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Using MATCONT to Generate Bifurcation Plots for Chemical Systems

Babita. K. Verma, Jason.R. Picardo, Anand.V. P. Gurumoorthy* and Rambabu Krishnamoorthy

Department of Chemical Engineering,School of Civil and Chemical Engineering, VIT University, Vellore - 632 014, India

Abstract : Bifurcation Analysis of a dynamical system calls for an interactive user friendly software. Dynamical systems involve differential equations and solving them analytically is tedious. So many software have been used but lately, MATCONT which is a continuation package of MATLAB with a graphical user interface is getting into trend. MATCONT can be used to study a variety of dynamical behavior including nonlinear behavior like steady state multiplicity, limit cycles, Hopf points, bifurcation plots, space plane, stability analysis etc. In this paper, this toolbox has been used to illustrate the nonlinear behavior exhibited by an electrochemical system. In particular, we consider an In^{3+}-HCN^{-} reaction at a hanging mercury Drop electrode as modeled by a system of two nonlinear differential equations.
Keywords: MATCONT, bifurcation analysis, electrochemical oscillators.

1. Introduction

It was somewhere in the 1950s when Boris P. Belousov, the Russian chemist first discovered an oscillatory reaction which changed color periodically from yellow to colorless due to repeated cycles of oxidation and reduction of cerium (III) and (IV) ions. His discovery was labeled impossible by certain editors and relegated to a less reputed forum where it remained obscure for years to come. Today the Belousov-Zhabotinsky (the latter name being that of a graduate student who revived the study of this system) family of reactions is a hallmark of non-equilibrium chemical dynamics.

In the ensuing decades, the advent of chaos and the science of non linear dynamical systems in general has caused the scientific community to rethink the way it understands nature and its patterns as well as the manner in which engineering systems are modelled, designed, operated and controlled. Complexity, as it pertains to the non linear behavior of systems which show multiplicity of steady states (point attractors), simple and mixed mode oscillations, quasiperiodicity and chaos, has been observed in a wide variety of natural and manmade systems[1]. From the Lorenz system of differential equations which first demonstrated sensitivity to initial conditions (butterfly effect), the hall mark of chaos, to the logistic difference equations extensively used in ecology and economics, the complex periodic and chaotic dynamics of several types of systems have been explored, resulting in an elevation in our intellectual standing. The fibrillation of the heart has been related to the onset of chaos (ref.) and dynamics of the acetylcholinestrase enzyme in the brain has been studied to understand Alzheimers and Parkinsons[2]. In the chemical engineering literature, reports of multiplicity of steady states, oscillations and chaotic behavior in lumped and distributed reactor systems is plentiful and the nonlinear analysis of some experimental reactors has borne out the predictions of theory[3]. Bio-fermentors with chaotic dynamics have been studied to exploit chaos for better yields. The modern field of chaos control looks to

control chaos in scenarios where it can be dangerous as in industrial reactors. In some cases is may be advantageous as in the bio-fermentor mentioned above while often it may be important to understand complex dynamics in order to achieve a complete understanding of a system as is often the case in biological systems such as species population interactions.

It is not the aim of the authors to provide a review of all the applications of non linear science and indeed the above mentioned list is only a small fraction of the work done by researchers in chemical and biological sciences alone. It has been provided to give the reader an understanding of the ever growing nature of the field and its proximity to workers who traditionally are not associate with advanced mathematics. Over the last three decades or so, much advancement has been made in mathematical bifurcation theory and physicists have extensively explored the dynamical behavior of a large variety of systems from lasers to hydrodynamics (the onset of turbulence has long been recognized as a transition to chaos). These advancements have allowed theoretically oriented researchers in chemical engineering to uncover the rich bifurcation structure of many chemical reactor systems greatly increasing our understanding of their inherent behavior. However, industrial interest in these phenomena remains at a low. This is partially due to the philosophy of avoiding these troublesome operating regions altogether. Given the great advancements made in dynamical modelling, computational power and digital control, it would seem that the time is ripe to move forward and explore the possible advantages of higher yield and efficiency which may be achieved in these non conventional operating regimes. The implications of these studies on the design, operation and control of chemical/biological reactors cannot be ignored in a world where the cost of energy and time is on the rise. Among the life sciences, it is becoming increasingly obvious that dynamical systems theory has a lot to contribute to our understanding of life and nature. The inherent non-monotonic dependencies of biological factors on environmental conditions along with the synergetic coupling between reaction and diffusion phenomena lead to complexity in many biological systems.

As such, great rewards seem to be in store for practically oriented engineers and life scientists who adopt the methods of non linear dynamics in their field of work. In fact one may go as far as to say that it is necessary for dynamical systems theory to percolate throughout science and engineering if we are to solve many of the complex problems which face our world today. A major hurdle in this regard is the lack of mathematical knowledge among many of the scientific groups who are faced with this challenge. Ironically the mathematics behind complex dynamical systems is itself quite complex. It may seem intimidating to the uninitiated engineer or life scientist and he may well choose an alternative if less rewarding path of investigation. Clearly what is required is a user friendly tool which can allow a worker to simulate the system for various parameter ranges, plot necessary bifurcation diagrams and explore the behavior of the system in its entirety. This would require the integration of advanced numerical algorithms for solution of mathematical differential and difference equations, bifurcation routines and algorithms for computing various dynamical parameters of interest (eigen values, periods of oscillations, floquet multipliers etc.) and an advanced, interactive visualization package.

2. Software for bifurcation of dynamical systems

The availability of a flexible, reliable and user friendly software package for bifurcation analysis is apparent. Such software could have a similar impact to that of the now hugely popular CFD packages (ANSYS, COMSOL etc) which have allowed engineers studying fluid systems to focus on the engineering problem at hand and try various design and operational possibilities with ease. This has made the optimization of processes so much easier and brought the complex mathematics behind CFD within the reach of non mathematical workers.

Over the past decade and a half various software packages have emerged with the objective of aiding investigators in exploration of dynamical systems via bifurcation analysis. The initial versions were simple codes made available under the names of AUTO86, LINLBF, BIFOR2, PATH and LOCA. The next generation saw interactive programs like AUTO86, XPPAUT and LOCBIF. AUTO survived to reappear as AUTO97 which was a very popular tool used by many workers[4]. The latest version is AUTO07 which is still in considerable use. In this paper we are interested in a relatively new software package called MATCONT. The successor to the CONTENT package released in the early 2000s, MATCONT[5] is a GUI (graphical user interface) package created for use within the Matlab computing environment. Matlab is now widely used in academia and industry and is popular for its strong computational and visualization capabilities. MATCONT

provides a user friendly experience with the added advantage of being able to generate visualizations directly without using any other software. As such it is possible to use MATCONT to investigate non linear systems with a minimum of mathematical knowledge thus allowing engineers and biologists to continue their work with only an intuitive feel of the mathematics and the basic knowledge of the important rules and theorems. Such a tool would be particularly useful in applied studies and while extending previous work under different system conditions and/or configurations.

However, apart from computational capabilities any software must be reliable for a range of system types and should be reasonable flexible as well. It is the goal of this paper to put this promising software to the test and evaluate its capabilities as a tool for the non mathematical worker who is interested in exploring a dynamical system of his interest.

3. An Illustrative Example – Electrochemical Oscillators

Electrochemistry exhibits various non-linear phenomena which has been a subject of interest to both non linear dynamist and electrochemist. One of the most fascinating non linear dynamical features is electrochemical oscillations. It has been studied in the literature for past three decades. Some electrochemical system exhibits spontaneous oscillation in current and potential at certain parameter value. Such oscillators can be classified into anodic oscillators[12-16] and cathodic oscillators[17-20]. Anodic oscillation is a more complicated phenomenon as it involves passive layer formations which add complexity to the system and hence these kinds of model are difficult to develop and analyse. Cathodic oscillation is a less complicated process as it does not involve any passive layer formation thence easier to model.

We focus on the study of cathodic oscillators under potentiostatic operations since they have been successfully modelled in the literature[24-30]. We here probe the model given by M.T.M. Koper and co-workers[3,9-10] for the indium/thiocynate reaction at the hanging mercury drop electrode (HMDE) which is actually a simplification and an extension of Keizer Scherson model[21]. An understanding of the cathodic oscillation under potentiostatic condition of the system has been discussed here.

3.1 Model

The model is an electrochemical cell that consists of hanging mercury drop electrode (HMDE) that play the role of cathode and a pond of mercury works as the anode. Electrolyte is a solution of In $(NO_3)_3.5H_2O$, NaSCN and HNO_3 in distilled water.

Here thiocyanate acts as a catalyst and forms complex with indium ion. This complex then dissociates at the cathode. The indium ion reduces and gets deposited at the HMDE forming amalgam and the thiocyanate ions get adsorbed to the electrode which adds complexity to the system. This is in conformation with the mechanism proposed by Pospisil and de levie[22].The mechanism is illustrated by the following equations:

$$In^{3+} + 2SCN^-_{ads} \xrightarrow{slow} In(SCN)_2^+{}_{,ads} \quad (1a)$$

$$In\,(SCN)_2^+{}_{,ads} + 3e^- \xrightarrow{fast} In^0 + 2SCN^-_{ads} \quad (1b)$$

The situation at the cathode can be represented by a general equivalent electrical circuit as shown in fig 1. The double layer is represented as a double layer capacitance C_d in parallel with the faradiac impedance Z_F. This faradiac impedance should not be confused with a series connection of charge transfer and working impedance as they have their usual meaning only for a.c. applied voltages. The capacitor and impedance are in turn connected in series with an external resistance R_s which typifies the solution resistance.

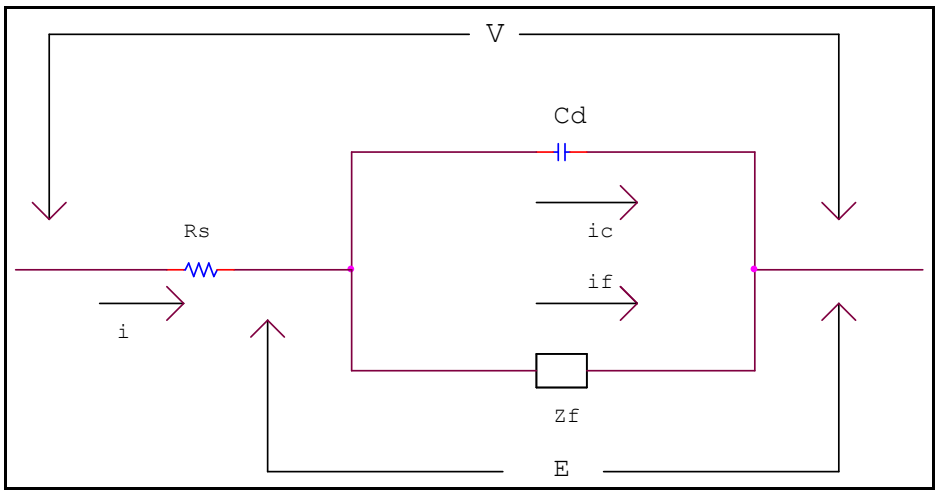

Fig 1. Equivalent electrical circuit representing the electrochemical cell

The following two are the base equations that are used to model the electrochemical oscillating behaviour of the system. The first equation is obtained by the conserving current in the circuit i.e. the current flowing through the capacitor and the impedance current should be equal to the total current flowing through the circuit. The second is the change in concentration of the electroactive species at the surface of the cathode by taking into account mass transfer diffusion which is assumed to be linear and the electrochemical phenomenon.

$$\frac{dE}{dt} = \frac{V-E}{R_S A C_d} - \frac{j_F}{C_d} \tag{2}$$

$$\frac{dC_0(t)}{dt} = -\frac{2k_f C_0(t)}{\delta} + \frac{2D}{\delta^2}\left(c_{bulk} - c_0(t)\right) \tag{3}$$

Where the nomenclature is as given in Table 1

Table 1. Notations

Notations	Description
E	Cell or Electrode potential
V	(controllable) Circuit potential
i_c	Charging current
i_F	Faradiac current
J_F	impedance current density
R_s	external resistance
A	area of the working electrode
C_0	surface concentration of the electroactive species
D	Diffusivity
Δ	Double layer thickness which is assume to be constant
Cd	Double layer capacitance
Z_F	faradiac impedance

For mathematical convenience, these equations are converted into dimensionless forms which are further modified by taking into account nonlinear processes involved. The electrochemical oscillation behaviour is then studied using bifurcation analysis technique.

$$\frac{de}{dt} = \frac{v-e}{r} - cx \tag{4}$$

$$\frac{dx}{dt} = -kx + d(1-x) \quad (5)$$

Where the dimensionless quantities are,
v = (F/RT) V
e= (F/RT) E
$x= c_0/c_{bulk}$
$t = (k' t/\delta)$

The above equations (4) and (5) are actually linear and do not display complex features. Nonlinear processes are then included in these dimensionless equations. To obtain oscillations they introduced relative surface activity of thiocyanate (θ) in the equations which varies with the potential applied.

$$\frac{de}{dt} = \frac{v-e}{r} - cx\theta^2 \quad (6)$$

$$\frac{dx}{dt} = d(1-x) - kx\theta^2 \quad (7)$$

The variation of θ with the potential was studied and found that no oscillation is observed when θ is constant with respect to the transition potential e_d . The model was observed to show oscillations on considering variable transition potential.

Further modifications was introduced by assuming an additional process occurring at the electrode with exponential dependence on the potential and also by considering the practicality of θ(e) which was chosen to follow a Gaussian plot. Thus, the final equations obtained were:

$$\frac{de}{dt} = \frac{v-e}{r} - c_1 x\theta^2 - c_2 x \exp(\eta\alpha(e - e^0)) \quad (8)$$

$$\frac{dx}{dt} = -k_1 x\theta^2 - k_2 x \exp(\eta\alpha(e - e^0)) + d(1-x) \quad (9)$$

Where,

$\theta = 1$ $\quad e \leq e_d$ (10)

$\exp(-b(e - e_d)^2)$ $\quad e > e_d$

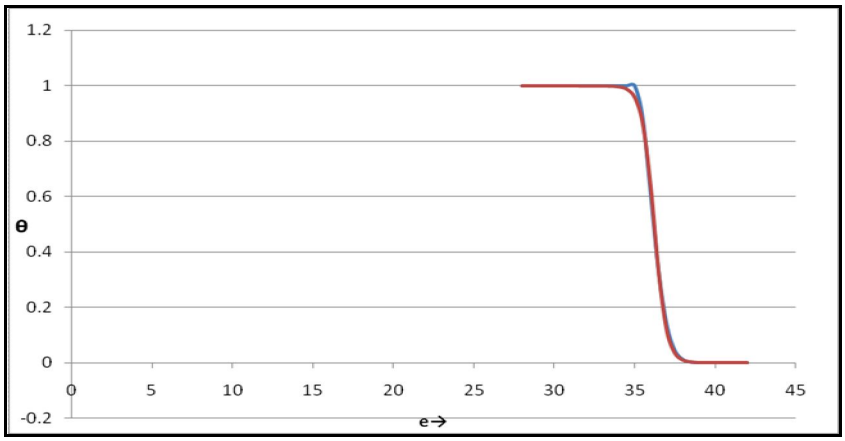

Fig 2: The relative surface activity θ as a continuous function of the potential e for b= 2.599174 which defines the steepness of the curve.

3.2 Hanging Mercury Drop Electrode

HMDE in an electrochemical system is a working electrode that develops mercury drop whose surface area and shape are monitored through a micrometer screw according to the need of the experiment. The design and construction of HMDE has greatly improved which has enhanced the reproducibility of mercury drops formed. One has to be very careful while using HMDE since Mercury is a poison. One of the merits of using HMDE is that no cleansing is required as in the case with ordinary electrode used.

In this example, one and the same mercury drop was taken into account. The size of this mercury drop is assumed to be about 0.03 cm^2 . This assumption is considerate since we are interested in the qualitative behavior of the system and no heed is given to the quantitative behavior of the model.

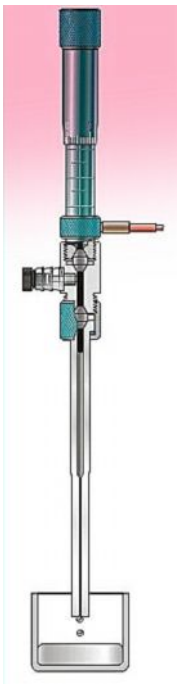

Fig 3: Schematic of HMDE

4 Results and Discussions

4.1 Oscillation profiles

The oscillating behaviour of the current(i) and the concentration of electroactive species(x) under potentiostatic condition have been studied and computed in MATCONT. The results obtained for the computed oscillating profile for i and x for different parameter values are given below. It was observed that at different parameter values the characteristics of amplitude is same as that obtained by M.T.M Koper et al which in turn is in agreement with the experimental results.

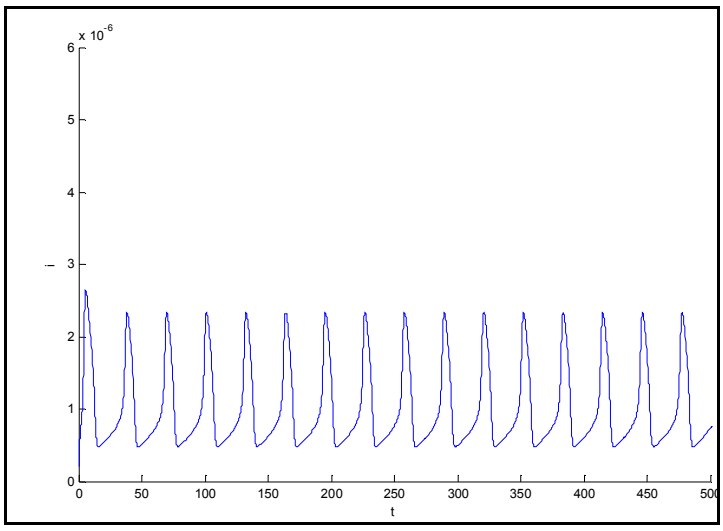

Fig 3(a)

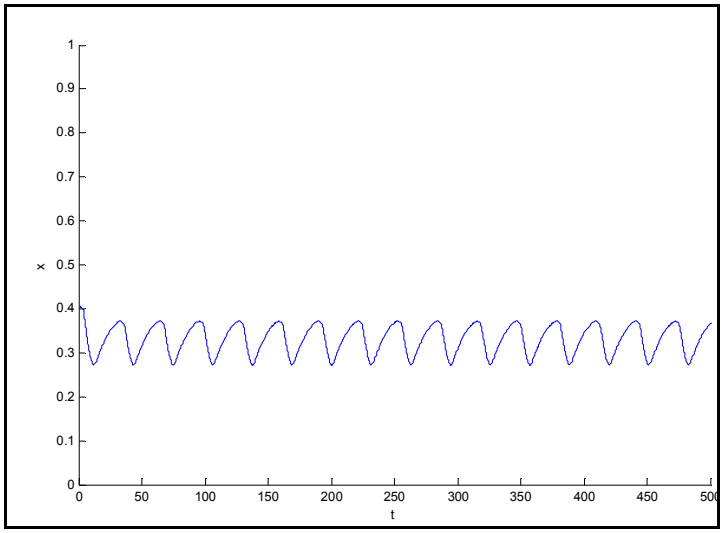

Fig 3(b)

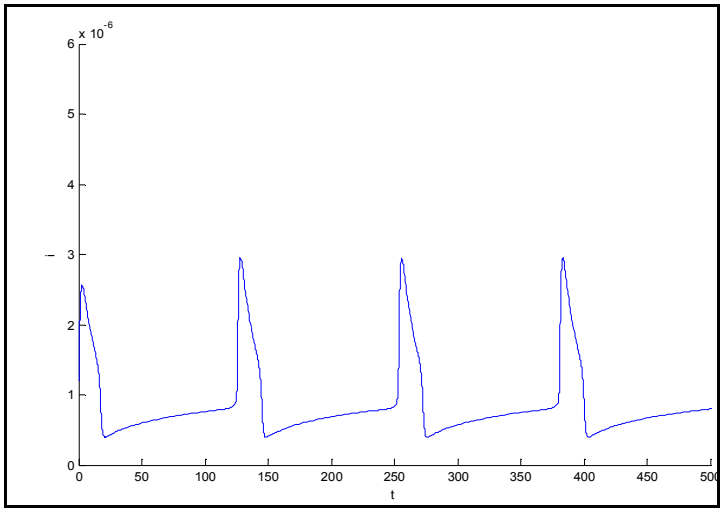

Fig 3(c)

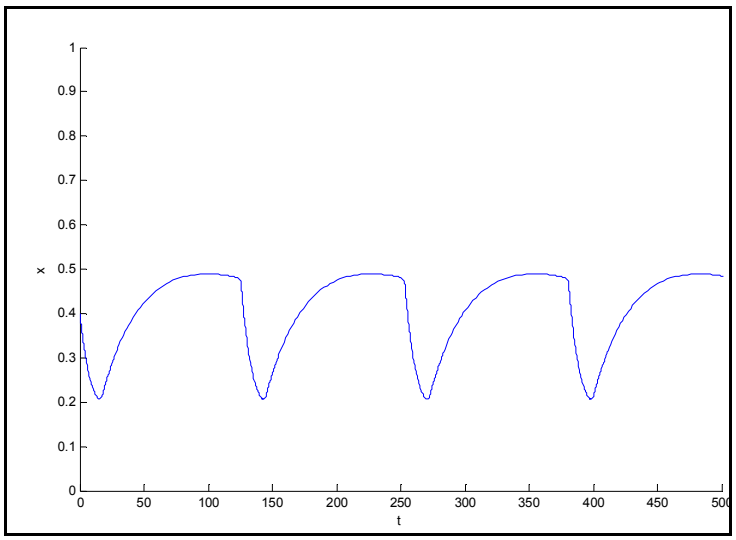

Fig 3(d)

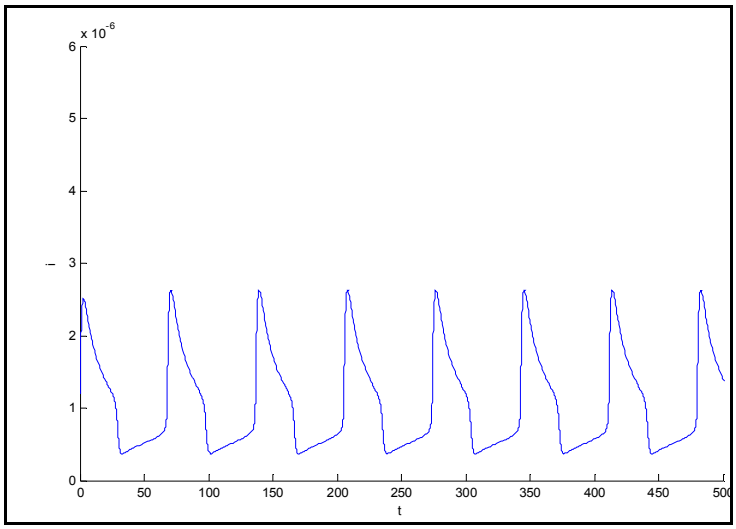

Fig 3(e)

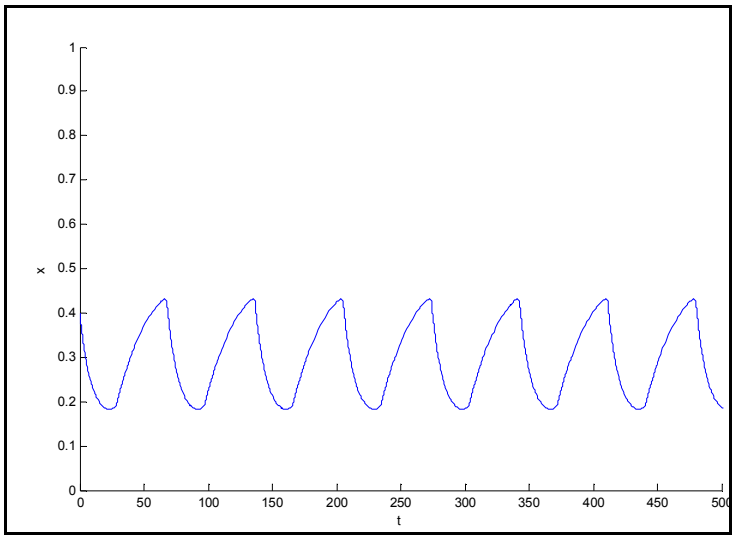

Fig 3(f) Parameter values are c1=12, c2=0.48,k1=0.1,k2=0.004,d=0.02,e^0=34,e_d=35,b=0.5
Fig3(a) &(b) : v=37,r=0.5 ; Fig3(c)&(d): v=38,r=1.1 ; Fig3(e)&(f): v=38,r=1.3

4.2 Bifurcation diagrams

4.2.1 Static bifurcation plots:

Through the bifurcation diagrams we examine how the behaviour of the system changes on changing the operating conditions via change of system parameters. The first bifurcation plot is globally stable since no special points where system could lose its stability were observed during its computation and there is no multiplicity.

MATCONT pauses when it encounters some special points like hopf points, Limit point cycles, branching point cycles etc. This was observed in computing the rest of the bifurcation plots. For instance, the second plot consists of two hopf points and Matcont pauses at these special points. On intermitting some important informations are displayed like the precise location of these special points, varying parmeter value along with some other dynamic parameters like first lyapunov coefficient which help us to study the stability of the system. Also we can study the stability of the equilibria and limit cycles through eigen values and floquet multipliers displayed on the numeric window in real time as the computation proceeds.

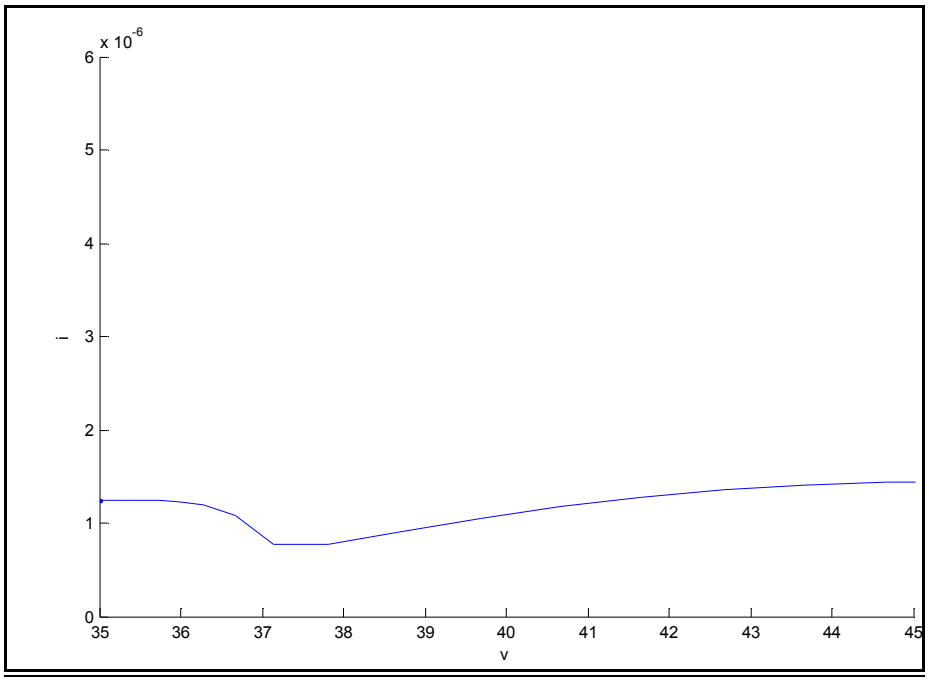

Fig 4(a) : r=0.4 (rest all parameter same as fig 3)

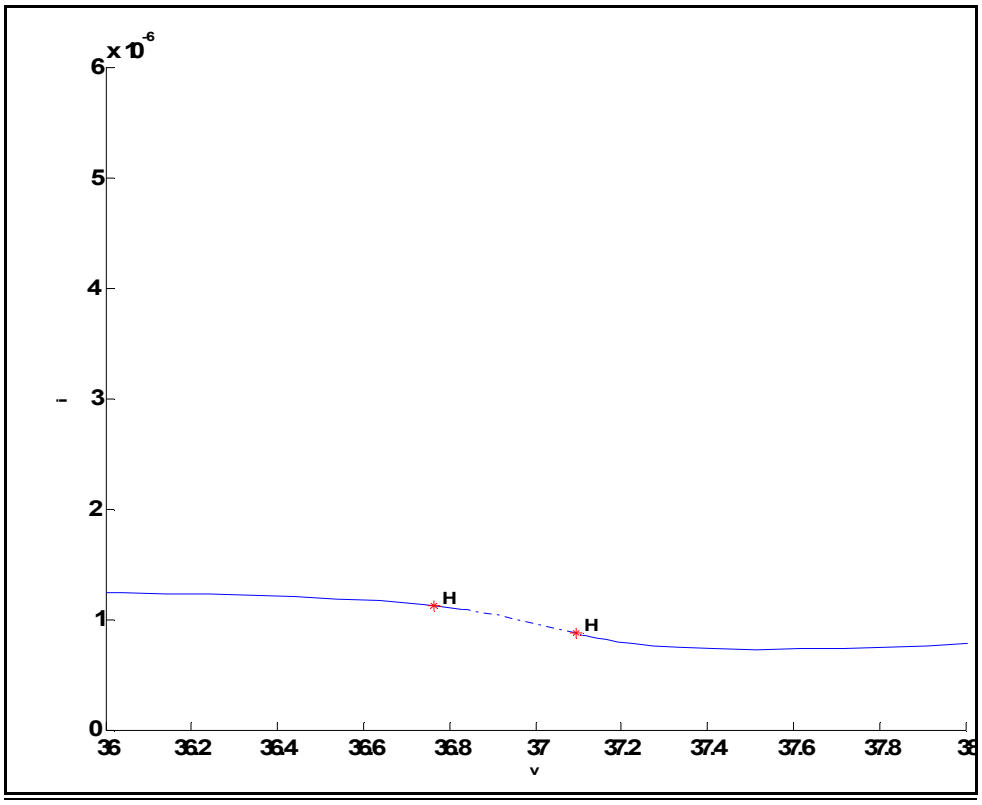

Fig4(b) : r=0.5 (rest all parameter same as fig 3)

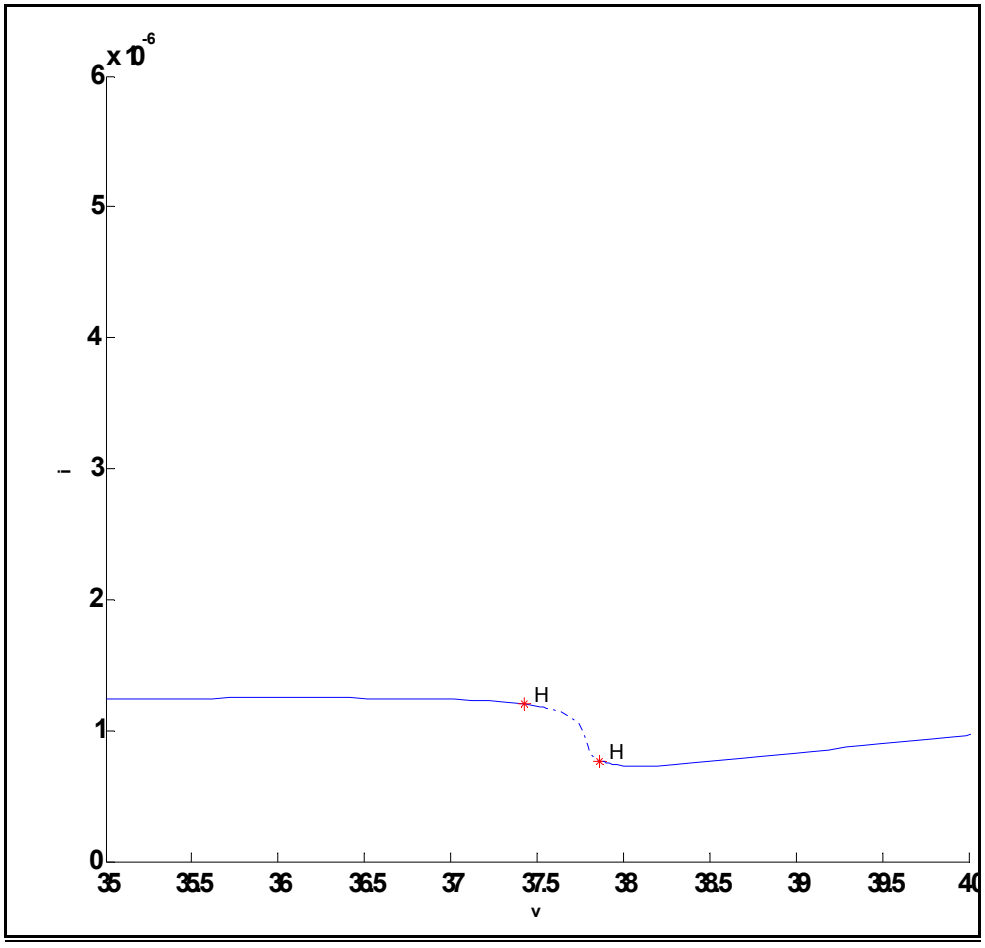

Fig4(c): r=1.0 (rest all parameter same as fig 3)

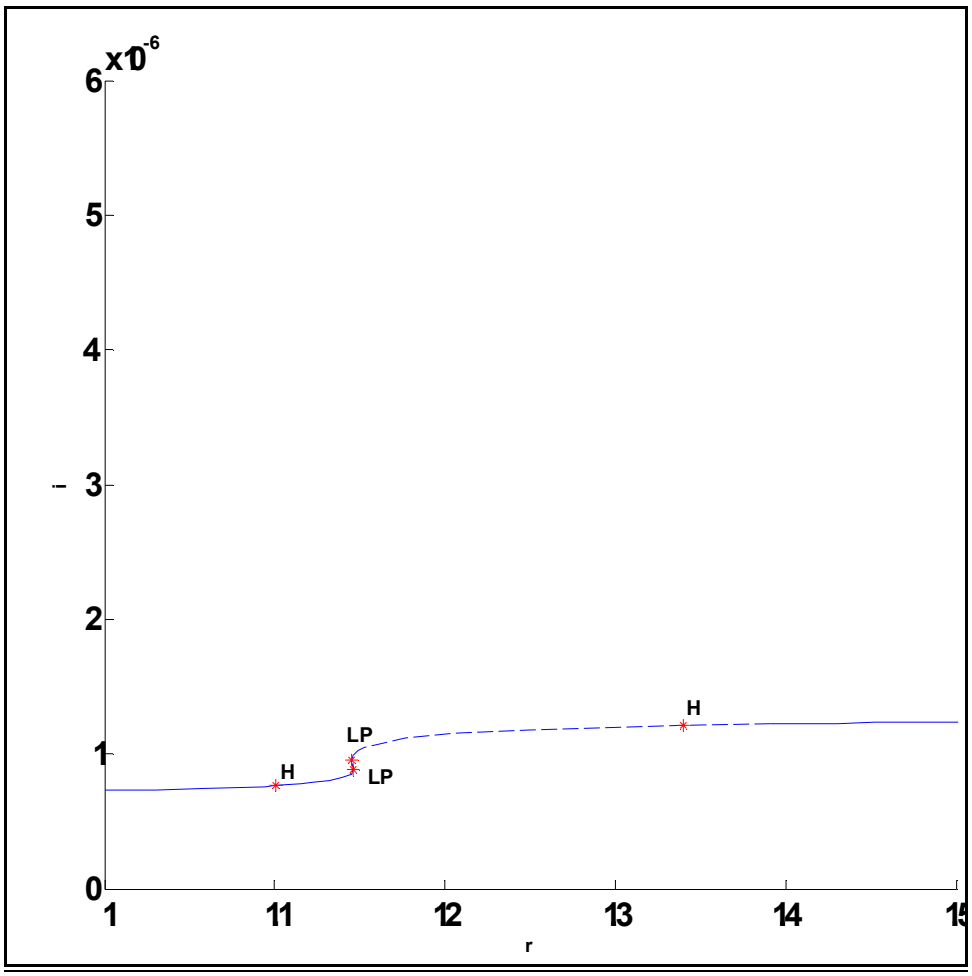

Fig 4(d): v=38 (rest all parameter same as fig 3)

4.2.2 Dynamic Equilibrium:

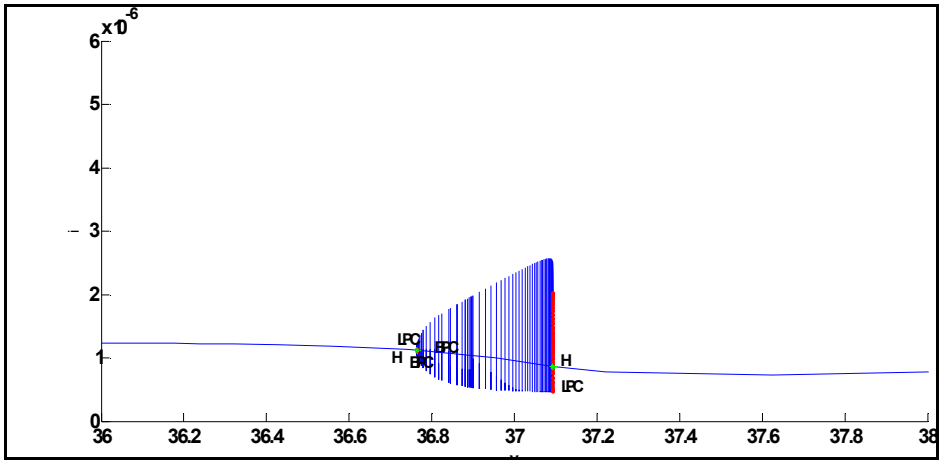

Fig 5(a): dynamic equilibrium plot for fig 4(b)

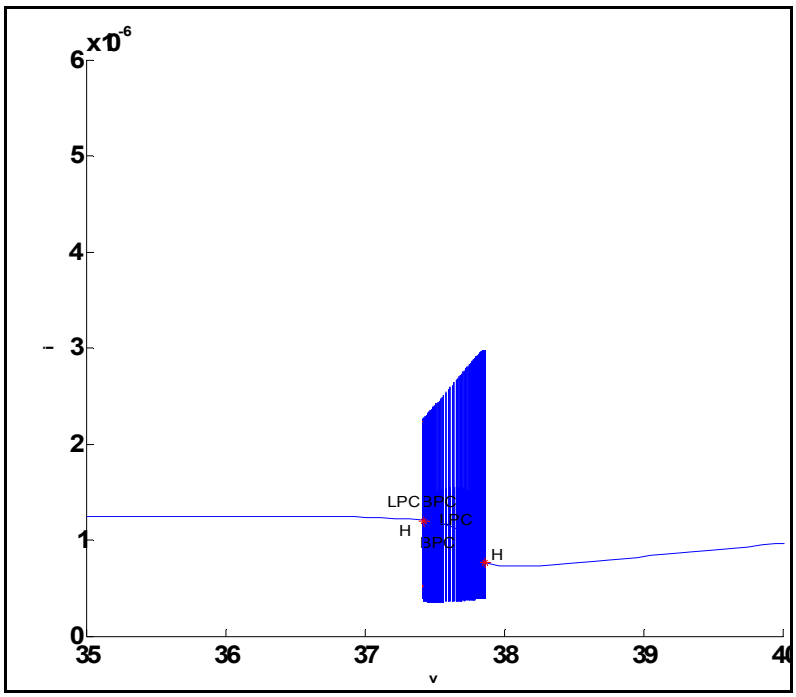

Fig 5(b): Dynamic equilibrium plot for fig 4(c)

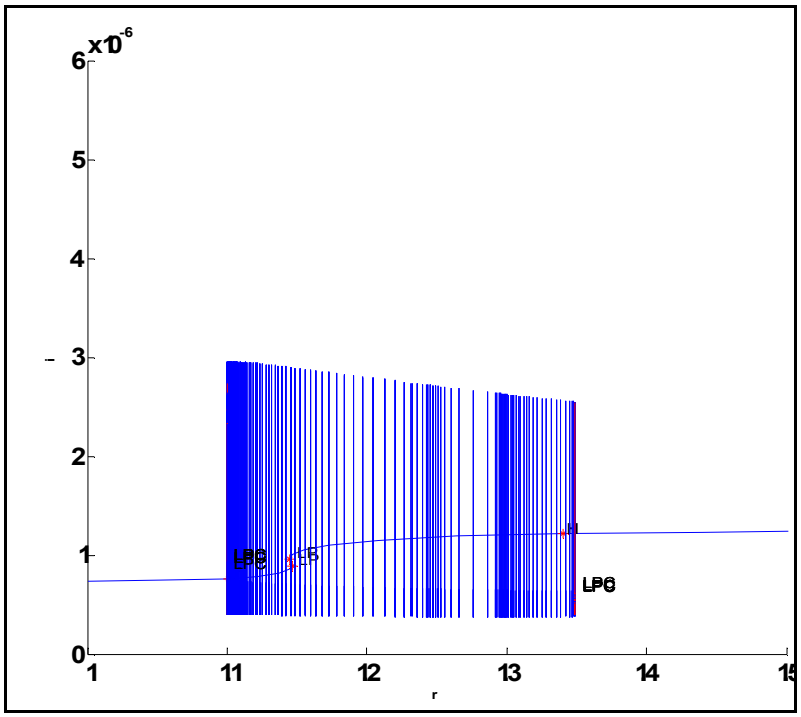

Fig 5(c): Dynamic equilibrium plot for fig 4(d)

5. Conclusions

In this work, the utility of MATCONT as a tool for studying multiplicity and dynamic oscillations of nonlinear systems has been demonstrated. It has proved to be user friendly especially for users of MATLAB. Its strengths include convenient access to powerful visualization tools and integrators and a large variety of features which encompass all the capabilities of present bifurcation software, with some additions.MATCONT has several advanced features, not discussed in this paper, which are helpful in studying complex dynamical behavior including quasi-periodicity and chaos. Apart from systems of differential equations it can also be used to study discrete dynamical maps (systems of iterative difference

equations). The possibility of interfacing MATCONT with other MATLAB toolboxes holds promise for the future. For e.g., a module which interfaces between MATCONT and the MATLAB optimization toolbox would make an excellent Tool for optimizing systems while considering changes in output due to bifurcations.

The Matcont team continues to work on adding new features and fixing bugs. This software is freely available for Download at Source Forge (http://sourceforge.net/projects/matcont) and can be installed and run easily by a MATLAB user. It is possible to use MATCONT to investigate nonlinear systems with a minimum of mathematical knowledge, thus allowing practically oriented engineers and electrochemist to analyze nonlinear systems with just an intuitive feel for the related mathematics and knowledge of essential rules and theorems. Such a tool would be particularly useful in applied engineering studies as well as in classroom courses on nonlinear dynamics and bifurcation theory.

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