The Andronov-Hopf bifurcation in the model

The sufficient conditions for the Andronov–Hopf bifurcation occurring in the system (1), (2) are [8]:

$$\xi_1 = 0, \tag{10}$$

$$\xi_1^2 - 4\xi_2 < 0. \tag{11}$$

Taking into account (10) we can rewrite (11) as

$$\xi_2 > 0. \tag{12}$$

The expressions (10) and (12) in more detailed form are

$$\frac{k_a}{\beta} e^{\gamma\theta^*/2} u^* \left(1 - \frac{\gamma}{2}(1-\theta^*)\right) + \frac{k_d}{\beta} e^{-\gamma\theta^*/2} \left(1 - \frac{\gamma\theta^*}{2}\right) + \frac{k_e}{\beta} e^{\alpha_0 f E}$$

$$= -k_a e^{\gamma\theta^*/2}(1-\theta^*) - 1, \tag{13}$$

$$\frac{k_a}{\beta} e^{\gamma\theta^*/2} \left(1 - k_e e^{\alpha_0 f E}\theta^*\right) \left(1 - \frac{\gamma}{2}(1-\theta^*)\right) + \frac{k_d}{\beta} e^{-\gamma\theta^*/2} \left(1 - \frac{\gamma\theta^*}{2}\right)$$

$$+ \frac{k_e}{\beta} e^{\alpha_0 f E} + \frac{k_a k_e}{\beta} e^{\gamma\theta^*/2}(1-\theta^*) e^{\alpha_0 f E} > 0. \tag{14}$$

Substituting (13) in (14) yields

$$k_a k_e e^{\gamma\theta^*/2}(1-\theta^*) e^{\alpha_0 f E} - \beta(k_a e^{\gamma\theta^*/2}(1-\theta^*) + 1) > 0. \tag{15}$$

Thus, the expressions (13) and (15) give us the sufficient condition for the Andronov-Hopf bifurcation in the system under consideration. It should be noted that for $\beta \to 0$ the condition (15) is fulfilled for all values of parameters. In the system (1), (2) the Andronov–Hopf bifurcation can occur either in the neighborhood of jump point A_1 or A_2. The Fig. 6 demonstrates the stable limit cycle of the system (1), (2) arising via the Andronov–Hopf bifurcation in the neighborhood of jump point A_1.

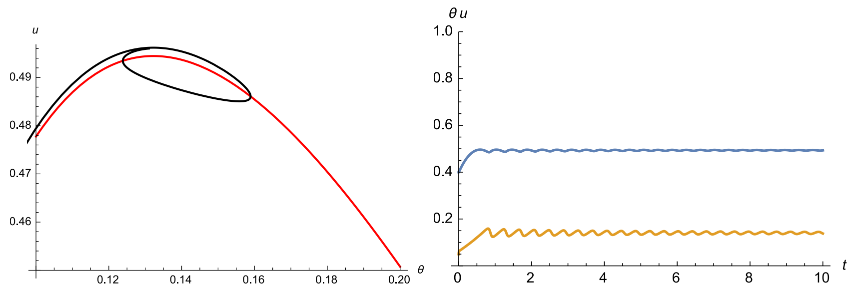

Fig. 6. (left) The slow curve (red line) and the limit cycle (black line) of the system (1), (2) and (right) plots of $u(t)$ (blue line), $\theta(t)$ (yellow line) for $k_e = 2.40855$

Canards

The canards and the parameter value k_e^* allow asymptotic expansions in powers of the small parameter β [4, 6, 11]:

$$u = \Phi(\theta, \beta) = u_0(\theta) + \beta u_1(\theta) + \beta^2 u_2(\theta) + \ldots, \tag{16}$$

$$k_e^* = \chi(\beta) = \chi_0 + \beta\chi_1 + \beta^2\chi_2 + \ldots \ . \tag{17}$$

In order to find these asymptotic expansions for the canard and the canard point we substitute the formal expansions (16) and (17) into the invariance equation [6]

$$\frac{du}{d\theta} g(u, \theta) = \beta f(u, \theta).$$

which follows from the system (1), (2). As a result we obtain the following equation:

$$\Big(k_a e^{\gamma\theta/2}(1-\theta)(u_0 + \beta u_1 + \beta^2 u_2 + \ldots) - (\chi_0 + \beta\chi_1 + \beta^2\chi_2 + \ldots)e^{\alpha_0 f E}\theta$$

$$-k_d e^{\gamma\theta/2}\theta\Big)(u_0' + \beta u_1' + \beta^2 u_2' + \ldots) = -\beta k_a e^{\gamma\theta/2}(1-\theta)(u_0 + \beta u_1 + \beta^2 u_2 + \ldots)$$

$$+\beta\left(k_d e^{\gamma\theta/2}\theta + 1 - u_0 - \beta u_1 - \beta^2 u_2 + \ldots\right). \tag{18}$$

On setting equal the coefficients of powers of β in the equation (18) we find the functions $u_0(\theta)$, $u_1(\theta)$, $\ldots$. To obtain the values χ_0, χ_1, $\ldots$ we require the continuity of the functions $u_i(\theta)$ $(i = 0, 1, ...)$ at the jump point. This requirement means that we glue the stable and the unstable integral manifolds at the jump point and, as a result, construct the canard passing through this point [4, 6, 9]. As a result we have:

$$u_0(\theta) = \frac{(k_d e^{-\gamma\theta/2} + \chi_0 e^{\alpha_0 f E})\theta}{k_a e^{\gamma\theta/2}(1-\theta)}, \tag{19}$$

$$u_1(\theta) = \frac{-k_a u_0(\theta)(1-\theta)e^{\gamma\theta/2} + k_d e^{-\gamma\theta/2}\theta + 1 - u_0(\theta) + \chi_1 e^{\alpha_0 f E}\theta u_0'(\theta)}{k_a e^{\gamma\theta/2} u_0'(\theta)}, \tag{20}$$

$$\chi_0 = \frac{k_a(1-\bar\theta)e^{\gamma\bar\theta/2} - k_d e^{-\gamma\bar\theta/2}\bar\theta}{(k_a(1-\bar\theta)e^{\gamma\bar\theta/2} - 1)e^{\alpha_0 f E}\bar\theta}, \tag{21}$$

$$\chi_1 = -\frac{k_a u_1(\bar\theta)(1-\bar\theta)e^{\gamma\bar\theta/2} + u_1(\bar\theta) + k_a u_1(\bar\theta)u_1'(\bar\theta)(1-\bar\theta)e^{\gamma\bar\theta/2}}{e^{\alpha_0 f E}\bar\theta u_1'(\bar\theta)}, \tag{22}$$

where the value $\theta = \bar\theta$ corresponding to the jump point can be calculate from the system (4). The equations (19)–(22) define the first–order approximations for the canard and the canard point of the system (1), (2) in a neighborhood of the jump point $(u(\bar\theta), \bar\theta)$. It should be noted that we can construct the canard either in the neighborhood of jump point A_1 (by gluing the stable slow integral manifold M_1 and the unstable one M_2, see Fig. 7) or in the neighborhood of A_2 (by gluing the stable slow integral manifold M_3 and M_2, see Fig. 8). If it is necessary to glue stable and unstable slow invariant manifolds at the both jump points simultaneously, we should use two control parameters and as a result we obtain a canard cascade [12].

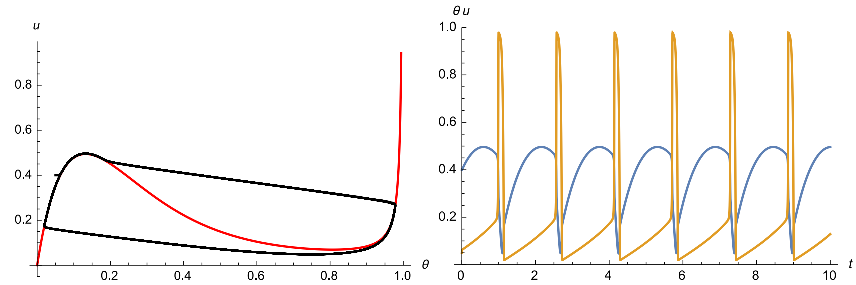

Fig. 7. (left) The slow curve (red line) and the canard (black line) of the system (1), (2) and (right) plots of $u(t)$ (blue line), $\theta(t)$ (yellow line) for $k_e = 2.4055$

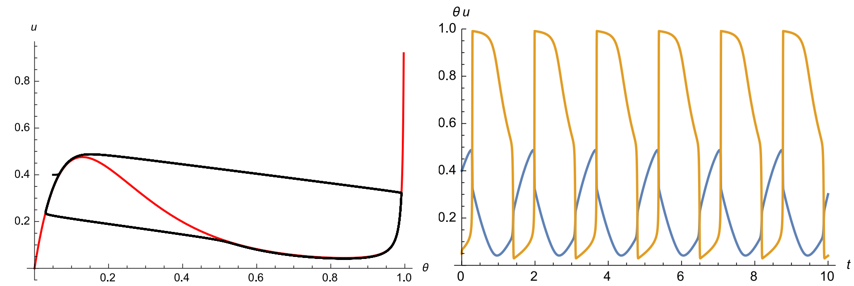

Fig. 8. (left) The slow curve (red line) and the canard (black line) of the system (1), (2) and (right) plots of $u(t)$ (blue line), $\theta(t)$ (yellow line) for $k_e = 0.9205283$

Conclusion

In the paper the dynamical model of the electrochemical reactor has been investigated. The critical regime separating the basic types of the regimes, slow and relaxation, was modelled with the help of the integral manifolds of variable stability. This approach was used in [13–23] for modelling of the critical phenomena in chemical systems.

The bifurcation point at which the supercritical Andronov–Hopf bifurcation takes place as well as the canard point of the control parameter at which the system has the canard cycle have been determined analytically. It is shown that the critical mode is modelled by the canard. The obtained results is of utmost importance for several applications in chemical kinetics, as they can be used to determine the dynamics of the process in the chemical system for given initial conditions.

Acknowledgements

This work is supported in part by the Russian Foundation for Basic Research (grant 14-01-97018-p) and the Ministry of Education and Science of the Russian Federation under the Competitiveness Enhancement Program of Samara University (2013-2020).

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