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SEARCH FOR THE OPTIMAL RATIO OF THE INITIAL SUBSTANCES OF A CHEMICAL REACTION BASED ON EVOLUTIONARY CALCULATIONS

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ABSTRACT

The article is devoted to the problem of developing methods for mathematical modeling in the sphere of optimal planning in a chemical experiment. In the article, the problem of finding the optimal ratio for initial concentrations of substances is formulated in general terms and an algorithm for solving this problem is constructed basing on the method of artificial immune systems. The developed algorithm for finding the optimal initial concentrations of substances allows solving the problem of experiment planning in chemistry at the computational experiment stage. In this case, the solution of the optimization problem found with its help does not depend on the choice of the initial approximation. The algorithm was tested for industrially meaningful process of benzilidenbenzilamin synthesis for which the optimum values of the initial concentrations were calculated in order to obtain maximum yield of the reaction product.

Keywords: chemical kinetics, artificial immune systems, initial concentration of substances.

1. INTRODUCTION

The solution of many problems in chemistry and chemical technology is associated with complex and expensive experiments. In the study of the chemical process at the computational experiment stage, it is advisable to identify its main regularities because of the complexity of the initial raw materials composition and the low content of valuable components in them. In this regard, the actual task is to develop methods for optimal planning of the experiment, which allow saving time and material resources for conducting a full-scale experiment.

The development of computer technology and information technology allows the use of mathematical methods in the planning of the chemical experiment. The methods of mathematical modeling allow determining the optimal concentrations of reagents to obtain the best yield of the final product and significantly reduce the cost of the synthesis of substances.

The calculation of the initial concentrations of the reactants in a chemical reaction is made by searching an extremum of the function for calculating the dynamics of the substances concentrations during the chemical experiment. Significant drawbacks of most numerical methods for finding the extremum of functions are the difficulties in achieving convergence of the process, which depends on the choice of the initial approximation.

Currently, metaheuristic optimization methods are widely used, which make it possible to efficiently find a global optimum in a reasonable time [1, 2, 3]. Their important feature is the ability to overcome the local extremum point of the target function in the search process. Therefore, they allow finding better solutions in comparison with classical heuristics [4, 5, 6, 7].

Among the metaheuristic algorithms, the method of artificial immune systems is distinguished. Its advantage is the presence of a memory mechanism. The memory mechanism makes it possible to use information about previously found best solutions, thereby increasing the efficiency of global search. An important feature of the method of artificial immune systems is the independence of the optimization problem solution from the initial approximation [8, 9, 10].

2. FORMULATION OF THE PROBLEM

Let us formulate in general terms the problem of finding the optimal ratio for initial concentrations of substances. A mathematical model for the dynamics of substances concentrations is a system of ordinary differential equations

$$\frac{dx}{dt} = f(t, x(t), T), \tag{1}$$

with initial conditions

$$x_i(0) = x_i^0, \quad i = \overline{1,n}, \tag{2}$$

where $x(t) = (x_1(t), x_2(t), \ldots, x_n(t))$ - the vector of the concentrations of the reacting substances, $t \in [t_1, t_2]$ - the time of reaction, T - reaction temperature [11].

At the initial moment of time, substances are interconnected by some ratio:

$$x_1(0) : \ldots : x_n(0) = \alpha_1 : \ldots : \alpha_n. \tag{3}$$

It is required to find ratio for initial concentrations of substances, which ensures the extremum of optimality criterion

$$Q(x) = \sum_{i=1}^{n} \lambda_i x_i(t_2) \to extr. \tag{4}$$

The optimality criterion shows the maximum yield of the target products or the minimum content of impurities at the final point in time.

3. THE ALGORITHM FOR THE METHOD OF ARTIFICIAL IMMUNE SYSTEMS TO CALCULATE OPTIMAL INITIAL CONCENTRATIONS OF SUBSTANCES

The method of artificial immune systems simulates the functioning of a living organism immune system, designed to destroy foreign bodies and improve the fight against them. Consider the main concepts of the method.

An antigen is an alien substance from which the body tries to protect itself with antibodies. An antibody is a substance that recognizes and destroys an antigen [12]. A memory cell is an immune cell that accumulates data about new antibodies that can recognize an antigen. The target function of the optimization problem is called the fitness function [13, 14].

As a function of fitness, we will use the maximum yield of the target reaction product at the final moment of the reaction. This requires the solution of a direct kinetic problem with a given ratio for the initial concentrations of the initial substances, that is, the solution of a system of differential equations (Eq. (1)) with the initial conditions (Eq. (2)).

We modify the algorithm to solve the problem of finding the optimal initial concentrations of the components in the reacting mixture. As a population of immune cells, we introduce sets of initial concentrations of substances $x^j(0) = (x_1^j(0), x_2^j(0), \ldots, x_n^j(0)), \quad j = \overline{1,k},$ where k is the number of immune cells in the population.

To calculate the value of the fitness function $Q(x)$, it is necessary to know the concentration of reagents at the final point in time. To do this, we introduce a block for solving a direct kinetic problem into the algorithm.

The problem of finding the minimum of the target function $Q(x)$ is reduced to the problem of finding the maximum by replacing the sign in front of the function with the opposite one: $Q(x^*) = \min Q(x) = \max [-Q(x)]$. We formulate this algorithm.

Step 1. The creation of an initial population for the starting substances concentrations.

Set the number of immune cells in the population k, the number of parental cells for the selection *r_sel*, the number of cells in the population with the worst value of the fitness function *n_bad*, the maximum number of iterations *i_max*, the clone operator parameter *n_cl*, the mutation parameter m, the iteration counter $num = 0$.

Randomly set the values of k cells of the initial population $x^j(0), j = \overline{1,k}, 0 \le x^j(0) < 1.$

Step 2. Calculation of fitness function values.

For sets $x^j(0)$ calculate the value of fitness function $Q(x^j)$, by solving a direct kinetic problem for each immune cell. That is, at this step it is necessary to find a numerical solution to the system of differential equations (Eq. (1)) with the initial conditions (Eq. (2)) by an explicit or implicit method. The initial conditions of the system (Eq. (2)) are the immune cell.

Step 3. Cloning.

Select *r_sel* parent cells from the population (a set of antibodies), which correspond to the best values of fitness function $Q(x)$. Generate *n_cl* clones for each cell.

Step 4. Mutation.

For each parent cell generate random numbers $l \in [0,1],\ h_1 \in [0, 1 - x_i^j(0)],\ h_2 \in [0, x_i^j(0)],\ i = \overline{1,n}.$

Perform a mutation of its clones by the rule: if $l > 0,5$, then $x_i^s(0) := x_i^s(0) + h_1 \cdot m$, else $x_i^s(0) := x_i^s(0) - h_2 \cdot m$, where $s = \overline{1, n\_cl}$, m – mutation parameter.

Step 5. Calculation of fitness function values.

For each mutant clone, calculate the value of the fitness function by Eq. (4).

Step 6. Selection and transition to a new population.

For each parent cell, find the mutant clone with the lowest value of the fitness function. Compare its value with the value of the fitness function of the parent cell. In the new population, leave the parent cell or replace it with a mutant clone with the best fitness function value.

Step 7. Renewal of a population.

In the population, find *n_bad* cells with the lowest value of fitness function $Q(x)$. Replace these cells with new ones, randomly generated in the interval [0, 1), and calculate the value of the fitness function $Q(x)$ for them.

Increase the iteration counter: $num = num + 1$.

Step 8. Checking the conditions for the end of search.

If $num < i\_max$, then go to step 3, else finish the search and go to step 9.

Step 9. Selection of optimal concentrations of substances from the population.

As a solution to the problem of finding the optimal concentrations of substances, select the cell with the highest fitness function value from the last population. The developed algorithm is implemented as a software tool in the visual programming environment Delphi.

4. COMPUTATIONAL EXPERIMENT

Based on the formulated algorithm, we calculate the optimal ratio of the initial concentrations for the reaction of the benzylidenebenzylamine synthesis in order to obtain the maximum yield of the reaction product. The mechanism of the chemical reaction for the synthesis of

benzylidenebenzylamine in the presence of a catalyst $FeCl_3 \cdot 6H_2O$ is represented by a set of stages [15]:

$$\begin{aligned} &X_1 + X_2 \to X_3 + X_4, \\ &X_3 \to X_5 + X_6, \\ &X_5 + X_1 \to X_7 + X_8, \\ &X_8 + X_6 \to X_9, \end{aligned} \quad (5)$$

where X_1 - benzylamine (C_7H_9N), X_2 - carbon tetrachloride (CCl_4), X_3 – chlorobenzylamine (C_7H_8NCl), X_4 - chloroform ($CHCl_3$), X_5 - 1-phenylmethanimine (C_7H_7N), X_6 - hydrogen chloride (HCl), X_7 - benzylidenebenzylamine ($C_{14}H_{13}N$), X_8 - ammonium (NH_3), X_9 - ammonium chloride (NH_4Cl).

The speed of each stage is determined according to the law of mass action:

$$\begin{aligned} &\omega_1 = k_1 x_1 x_2, \\ &\omega_2 = k_2 x_3, \\ &\omega_3 = k_3 x_5 x_1, \\ &\omega_4 = k_4 x_8 x_6, \end{aligned} \quad (6)$$

where x_i – concentration of the i-th substance ($i = \overline{1,9}$) (mole fraction), k_j – rate constant of the j-th reaction stage $\left(j = \overline{1,4}\right)$, calculated according to the Arrhenius equation $k_j(T) = k_{0j} \cdot \exp\left(-\frac{E_j}{RT}\right)$, where E_j – energy of activation of the j-th stage (kJ/mol), T – reaction temperature (K), R – universal gas constant (8,31 J/(mol·K)).

The matrix of stoichiometric coefficients of substances (γ_{ij}) ($i = \overline{1,4}$, $j = \overline{1,9}$) is given in Table-1.

Table-1. Matrix of stoichiometric coefficients of the reaction of synthesis of benzylidenebenzylamine.

	ω_1	ω_2	ω_3	ω_4
X_1	-1	0	-1	0
X_2	-1	0	0	0
X_3	1	-1	0	0
X_4	1	0	0	0
X_5	0	1	-1	0
X_6	0	1	0	-1
X_7	0	0	1	0
X_8	0	0	1	-1
X_9	0	0	0	1
δ	0	1	0	-1

Since there are nonzero elements among the elements of the last line δ, the reaction proceeds with a change in the reaction volume [16, 17]. Then the kinetic model of the reaction is a system of differential equations:

$$\frac{dx_i}{dt} = \frac{F_i(x,T) - x_i \cdot F_n(x,T)}{N}, \quad (7)$$

where $F_i = \sum_{j=1}^{4} \gamma_{ij} W_j$, $i = \overline{1,9}$, $\frac{dN}{dt} = F_n(x,T)$,

$F_n = \sum_{j=1}^{4} W_j \sum_{i=1}^{9} \gamma_{ij}$, with initial conditions:

$$x_i(0) = x_i^0, \quad i = \overline{1,9}, \quad N(0) = 1, \quad (8)$$

where N – variable reaction volume, $W_j = \frac{\omega_j}{C_0}$ – values of rate of reaction stages ($j = \overline{1,4}$) (h^{-1}), C_0 – initial total concentration of substances (mol/l).

The functions $F_n(x,T)$, $F_i(x,T)$ $(i = \overline{1,9})$ have the form:

$$\begin{aligned} &F_1(x,T) = -W_1(x,T) - W_3(x,T), \\ &F_2(x,T) = -W_1(x,T), \\ &F_3(x,T) = W_1(x,T) - W_2(x,T), \\ &F_4(x,T) = W_1(x,T), \\ &F_5(x,T) = W_2(x,T) - W_3(x,T), \\ &F_6(x,T) = W_2(x,T) - W_4(x,T), \\ &F_7(x,T) = W_3(x,T), \\ &F_8(x,T) = W_3(x,T) - W_4(x,T), \\ &F_9(x,T) = W_4(x,T), \\ &F_n(x,T) = W_2(x,T) - W_4(x,T). \end{aligned} \quad (9)$$

The initial substances of the reaction are benzylamine (X_1) and carbon tetrachloride (X_2), the concentrations of which are related by the ratio: $x_1(0) + x_2(0) = 1$.

For other substances $x_i(0) = 0$, $i = \overline{3,9}$.

Since the target substance of the reaction scheme is benzylideneaniline (X_7), the optimization problem is formulated as follows: find the ratio for the initial concentrations $x_1(0) : x_2(0)$ of the source substances X_1 and X_2, at which at the final time of the reaction the maximum yield of benzylidenebenzylamine X_7 is reached, i.e. $Q(x) = x_7(t_2) \to \max$.

The solution of this problem is obtained at the temperature $T = 23\,^{\circ}C$ and time of the reaction $t_2 = 4$ h. The solution of the system (Eq. (7)) with initial conditions (Eq. (8)) is obtained by the implicit Euler method.

The result of the calculation obtained the optimal ratio for the initial concentrations of the source substances:

$$x_1(0) : x_2(0) = 0,51 : 0,49. \quad (10)$$

The maximum yield of the reaction (benzylideneaniline) is 0,013 mole fractions.

Figure-1 shows the dynamics of the benzylidenebenzylamine concentration at optimal initial concentrations.

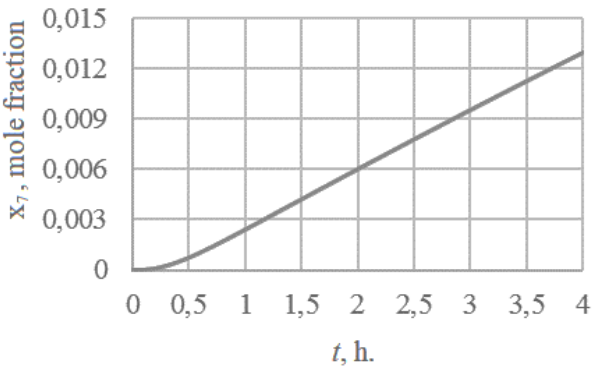

Figure-1. Dynamics of the optimal concentration of benzylidenebenzylamine.

5. CONCLUSIONS

Let's consider the solution of a direct kinetic problem for the reaction scheme (Eq. (5)) with arbitrary sets for initial concentrations of substances.

According to Table-2, the maximum concentration of benzylidenebenzylamine is observed when there is the ratio of the source substances (Eq. (10)). It confirms the correct operation of the algorithm.

Table-2. Dependence of the concentration of benzylidenebenzylamine X_7 from the ratio of source substances X_1 and X_2.

x_1, mole fraction	x_2, mole fraction	x_7, mole fraction
0,1	0,9	0,004
0,2	0,8	0,008
0,3	0,7	0,010
0,4	0,6	0,012
0,51	0,49	0,013
0,7	0,3	0,011
0,8	0,2	0,009
0,9	0,1	0,005

Thus, the developed algorithm for finding the optimal initial concentrations of the initial substances makes it possible to solve the problem of planning an experiment in chemistry at the stage of a computational experiment. The solution of the optimization problem will be found for any set of values of the initial concentrations of substances, since the work of the artificial immune systems method does not depend on the initial approximation.

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