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Article

Analytical Solution of Nonlinear Equation in NAPP Synthesis

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Abstract: The time dependent analytical expression for the concentrations of Hydroxylamine - O – Sulfonique acid (HOSA), Piperidine, N- aminopiperdine (NAPP), Sodium hydroxide (NaOH) and Diazene are presented by solving systems of non-linear differential equations. We employ the analytical method to solve the non-linear differential equations containing a non-linear term related to basic kinetic reaction. Closed and simple analytical expressions of concentrations have been derived in terms of parameters k_1 and k_2. The numerical solution of the problem is also reported using the Matlab program. Our analytical results are compared with our simulation and available experimental results. A good agreement is noted between analytical and experimental results.

Keywords: Kinetic modeling, Time dependent analytical solution, Mathematical modeling, Non-linear reaction equations, Simulation.

Mathematics Subject Classification (2000): 34B15, 34A34, 34G25, 34G20, 35E15, 65L05.

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1. Introduction

The extensive use of hydrogen as storable liquid rocket fuels has led to a renewal of interest in their synthesis. In most instances, the synthetic methods available are cumbersome, requiring multiple step separations from dilute aqueous solutions and therefore are expensive. Recently adopted an alternate

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procedure wherein the synthesis of monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) could be carried out in non-aqueous solvents instead, using the hydrous chloramine process [1]. The N-aminopiperidine, hydrazine of great interest, is often used in pharmaceutical applications. It is produced by the reaction between the hydroxylamine-O-sulfonic acid and a large excess of piperidine ($C_5H_{10}NH$) [2]. N-aminopiperidine (NAPP) is an exocyclic hydrazine often used in pharmaceutical industries [3]. Heterocyclic compounds, including an unsymmetrical hydrazine group are used in the pharmaceutical industry as precursors of medicinal drugs. In particular N–aminopiperidine (1, NAPP, $C_5H_{12}N_2$) is a precursor of a selective CB1 endocannabinoid receptor antagonist, commercially known as Rimonabant, which is used for the treatment of obesity and for smoking cessation [4].

The preparation of an unsymmetrical substituted hydrazine − 1-aminopiperidine − in an ammoniacal hypochlorite medium, which is used in the pharmaceutical industry as a precursor of medicinal drugs [5, 8]. These results are important to design a new process for the recovery of amine from an aqueous mixture of leaching with sodium hydroxide [6]. N- aminopiperdine (NAPP) is a precursor for the pharmaceutical industry. It is used for plant protection, in cosmetology and photographic chemistry. Other applications are the fabrication of paper and transparent recording films, the formulation of inhibitors and substances resistant to amine based solvents [7].

Labarthe. et al. [7] solved the system of differential equations in NAPP synthesis numerically by the Runge – Kutta method. However, to the best of our knowledge, to date, no analytical expressions corresponding to the concentrations of HOSA, Piperidine, NAPP, NAOH and Diazene are derived. The purpose of this communication is to derive an approximate analytical expression for the concentrations for all values of parameters.

2. Mathematical Formulation and Analysis of the Initial Value Problem

The reaction rate of concentrations of HOSA $(x(t))$, Piperidine $(a(t))$, NAPP $(u(t))$, NaOH $(b(t))$ and Diazene $(f(t))$ for all values of parameters k_1 and k_2 are described by the following system of non-linear differential equations [7]:

$$\frac{d}{dt}x(t) = -k_1 x(t)a(t) - k_2\, x(t)u(t) \tag{1}$$

$$\frac{d}{dt}a(t) = -k_1 x(t)a(t) \tag{2}$$

$$\frac{d}{dt}u(t) = k_1 x(t)a(t) - k_2\, x(t)u(t) \tag{3}$$

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$$\frac{d}{dt}b(t) = -2\left(k_1 x(t)\,a(t) + k_2\, x(t)u(t)\right) \tag{4}$$

$$\frac{d}{dt}f(t) = k_2 x(t)u(t) \tag{5}$$

where k_1 represents rate constant of the oxidation of NAPP by HOSA and k_2 represents rate constant of the reaction between HOSA and Piperdine. The initial conditions for the above equations for the above equations are given as follows:

$$\text{At } t=0:\ x = x_0,\ a = a_0,\ b = b_0 \quad and \quad u = f = 0 \tag{6}$$

From Eqns. (1-3), we get the following equation

$$\frac{dx(t)}{dt} - 2\frac{da(t)}{dt} - \frac{du(t)}{dt} = 0 \tag{7}$$

The integration of this equation with the boundary conditions (Eqn. (6)) leads to

$$x(t) = x_0 - 2a_0 + 2a(t) + u(t) \tag{8}$$

The instantaneous concentration of Piperdine and HOSA were determined experimentally from the NAPP concentration by using the following equations [7]:

$$a(t) = a_0 - u(t) \tag{9}$$

$$x(t) = x_0 - u(t) \tag{10}$$

From the above equations we get

$$x(t) = x_0 - a_0 + a(t) \tag{11}$$

Now the Eqn. (2) becomes

$$\frac{da(t)}{dt} = -k_1 a(t)\left(x_0 - a_0 + a(t)\right) \tag{12}$$

Solving the above equation using the initial condition $a\ (t=0) = a_0$, we get

$$a(t) = \frac{a_0\left(x_0 - a_0\right)}{x_0 e^{(x_0 - a_0)k_1 t} - a_0} \tag{13}$$

We can modify Eqns. (2) and (3) by dividing Eqn. (3) by Eqn. (2)

$$\frac{du(t)}{da} = -1 + \left(\frac{k_1}{k_2}\right)\left(\frac{u(t)}{a}\right) \tag{14}$$

Solving the above equation, we obtain

$$u(t) = \frac{k_1}{\left(k_2 - k_1\right)} a(t)\left(1 - \left(\frac{a(t)}{a_0}\right)^{\left(\frac{k_2}{k_1} - 1\right)}\right) \tag{15}$$

From Eqns. (1) and (4), we get the following relation:

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$$\frac{db(t)}{dt} = 2\left(\frac{dx(t)}{dt}\right) \tag{16}$$

Integrating the above equation, we get

$$b(t) = 2(x_0 - a_0 + a(t)) \tag{17}$$

Also from the Eqns. (1), (2) and (5), the following relation is obtained.

$$\frac{dx(t)}{dt} - \frac{da(t)}{dt} - \frac{df(t)}{dt} = 0 \tag{18}$$

By integrating the above equation we get the concentration of Diazene $(f(t))$ as follows:

$$f(t) = x_0 - a_0 + a(t) - x(t) \tag{19}$$

From the above results, we can summarize the concentrations HOSA, Piperidine, NAPP, NaOH and Diazene as follows:

$$x(t) = x_0 - a_0 + a(t) \tag{20}$$

$$a(t) = \frac{a_0(x_0 - a_0)}{x_0 e^{(x_0 - a_0)k_1 t} - a_0} \tag{21}$$

$$u(t) = \frac{k_1}{(k_2 - k_1)} a(t)\left(1 - \left(\frac{a(t)}{a_0}\right)^{\frac{k_1}{(k_2 - k_1)}}\right) \tag{22}$$

$$b(t) = 2(x_0 - a_0 + a(t)) \tag{23}$$

$$f(t) = x_0 - a_0 + a(t) - x(t) \tag{24}$$

When time $t \to \infty$, we can obtain steady state concentrations when $x_0 > a_0$ (or) $a_0 \geq u_0$, from Eqns. (20) - (24) as follows:

Steady state Concentration	When $a_0 \geq u_0$	When $x_0 > a_0$
HOSA	$x_s = 0$	$x_s = x_0 - a_0$
Piperidine	$a_s = a_0 - x_0$	$a_s = 0$
NAPP	$u_s = \frac{k_1(a_0 - x_0)}{k_2 - k_1}\left[1 - \left(\frac{a_0 - x_0}{a_0}\right)^{\frac{k_1}{k_1 - k_2}}\right]$	$u_s = \frac{k_1(x_0 - a_0)}{k_2 - k_1}\left[1 - \left(\frac{x_0 - a_0}{a_0}\right)^{\frac{k_1}{k_1 - k_2}}\right]$
NAOH	$b_s = 0$	$b_s = 2(x_0 - a_0)$
Diazene	$f_s = 0$	$f_s = 0$

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3. Numerical Simulation

The non-linear differential equations (1 - 5) for the given initial conditions (Eqn. 6) are being solved numerically. The function mat1, in Matlab software is used to solve the ordinary differential equations. The Matlab program is given in Appendix A. The numerical solution is compared with analytical solution for some experimental values of the parameters in Figs. 1- 6. Satisfactory agreement is noted between the analytical and numerical result.

4. Result and Discussion

Equations (20) – (24) represent the approximate simple and closed form analytical expressions of concentration of HOSA $(x(t))$, Piperdine $(a(t))$, NAPP $(u(t))$, NaOH $(b(t))$ and Diazene $(f(t))$. The analytical results Eqns. (20) – (24) are compared with numerical solution, which is provided in Figures (1–6). Fig. 1 shows the plots of all the concentration versus time t different values of the parameters k_1 and k_2. From this figure, it is inferred that the concentration of HOSA, Piperdine, NaOH $(b(t))$ and Diazene $(f(t))$ are decrease when time t increases. Whereas the concentration of $(u(t))$ increases when t increases.

From Figure. 2. (a), it is observed that the concentration of HOSA decreases when k_1 is large. Also the concentration of HOSA is uniform, when $k_1 \leq 0.01$. From Fig. 2. (b), it is inferred that the concentration decreases when the initial concentration of Piperdine a_0 increases.

Fig. 3 represents the concentration of Piperdine versus time t for various values of parameters. From Fig. 3. (a), it is inferred that the concentration of Piperdine decreases when the initial concentration of HOSA x_0 increases. When x_0 is small, concentration of Piperdine remains constant. From Fig. 3. (b), it is observed that the concentration of piperdine decreases when the rate constant k_1 increases for some fixed values of x_0 and a_0.

Fig. 4. shows the concentration of NAPP versus time t for various values of parameters. From Fig. 4. (a), we have investigated that the concentration of NAPP increases when k_1 increases for the some fixed values of x_0 and k_2. From Fig. 4. (b), it is investigated that the concentration NAPP increases when the initial concentration Piperdine a_0 increases. Also the concentration of NAPP is uniform when a_0 is very small.

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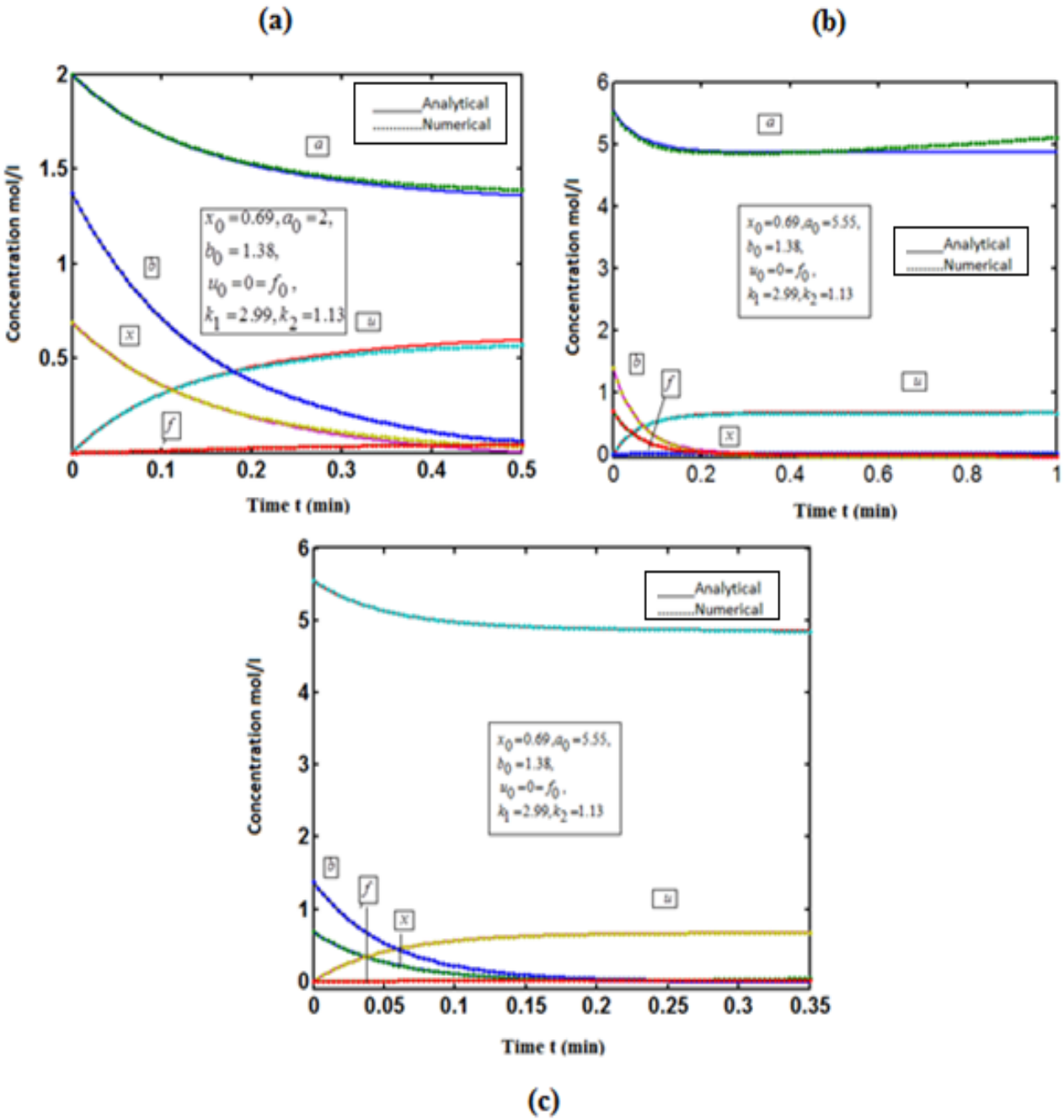

Fig. 1. Plot of concentrations of HOSA $(x(t))$, Piperdine $(a(t))$, NAPP $(u(t))$, NaOH $(b(t))$ and Diazene $(f(t))$ versus time t for different values of the parameters k_1 and k_2. The curves are plotted using Eqns. (20-24), for some fixed values of the following parameters:

(a) $x_0 = 0.69, a_0 = 2, b_0 = 1.38, u = f = 0, k_1 = 2.99, k_2 = 1.13.$

(b) $x_0 = 0.69, a_0 = 5.55, b_0 = 1.38, u = f = 0, k_1 = 2.99, k_2 = 1.13$

(c) $x_0 = 0.69, a_0 = 5.55, b_0 = 1.38, u = f = 0, k_1 = 2.99, k_2 = 1.13$

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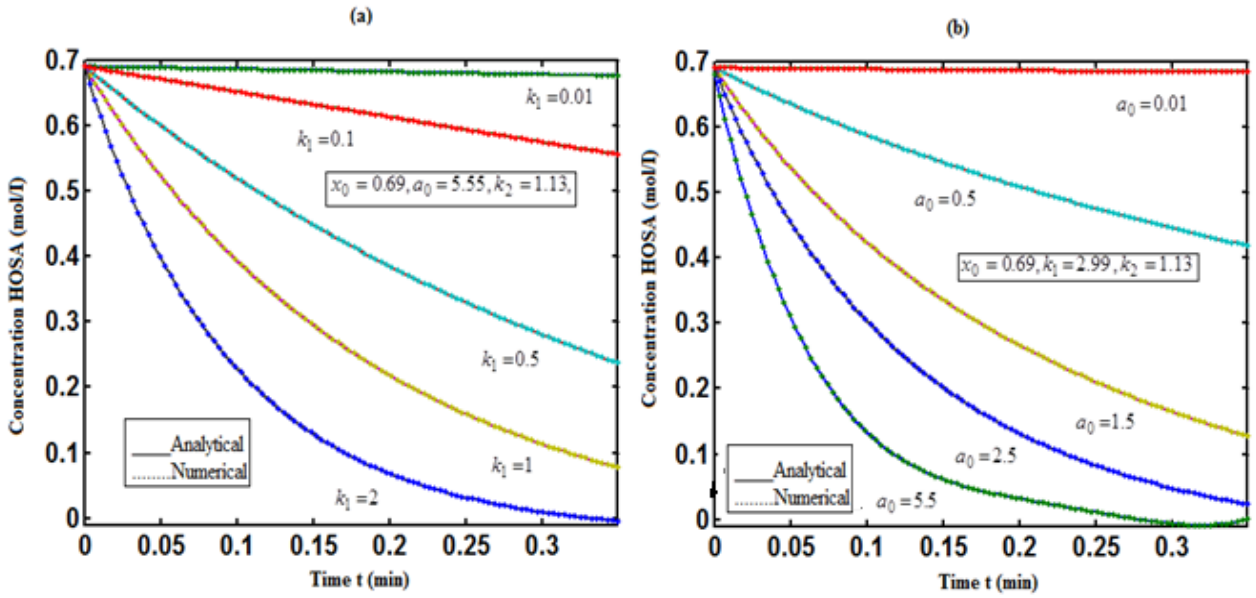

Fig. 2. Concentration profiles of HOSA $x(t)$ are plotted using Eq. (20). (a) For various values of the parameter k_1 and for some fixed (experimental) values of the parameters $x_0 = 0.69, a_0 = 5.55, k_2 = 1.13$. (b) For various values of the parameter a_0 and for some fixed (experimental) values of the parameters $x_0 = 0.69, k_1 = 2.99$ and $k_2 = 1.13$.

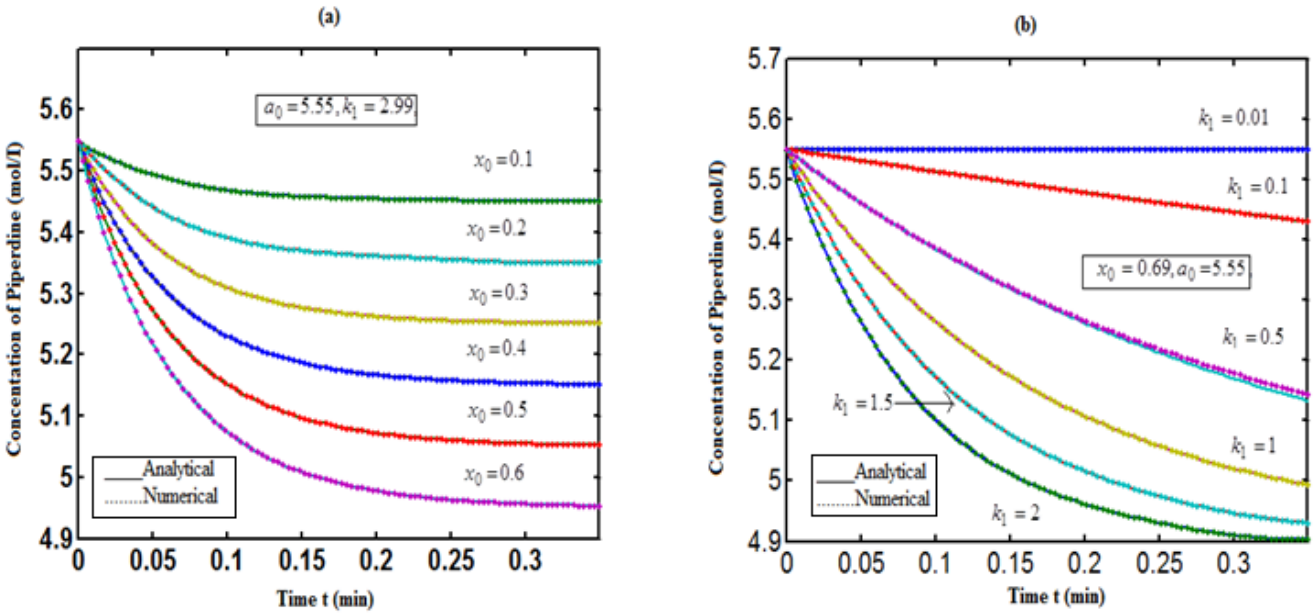

Fig. 3. Concentration profiles of Piperdine $a(t)$ versus time t using Eq. (21). (a) For various values of the parameter x_0 and for some fixed (experimental) values of the parameters $a_0 = 5.55$ and $k_1 = 2.99$. (b) For various values of the parameter k_1 and for some fixed (experimental) values of the parameters $x_0 = 0.69$ and $a_0 = 5.55$.

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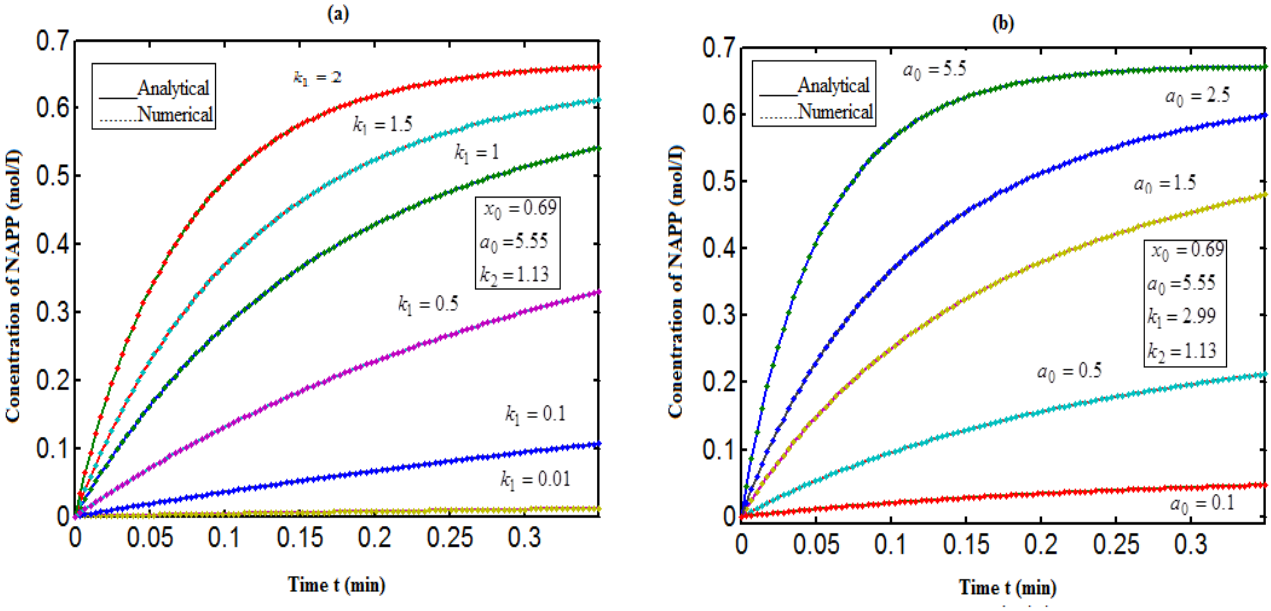

Fig. 4. Concentration profiles of NAPP $u(t)$ versus time t plotted using Eq. (22). (a) For various values of the parameter k_1 and for some fixed (experimental) values of the parameters $x_0 = 0.69, a_0 = 5.55$ and $k_2 = 1.13$. (b) For various values of the parameter a_0 and for some fixed (experimental) values of the parameters $x_0 = 0.69, a_0 = 5.55, k_1 = 2.99$ and $k_2 = 1.13$.

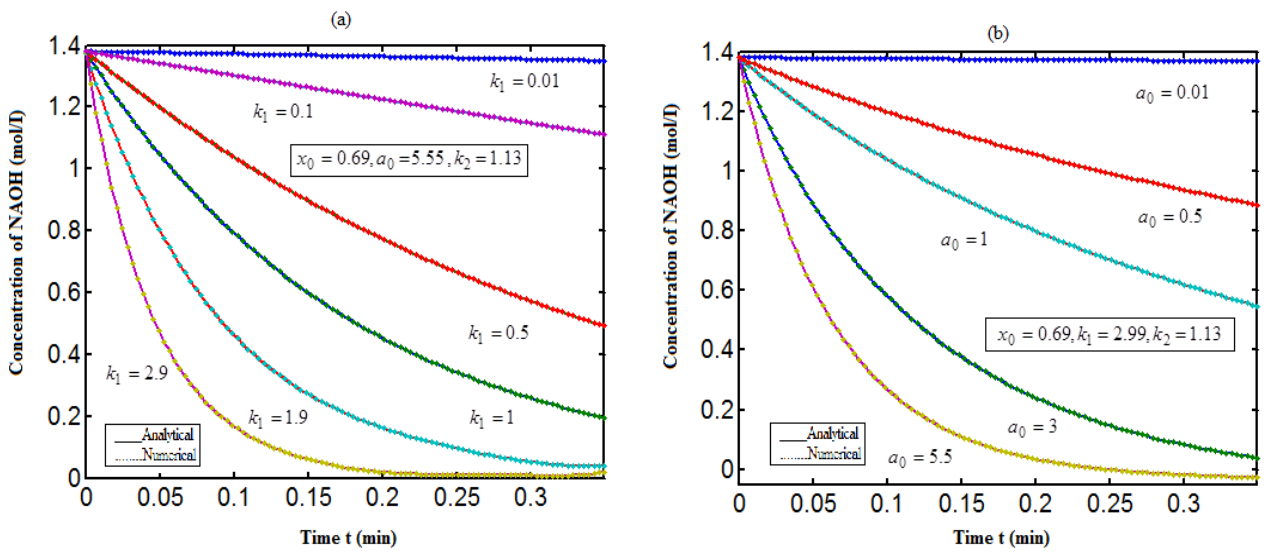

Fig. 5. Concentration profiles of NaOH $b(t)$ versus time t plotted using Eq. (23)

(a) For various values of the parameter k_1 and for some fixed (experimental) values of the parameters $x_0 = 0.69, a_0 = 5.55$ and $k_2 = 1.13$.

(b) For various values of the parameter a_0 and for some fixed (experimental) values of the parameters $x_0 = 0.69, k_1 = 2.99$ and $k_2 = 1.13$.

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Fig. 5 represents the plot of concentration NaOH versus time t for various values of reaction parameters. Fig. 5. (a), proves that the concentration of NaOH decreases when rate constant k_1 increases. It remains constant when k_1 (≤ 0.01) is small. From Fig. 5. (b), it is observed that the concentration of NAOH decreases when a_0 increases. Concentration of NaOH is uniform for small values of a_0 (≤ 0.01).

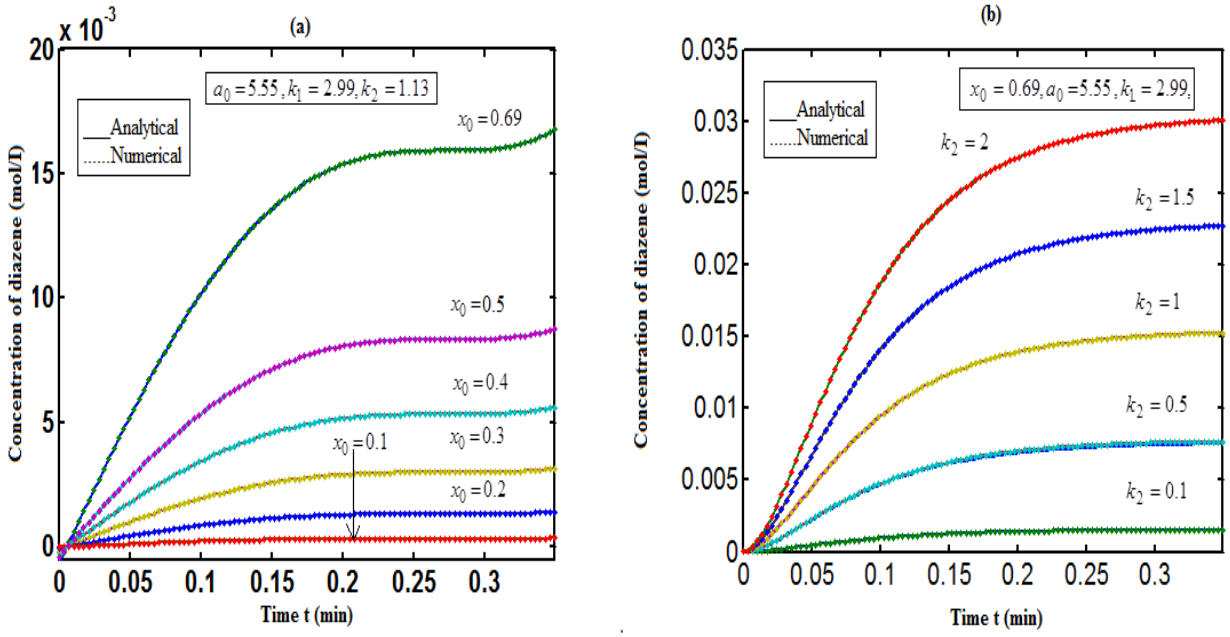

Fig. 6. Concentration profiles of Diazene $f(t)$ versus time t using Eqn. (24).

(a) For various values of the parameter x_0 and for some fixed (experimental) values of the parameters $a_0 = 5.55, k_1 = 2.99$ and $k_2 = 1.13$.

(b) For various values of the parameter k_2 and for any fixed (experimental) values of the parameters $x_0 = 0.69, a_0 = 5.55$ and $k_2 = 1.13$.

Fig. 6. denotes the plot concentration of Diazene $f(t)$ versus time t for various values of rate constant k_1 and k_2. From Fig. 6. (a), it is observed that the concentration of Diazene increases when the initial concentration of HOSA, x_0 increases. The concentration of Diazene attains its steady state value when $x_0 (\leq 0.01)$ is very small. From Fig. 6. (b), it is inferred that concentration of Diazene increases when the rate constant k_2 increases and the concentration of Diazene attains the costant value when the rate constant $x_0 = 0.69, a_0 = 5.55, k_2 = 1.13$.

Experimental result is compared with our analytical result (Eqn. (3)) for the concentration NAPP in Table 1. Satisfactory agreement is noted. Plot of rate of change of concentration of piperdine versus $x(t), a(t)$ is linear with a slope of k_1. From this simulation, we can obtain the value of the rate constant k_1. Similarly from the Eqn. (5), we can obtain the value of the rate constant k_2.

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Table: 1. Comparison of experimental result with our analytical result (Eqn. 3) of NAPP

Time t (min)	k_1 $(mol^{-1}\min^{-1})$	k_2 $(mol^{-1}\min^{-1})$	[NAPP] x 10^3(mol/I)	
			Experimental [7]	This work Analytical
7	3.50	1.16	0.32	0.314
14	3.48	1.16	0.55	0.54
21	3.53	1.16	0.72	0.71
28	3.43	1.16	0.84	0.82
35	3.44	1.16	0.93	0.91
42	3.46	1.16	1.01	0.98
49	3.41	1.16	1.06	1.03
56	3.36	1.16	1.09	1.07
63	3.32	1.16	1.12	1.09
70	2.99	1.16	1.12	1.09

5. Conclusion

The time dependent non-linear reaction diffusion equation in NAPP Synthesis has been solved analytically. The obtained results have a good agreement with those numerical and experimental results. The primary result of this work is a simple approximate calculation of concentration for all possible values of reaction parameters k_1 and k_2. The analytical results obtained in this paper can also be used to predict the behavior of the system.

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Appendix A: Scilab/Matlab program for the numerical solution of equation (5).

```
function mat1
options= odeset('RelTol',1e-6,'Stats','on');
%initial conditions
x0 = [0.69;5.5;0;1.38;0];
tspan = [0,0.35];
tic
[t,x] = ode45(@TestFunction,tspan,x0,options);
toc
figure
hold on
plot(t, x(:,1))
plot(t, x(:,2))
plot(t, x(:,3))
plot(t, x(:,4))
plot(t, x(:,5))
legend('x1','x2','x3','x4','x5')
ylabel('x')
xlabel('t')
return
function [dx_dt]= TestFunction(t,x)
k1=1.83;k2=1.83;
dx_dt(1)=-k1*x(1)*x(2)-k2*x(1)*x(3);
dx_dt(2) =-k1*x(1)*x(2);
dx_dt(3)=k1*x(1)*x(2)-k2*x(1)*x(3);
dx_dt(4)=-2*(k1*x(1)*x(2)+k2*x(1)*x(3));
dx_dt(5)=k2*x(1)*x(3);
dx_dt = dx_dt';
return
```

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Appendix B.

Nomenclature

Symbol	Meaning	Usual dimension
x	Concentration of Hydroxylamine – O –Sulfonique Acid (HOSA)	mol/l
a	Concentration of Piperidine (PP)	mol/l
b	Concentration of Sodium hydroxide (NAOH)	mol/l
f	Concentration of Diazene	mol/l
x_0	Initial concentration of Hydroxylamine – O –Sulfonique Acid (HOSA)	mol/l
a_0	Initial concentration of Piperidine (PP)	mol/l
b_0	Initial concentration of Sodium hydroxide (NAOH)	mol/l
f_0	Initial Concentration of Diazene	mol/l
b	Initial concentration of Hydroxylamine – O –Sulfonique Acid (HOSA)	mol/l
x_s	Steady state solution of Concentration of Hydroxylamine – O – Sulfonique Acid (HOSA)	mol/l
a_s	Steady state solution of Concentration of Piperidine (PP)	mol/l
b_s	Steady state solution of Concentration of Sodium hydroxide (NAOH)	mol/l
f_s	Steady state solution of Concentration of Diazene	mol/l
k_2	Rate constant of the oxidation of NAPP by HOSA	$mol^{-1}\min^{-1}$
k_1	Rate constant of the reaction between HOSA and Piperdine	$mol^{-1}\min^{-1}$
t	Time factor	min

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