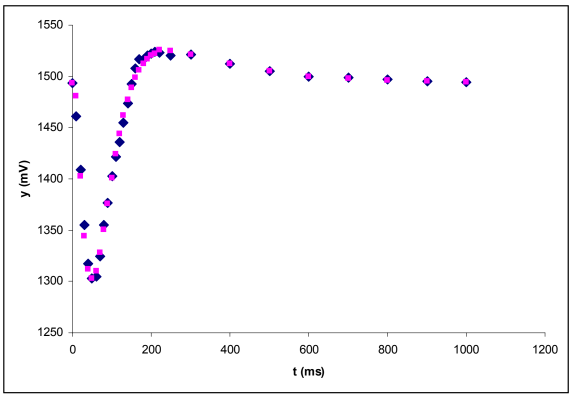

Fig. 2. Superposition experimental curve (■) to the simulated curve (▲)

It was simulating and modelling the kinetic of rapid redox reaction between Cu^{2+} and $S_2O_3^{2-}$ (fig. 2). This method can present a good compromise, between theoretic rigorous formalism and possibilities – sometimes very limited – of experimental methods of the evaluation.

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