ХИМИЧЕСКИЕ НАУКИ

УДК: 547.662. 66.011

Ziyadullaev A.E.
Doctorate of 3-course of the
Tashkent Chemical Technology Institute
Nurmonov S.E.
Doctor of technical sciences, professor,
Faculty of chemistry of the National University of Uzbekistan
Parmonov A.B.
Lecturer at the Faculty
of Chemistry of National University of Uzbekistan
Jumartova U.U.
Student of 2-course of the Faculty of Chemistry
National University of Uzbekistan
Mavloniy M.I.
Head Laboratories Institute of Microbiology
Academy of Sciences of the Republic of Uzbekistan,
Doctor of Biological Sciences, academician

MATHEMATICAL PROCESSING OF THE RESULTS OF SYNTHESIS OF VINYL ETHERS OF CYANURIC ACID

Зиядуллаев А.Э.
Докторант 3-курса
Ташкентский химико- технологический института
Нурманов С.Э.
Доктор технических наук, профессор,
факультет химия Национального университета Узбекистана
Парманов А.Б.
Преподаватель химического факультета
Национальный Университет Узбекистана
Жумартова У.У.
Магистрантка 2-курса химического факультета
Национальный Университет Узбекистана
Мавлоний М.И.
Зав. Лаборатории Институт Микробиологии
Академия наук Республики Узбекистан,
доктор биологических наук, академик

МАТЕМАТИЧЕСКАЯ ОБРАБОТКА РЕЗУЛЬТАТОВ СИНТЕЗА ВИНИЛОВЫХ ЭФИРОВ ЦИАНУРОВОЙ КИСЛОТЫ

Аннотация. В статье приведены результаты исследования процесса гомогенного каталитического винилирования 2,4,6-тригидрокси 1,3,5-триазина ацетиленом на основе высоко-основны систем: ДМСО, ДМФА; гидроксидов лития, натрия и калия. Определено, что в процессе синтеза образуются моно-, ди- и три-виниловые эфиры триазин. Найдены оптимальные параметры процесса, определено влияние продолжительности проведения реакции и температуры, количества и скорости подачи ацетилена, природы катализаторов и растворителей на выход целевых продукта. Структура синтезированных виниловых эфиров подтверждена данными ИК, ^{1}H, ^{13}C-ЯМР спектральные анализов. Полученные разработаны математическими моделями и методами. Анализ полученных экспериментальных результатов химического процесса показал их соответствие с теоретическими данными. Разработаны диаграммы результатов энергии активации и динамика изменения кинетических параметров, а также приведи графики аналитических функций.

Определена значение выхода продуктов: показало, что при температуре 80–120 ^{o}C продолжительности реакции 6 часов выход виниловых эфиров циануровый кислоты увеличивается: (12,2–18,2) моно-винилового эфира, (14,6-21,8) ди-винилового эфира и (12,4-22,6) % три- винилового эфира соответственно. Установлена, что дальнейшее повышение температуры реакции (140 ^{o}C) приводит к умещению выхода продуктов до 16,4; 16 и 10,8 % соответственно для моно-, ди- и три-виниловых эфиров. Установлено, что оптимальным режим от проведения экспериментов является: продолжительность 6 часов, температура 120 ^{o}C, количество катализатора относительно кислот 10 % от массы кислоты, скорость подачи ацетилена 4,5 л/сек. Вылены условия максимального выхода общая винилового эфира (62.6%) циануровой кислоты.

Abstract. In article results by investigation of catalytic homogeneous vinylation of 2,4,6-trihydroxy-1,3,5-triazine (cyanuric acid) by acetylene on the base high-based system: DMSO, DMF; hydroxides of lithium, potassium and sodium. It was determined that in process of synthesis mono-, two- and three-vinyl ethers of cyanuric acid have been formed. Optimal parameters of investigated process were determined: influence of duration of reaction temperature and rate of feeding acetylene, nature of using catalysts and solvents on yield of forming products. Structure of the synthesized vinyl ethers was been proved by data of such methods IR, ^{1}H, ^{13}C-NMR spectral analyzes. Obtain results were treated wish using mathematical models and methods. Analysis of obtained experimental results of investigated chemical process has shown corresponding to theoretical data. Diagrams of results of activation energy and dynamics of changing of kinetic parameters have been elaborated and also graphs of analytical functions are also presented. Values of products yields have been determined: it was shown that at temperature of 80–120 ^{o}C for and duration of reaction 6 h, yield of vinyl ethers of cyanuric acid have increased: (12.2–18.2) of mono-vinyl ether, (14.6–21.8) two-vinyl ether and (12.4 - 22.6) % three-vinyl ether, correspondence. It was determined that further increase of temperature (140 ^{o}C) has carried out to he creasing of yields of products to 16.4; 16 and 10.8 % correspondence for mono-, two- and thee-vinyl ethers. It was determined that optimal optimal regime for carrying out of experiments was: duration of reaction 6 hours, temperature 120 ^{o}C, quantity of catalyst relatively of initial reagent (cyanuric acid) - 10 mas %, (from it’s mass) and rate feeding of acetylene 4.5 l / sec. The conditions for the maximum yield of total vinyl ester (62.6%) of cyanuric acid were determined.

Ключевые слова: ацетилен, винилирование, виниловый эфир, циануровой кислоты, моно,- ди- и три винил цианурат.

Key words: acetylene, vinylation, ethers of cyanuric acid, mono,- two- and three vinyl cyanurates.

INTRODUCTION

Obtaining complex compounds with the participation of cyanuric acid is becoming relevant in the world industry. The formation of certain cyanuric acid derivatives due to the exchange of a hydrogen atom and sulfur containing compounds by oxygen substitution has been theoretically studied [1]. Also, with the participation of cyanuric acid and melamine, supramolecular clusters were obtained [2-5]. The use of cyanuric acid and some of its homologs is becoming more promising in metallurgy. It should be emphasized that due to the content of the hydrogen atom in the composition of cyanuric acid, it has a special tendency to form the Hamilton complex [6,7]. Because of these properties, cyanuric acid has gained importance for the biochemical and pharmaceutical industries [8-12].

Currently, vinyl esters and ethers are widely used in various industries: including as biological active substances in medicine; monomers for the production of polymers and plastic materials; inhibitors in the oil and gas industry; crosslinking agents in the manufacture of rubber and rubber; adhesives in microelectronics; various solvents in the textile industry [13-15].

Cyanuric acid and its derivatives are widely used in various industries. The introduction of a vinyl group into a cyanuric acid molecule has increased its biological activity and expands the scope of its using [16-18]. Mathematical processing the results obtained in chemical reactions, finding a mathematical formula for the course of such processes is important at elaboration of technology and determining the technological parameters of the synthesis of organic compounds [19].

In this paper is presented the mathematical processing of the obtained experimental results by catalytic vinylation of cyanuric acid with acetylene.

EXPERIMENTAL

The least squares method has allowed the experimental data to select such analytical function that passes as close to the experimental points as possible. In the general case, the problem can be formulated as follows. Let result of the experiments in a certain experimental dependence y (x), was obtained which in is presented in table:

x	x_1	x_2	x_3	…	x_{n-1}	x_n
y	y_1	y_2	y_3	…	y_{n-1}	y_n

It is necessary to build an analytical dependence $f(x, a_1, a_2, \dots, a_k)$, that most accurately describes the results of the experiment. To building function parameters $f(x, a_1, a_2, \dots, a_k)$ the least squares method. Was used which is concluded that function $f(x, a_1, a_2, \dots, a_k)$ it in necessaries, by such method so that the sum of the squared deviations of the measured values y_i from calculated $Y_i = f(x, a_1, a_2, \dots, a_k)$ would be the smallest (Fig.1):

$$S(a_1, a_2, \dots, a_k) = \sum_{i=1}^{n} [y_i - Y_i]^2 = \sum_{i=1}^{n} [y_i - f(x, a_1, a_2, \dots, a_k)]^2 \to min \quad (1)$$

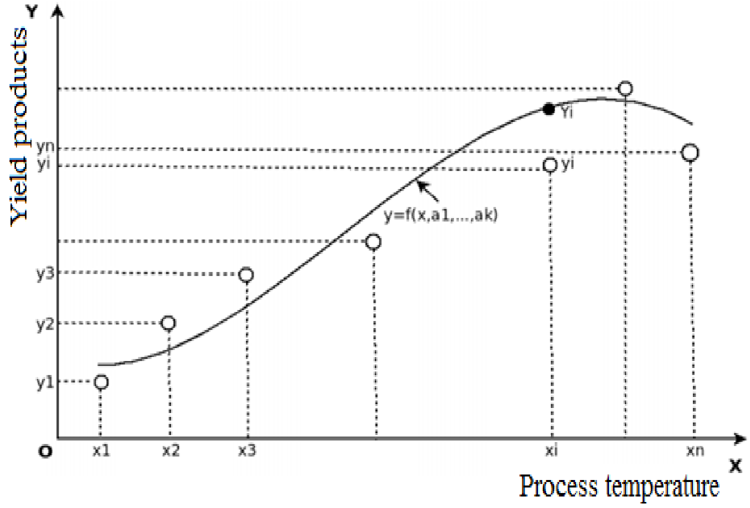

Fig 1. Analytical dependence of product yield on temperature

The task consists of two stages:

1. By use it's the results of the experiments, to determine the appearance of the selected dependence.

2. Choose the coefficients of dependence $Y = f(x, a_1, a_2, \dots, a_k)$. Mathematical, the problem of selecting the coefficients of dependence is reduced to determining the coefficients a_i from the condition (1).

The sufficient condition for the minimum function $S(a_1, a_2, \dots, a_k)$ (1) is the equality to zero of all its partial derivatives. Therefore, the problem of finding the minimum of function (1) is equivalent to solving a system of algebraic equations:

$$\begin{cases} \frac{\partial S}{\partial a_1} = 0 \\ \frac{\partial S}{\partial a_2} = 0 \\ \dots \\ \frac{\partial S}{\partial a_k} = 0 \end{cases} \qquad (2)$$

If the parameters a_i are introduced in dependence $Y = f(x, a_1, a_2, \dots, a_k)$ linearly, then system (3) consisting from k linear equations with k unknowns will be obtained:

$$\begin{cases} \sum_{i=1}^{n} 2[y_i - f(x, a_1, a_2, \dots, a_k)] \frac{\partial f}{\partial a_1} = 0 \\ \sum_{i=1}^{n} 2[y_i - f(x, a_1, a_2, \dots, a_k)] \frac{\partial f}{\partial a_2} = 0 \\ \dots \\ \sum_{i=1}^{n} 2[y_i - f(x, a_1, a_2, \dots, a_k)] \frac{\partial f}{\partial a_k} = 0 \end{cases} \qquad (3)$$

In general, a system of equations for calculating parameters a_i polynomial $k-1-$st degree $Y = \sum_{i=1}^{k} a_i x^{i-1}$ has the form:

$$\begin{cases} a_1 n + a_2 \sum_{i=1}^{n} x_i + a_3 \sum_{i=1}^{n} x_i^2 + \dots + a_k \sum_{i=1}^{n} x_i^{k-1} = \sum_{i=1}^{n} y_i \\ a_1 \sum_{i=1}^{n} x_i + a_2 \sum_{i=1}^{n} x_i^2 + a_3 \sum_{i=1}^{n} x_i^3 + \dots + a_k \sum_{i=1}^{n} x_i^{k} = \sum_{i=1}^{n} x_i y_i \\ \dots \\ a_1 \sum_{i=1}^{n} x_i^k + a_2 \sum_{i=1}^{n} x_i^{k+1} + a_3 \sum_{i=1}^{n} x_i^{k+2} + \dots + a_k \sum_{i=1}^{n} x_i^{2k-2} = \sum_{i=1}^{n} x_i^k y_i \end{cases} \qquad (4)$$

System (4) can be written in matrix form:

$$Ca = g, \qquad (5)$$

Elements of the matrix C and vector g are calculated by the formulas:

$$C_{i,j} = \sum_{k=1}^{n} x_k^{i+j-2},$$

$$i = 1, \dots, k+1, j = 1, \dots, k+1, \qquad (6)$$

$$g_i = \sum_{k=1}^{n} y_k x_k^{i-1}, i = 1, \dots, k+1. \qquad (7)$$

Having solved system (4), parameters of dependence $Y = a_1 + a_2 x + a_3 x^2 + \dots + a_{k+1} x^k$ can be determined.

RESULTS AND DISCUSSION

The influence of the nature of the solvent and catalyst, the temperature and the feed rate of acetylene on the formation of vinyl compounds on the base of cyanuric acid has been investigated. Cyanuric acid vinyl compounds were synthesized by catalytic vinylation involving acetylene owing to its active hydrogen atoms [20].

DMSO, DMF were used as a solvent, and LiOH, NaOH, and KOH as catalysts. In this case, the formation of mono-, two- and three-vinyl ethers of cyanuric acid was established. The results showed that with an increasing of the amount of catalyst, the yield of products has increased.

The activation energy and reaction rate were calculated in order to determine the kinetic parameters of the synthesis of mono-, two- and three vinyl ethers of cyanuric acids (table 1).

Table 1.

Kinetic parameters of the synthesis of mono, two, three-vinyl ethers of cyanuric acid (DMSO solvent, KOH catalyst)

The duration of the reaction, hour	Temperature, ºC	Product yield:		Average reaction rate	
		%	mol/l	% / hour	mol / l.h
Synthesis mono-vinyl ether of cyanuric acid					
6	80	12,2	0,99	4,41	0,22
	100	16,7	1,35	6,03	0,30
	120	18,2	1,47	6,57	0,32
	140	16,4	1,32	5,92	0,28
Synthesis two-vinyl ether of cyanuric acid					
6	80	14,6	1,19	5,28	0,26
	100	18,6	1,51	6,73	0,34
	120	21,8	1,78	7,89	0,40
	140	16,0	1,30	5,27	0,29
Synthesis three-vinyl ether of cyanuric acid					
6	80	12,4	1,01	4,48	0,22
	100	14,8	1,20	5,33	0,26
	120	22,6	1,86	8,15	0,42
	140	10,8	0,88	3,89	0,20

Using the tables, it is possible to elaborate a mathematical model of the reactions. Mathematical model and has been composed an analytic function for each table has been found. According to the results, the most effective reaction is the reaction, the duration of which is 6 hours. For brevity, mathematically a model of these reactions in presented:

1-table model:

t_i	80	100	120	140
u_i	12.2	16.7	18.2	16.4

$$S(a_1, a_2, \dots, a_k) = \sum_{i=1}^{4} [u_i - U_i]^2 = \sum_{i=1}^{4} [u_i - f(t_i, a_1, a_2, a_3, a_4)]^2 \to min$$

$$f(t_i, a_1, a_2, a_3, a_4) = a_1 + a_2 t_i + a_3 {t_i}^2 + a_4 {t_i}^3$$

From (2) we obtain system (8) from 4 linear equations with 4 unknowns:

$$\begin{cases} \sum_{i=1}^{4} 2[u_i - a_1 - a_2 t_i - a_3 {t_i}^2 - a_4 {t_i}^3] = 0 \\ \sum_{i=1}^{4} 2[u_i - a_1 - a_2 t_i - a_3 {t_i}^2 - {t_i}^3]\, t_i = 0 \\ \sum_{i=1}^{4} 2[u_i - a_1 - a_2 t_i - a_3 {t_i}^2 - a_4 {t_i}^3]\, {t_i}^2 = 0 \\ \sum_{i=1}^{4} 2[u_i - a_1 + a_2 t_i + a_3 {t_i}^2 + a_4 {t_i}^3]\, {t_i}^3 = 0 \end{cases} \quad (8)$$

From here we get the system:

$$\begin{cases} 4a_1 + a_2 \sum_{i=1}^{4} t_i + a_3 \sum_{i=1}^{4} t_i^2 + a_4 \sum_{i=1}^{4} t_i^3 = \sum_{i=1}^{4} u_i \\ a_1 \sum_{i=1}^{4} t_i + a_2 \sum_{i=1}^{4} t_i^2 + a_3 \sum_{i=1}^{4} t_i^3 + a_4 \sum_{i=1}^{4} t_i^4 = \sum_{i=1}^{4} t_i u_i \\ a_1 \sum_{i=1}^{4} t_i^2 + a_2 \sum_{i=1}^{4} t_i^3 + a_3 \sum_{i=1}^{4} t_i^4 + a_4 \sum_{i=1}^{4} t_i^5 = \sum_{i=1}^{4} t_i^2 u_i \\ a_1 \sum_{i=1}^{4} t_i^3 + a_2 \sum_{i=1}^{4} t_i^4 + a_3 \sum_{i=1}^{4} t_i^5 + a_{k+1} \sum_{i=1}^{4} t_i^6 = \sum_{i=1}^{n} t_i^3 u_i \end{cases} \quad (9)$$

In matrix form, system (9) can be written as:

$$\begin{pmatrix} 4 & 440 & 50400 & 5984000 \\ 440 & 50400 & 5984000 & 73248 \cdot 10^4 \\ 50400 & 5984000 & 73248 \cdot 10^4 & 919424 \cdot 10^5 \\ 5984000 & 73248 \cdot 10^4 & 919424 \cdot 10^5 & 11777664 \cdot 10^6 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} = \begin{pmatrix} 63,5 \\ 7126 \\ 828600 \\ 99397600 \end{pmatrix}$$

Having solved system (9), we determine the dependence parameters

$$a_1 = -29{,}8; a_2 = 0{,}715; a_3 = -18{,}75 \cdot 10^{-4}; a_4 = -62{,}496 \cdot 10^{-7}$$

and function $f = -29{,}8 + 0{,}715x - 18{,}75 \cdot 10^{-4}x^2 - 62{,}496 \cdot 10^{-7}x^3$.

Now using the Maple18 program, it is possible to construct a graph of this function and a diagram of the results (Fig. 2).

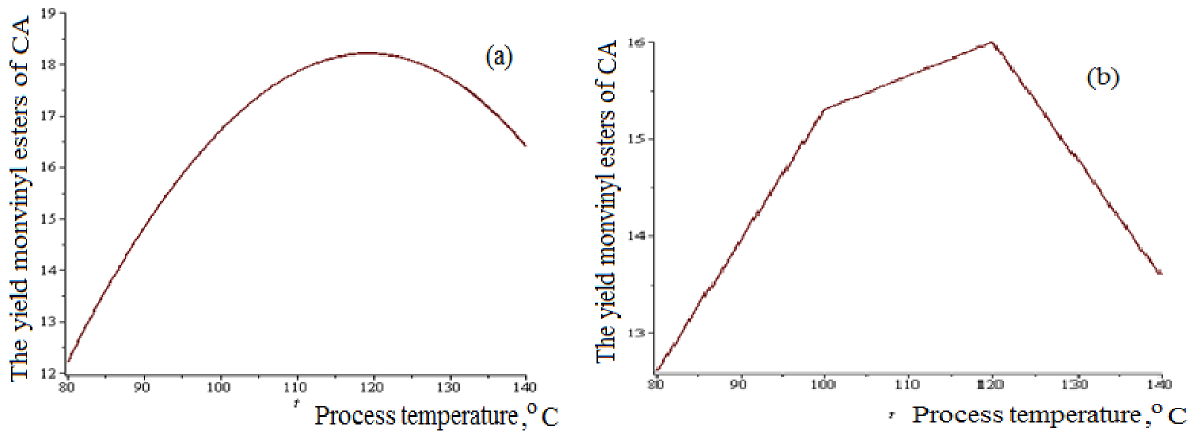

Fig 2. The in fluense of temperature on the yield of mono-vinyl ester of cyanuric acid; (a) experimentally; (b) the results of mathematical processing.

t_i	80	100	120	140
ϑ_i	4,41	6,03	6,57	5,92
u_i	12.2	16.7	18.2	16.4

$$S(a_1, a_2, \dots, a_k) = \sum_{i=1}^{4}[u_i - U_i]^2 = \sum_{i=1}^{4}[u_i - f(t_i, \vartheta_i, a_1, a_2, a_3, a_4)]^2 \to min$$

$$f(t_i, \vartheta_i, a_1, a_2, a_3, a_4) = a_1 t_i + a_2 {t_i}^2 + a_3 t_i \vartheta_i + a_4 {\vartheta_i}^2$$

From (2) we obtain system (10) from 4 linear equations with 4 unknowns:

$$\begin{cases} \sum_{i=1}^{4} 2[u_i - (a_1 t_i + a_2 {t_i}^2 + a_3 t_i \vartheta_i + a_4 {\vartheta_i}^2)]t_i = 0 \\ \sum_{i=1}^{4} 2[u_i - (a_1 t_i + a_2 {t_i}^2 + a_3 t_i \vartheta_i + a_4 {\vartheta_i}^2)]\, {t_i}^2 = 0 \\ \sum_{i=1}^{4} 2[u_i - (a_1 t_i + a_2 {t_i}^2 + a_3 t_i \vartheta_i + a_4 {\vartheta_i}^2)]\, t_i \vartheta_i = 0 \\ \sum_{i=1}^{4} 2[u_i - (a_1 t_i + a_2 {t_i}^2 + a_3 t_i \vartheta_i + a_4 {\vartheta_i}^2)]\, {\vartheta_i}^2 = 0 \end{cases} \quad 10)$$

From here the following system will be obtained:

$$\begin{cases} a_1 \sum_{i=1}^{4} t_i^2 + a_2 \sum_{i=1}^{4} t_i^3 + a_3 \sum_{i=1}^{4} t_i^2 \vartheta_i + a_4 \sum_{i=1}^{4} t_i {\vartheta_i}^2 = \sum_{i=1}^{4} u_i t_i \\ a_1 \sum_{i=1}^{4} t_i^3 + a_2 \sum_{i=1}^{4} t_i^4 + a_3 \sum_{i=1}^{4} t_i^3 \vartheta_i + a_4 \sum_{i=1}^{4} t_i^2 {\vartheta_i}^2 = \sum_{i=1}^{4} u_i t_i^2 \\ a_1 \sum_{i=1}^{4} t_i^2 \vartheta_i + a_2 \sum_{i=1}^{4} t_i^3 \vartheta_i + a_3 \sum_{i=1}^{4} t_i^2 {\vartheta_i}^2 + a_4 \sum_{i=1}^{4} t_i {\vartheta_i}^3 = \sum_{i=1}^{4} u_i t_i \vartheta_i \\ a_1 \sum_{i=1}^{4} t_i {\vartheta_i}^2 + a_2 \sum_{i=1}^{4} t_i^2 {\vartheta_i}^2 + a_3 \sum_{i=1}^{4} t_i {\vartheta_i}^3 + a_{k+1} \sum_{i=1}^{4} {\vartheta_i}^4 = \sum_{i=1}^{n} u_i {\vartheta_i}^2 \end{cases} \quad (11)$$

System (11) can be written in matrix form:

$$\begin{pmatrix} 50400 & 5984000 & 299164 & 15278{,}222 \\ 5984000 & 73248 \cdot 10^4 & 35885360 & 1796560{,}84 \\ 299164 & 35885360 & 1796560{,}84 & 91864{,}57586 \\ 15278{,}222 & 1796560{,}84 & 91864{,}57586 & 4791{,}802388 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} = \begin{pmatrix} 7126 \\ 828600 \\ 42315{,}46 \\ 2204{,}85599 \end{pmatrix}$$

Having solved system (11), the dependence parameters $a_1 = 0{,}151887768503185$; $a_2 = -8{,}17174362595097 \cdot 10^{-6}$; $a_3 = -0{,}0222409649173869$; $a_4 = 0{,}432874298761817$ and function $f(t_i, \vartheta_i, a_1, a_2, a_3, a_4) = 0{,}151887768503185 t_i - 0{,}00000817174362595097 {t_i}^2 - 0{,}0222409649173869 t_i \vartheta_i + 0{,}432874298761817 {\vartheta_i}^2$ have been determined.

2-table model:

t_i	80	100	120	140
u_i	14.6	18.6	21.8	16

$$S(a_1, a_2, \dots, a_k) = \sum_{i=1}^{4} [u_i - U_i]^2 = \sum_{i=1}^{4} [u_i - f(t_i, a_1, a_2, a_3, a_4)]^2 \to min$$

$$f(t_i, a_1, a_2, a_3, a_4) = a_1 + a_2 t_i + a_3 {t_i}^2 + a_4 {t_i}^3$$

From (2) system (12) of 4 linear equations with 4 unknowns was obtained:

$$\begin{cases} \sum_{i=1}^{4} 2[u_i - a_1 - a_2 t_i - a_3 {t_i}^2 - a_4 {t_i}^3] = 0 \\ \sum_{i=1}^{4} 2[u_i - a_1 - a_2 t_i - a_3 {t_i}^2 - {t_i}^3]\, t_i = 0 \\ \sum_{i=1}^{4} 2[u_i - a_1 - a_2 t_i - a_3 {t_i}^2 - a_4 {t_i}^3]\, {t_i}^2 = 0 \\ \sum_{i=1}^{4} 2[u_i - a_1 + a_2 t_i + a_3 {t_i}^2 + a_4 {t_i}^3]\, {t_i}^3 = 0 \end{cases} \quad (12)$$

From here the following system can be obtained:

$$\begin{cases} 4a_1 + a_2 \sum_{i=1}^{4} t_i + a_3 \sum_{i=1}^{4} t_i^2 + a_4 \sum_{i=1}^{4} t_i^3 = \sum_{i=1}^{4} u_i \\ a_1 \sum_{i=1}^{4} t_i + a_2 \sum_{i=1}^{4} t_i^2 + a_3 \sum_{i=1}^{4} t_i^3 + a_4 \sum_{i=1}^{4} t_i^4 = \sum_{i=1}^{4} t_i u_i \\ a_1 \sum_{i=1}^{4} t_i^2 + a_2 \sum_{i=1}^{4} t_i^3 + a_3 \sum_{i=1}^{4} t_i^4 + a_4 \sum_{i=1}^{4} t_i^5 = \sum_{i=1}^{4} t_i^2 u_i \\ a_1 \sum_{i=1}^{4} t_i^3 + a_2 \sum_{i=1}^{4} t_i^4 + a_3 \sum_{i=1}^{4} t_i^5 + a_{k+1} \sum_{i=1}^{4} t_i^6 = \sum_{i=1}^{n} t_i^3 u_i \end{cases} \quad (13)$$

System (13) in matrix form can be written as:

$$\begin{pmatrix} 4 & 440 & 50400 & 5984000 \\ 440 & 50400 & 5984000 & 73248 \cdot 10^4 \\ 50400 & 5984000 & 73248 \cdot 10^4 & 919424 \cdot 10^5 \\ 5984000 & 73248 \cdot 10^4 & 919424 \cdot 10^5 & 11777664 \cdot 10^6 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} = \begin{pmatrix} 71 \\ 7884 \\ 906960 \\ 107649600 \end{pmatrix}$$

Solving the system (13), parameters dependence $a_1 = 154{,}6$; $a_2 = -4{,}67666$; $a_3 = 0{,}05025$; $a_4 = 0{,}0001708336$ and function $f = 154{,}6 - 4{,}67666x + 0{,}05025x^2 + 0{,}0001708336x^3$., can been determined.

Now, using the program Maple18, a graph of this function and a diagram of the results can been determined (Fig. 3).

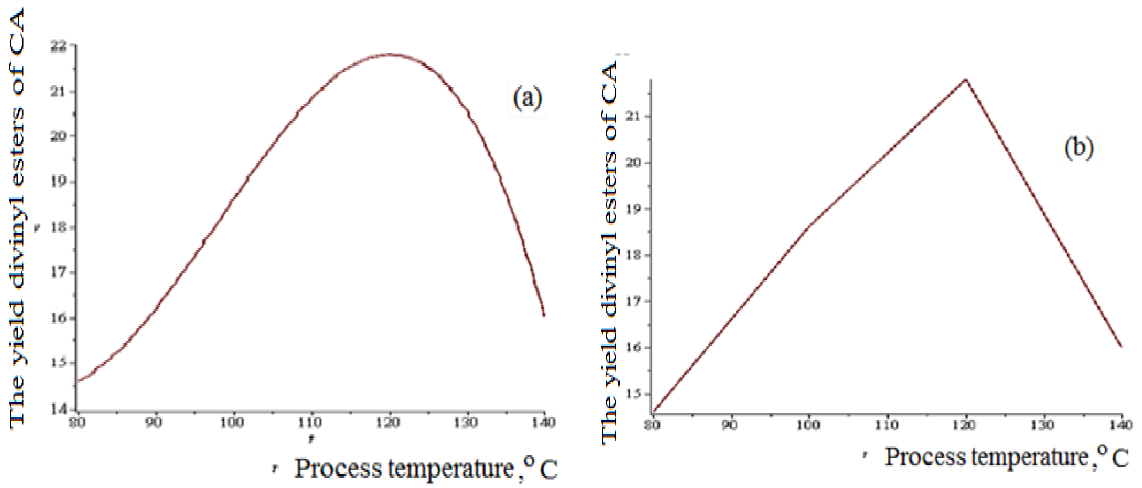

Fig. 3. Effect of temperature on the yield two-vinyl ether of cyanuric acid: (a) experimentally; (b) the results of mathematical processing

t_i	80	100	120	140
ϑ_i	5,28	6,73	7,89	5,27
u_i	14.6	18.6	21.8	16

$$S(a_1, a_2, \dots, a_k) = \sum_{i=1}^{4} [u_i - U_i]^2 = \sum_{i=1}^{4} [u_i - f(t_i, \vartheta_i, a_1, a_2, a_3, a_4)]^2 \to min$$

$$f(t_i, \vartheta_i, a_1, a_2, a_3, a_4) = a_1 t_i + a_2 t_i^2 + a_3 t_i \vartheta_i + a_4 \vartheta_i^2$$

From (2) system (14) from 4 linear equations with 4 unknowns will be obtained.

$$\begin{cases} \sum_{i=1}^{4} 2[u_i - (a_1 t_i + a_2 t_i^2 + a_3 t_i \vartheta_i + a_4 \vartheta_i^2)] t_i = 0 \\ \sum_{i=1}^{4} 2[u_i - (a_1 t_i + a_2 t_i^2 + a_3 t_i \vartheta_i + a_4 \vartheta_i^2)]\, t_i^2 = 0 \\ \sum_{i=1}^{4} 2[u_i - (a_1 t_i + a_2 t_i^2 + a_3 t_i \vartheta_i + a_4 \vartheta_i^2)]\, t_i \vartheta_i = 0 \\ \sum_{i=1}^{4} 2[u_i - (a_1 t_i + a_2 t_i^2 + a_3 t_i \vartheta_i + a_4 \vartheta_i^2)]\, \vartheta_i^2 = 0 \end{cases} \quad (14)$$

From here we get the system:

$$\begin{cases} a_1 \sum_{i=1}^{4} t_i^2 + a_2 \sum_{i=1}^{4} t_i^3 + a_3 \sum_{i=1}^{4} t_i^2 \vartheta_i + a_4 \sum_{i=1}^{4} t_i \vartheta_i^2 = \sum_{i=1}^{4} u_i t_i \\ a_1 \sum_{i=1}^{4} t_i^3 + a_2 \sum_{i=1}^{4} t_i^4 + a_3 \sum_{i=1}^{4} t_i^3 \vartheta_i + a_4 \sum_{i=1}^{4} t_i^2 \vartheta_i^2 = \sum_{i=1}^{4} u_i t_i^2 \\ a_1 \sum_{i=1}^{4} t_i^2 \vartheta_i + a_2 \sum_{i=1}^{4} t_i^3 \vartheta_i + a_3 \sum_{i=1}^{4} t_i^2 \vartheta_i^2 + a_4 \sum_{i=1}^{4} t_i \vartheta_i^3 = \sum_{i=1}^{4} u_i t_i \vartheta_i \\ a_1 \sum_{i=1}^{4} t_i \vartheta_i^2 + a_2 \sum_{i=1}^{4} t_i^2 \vartheta_i^2 + a_3 \sum_{i=1}^{4} t_i \vartheta_i^3 + a_{k+1} \sum_{i=1}^{4} \vartheta_i^4 = \sum_{i=1}^{n} u_i \vartheta_i^2 \end{cases} \quad (15)$$

System (15) can be written in matrix form

$$\begin{pmatrix} 50400 & 5984000 & 318000 & 18118{,}02 \\ 5984000 & 73248 \cdot 10^4 & 37528160 & 2072129{,}84 \\ 318000 & 37528160 & 2072129{,}84 & 121689{,}0917 \\ 18118{,}02 & 2072129{,}84 & 121689{,}0917 & 7475{,}309905 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} = \begin{pmatrix} 7884 \\ 906960 \\ 51129{,}88 \\ 3050{,}93476 \end{pmatrix}$$

Having solved system (15), the dependence parameters $a_1 = 0{,}18257393692835$; $a_2 = -3{,}05057318158219 \cdot 10^{-4}$; $a_3 = -0{,}0174143349854603$; $a_4 = 0{,}333673055662075$ and function $f(t_i, \vartheta_i, a_1, a_2, a_3, a_4) = 0{,}18257393692835 t_i - 3{,}05057318158219 \cdot 10^{-4} t_i^2 - 0{,}0174143349854603 t_i \vartheta_i + 0{,}333673055662075 \vartheta_i^2$can be determined.

3-table model:

6	80	12,4	1,01	4,48	0,22
	100	14,8	1,20	5,33	0,26
	120	22,6	1,86	8,15	0,42
	140	10,8	0,88	3,89	0,20

t_i	80	100	120	140
u_i	12.4	14.8	22.6	10,8

$$S(a_1, a_2, \dots, a_k) = \sum_{i=1}^{4} [u_i - U_i]^2 = \sum_{i=1}^{4} [u_i - f(t_i, a_1, a_2, a_3, a_4)]^2 \to min$$

$$f(t_i, a_1, a_2, a_3, a_4) = a_1 + a_2 t_i + a_3 t_i^2 + a_4 t_i^3$$

From (2) system (16) from 4 linear equations with 4 unknowns will be obtained:

$$\begin{cases} \sum_{i=1}^{4} 2[u_i - a_1 - a_2 t_i - a_3 t_i^2 - a_4 t_i^3] = 0 \\ \sum_{i=1}^{4} 2[u_i - a_1 - a_2 t_i - a_3 t_i^2 - t_i^3]\, t_i = 0 \\ \sum_{i=1}^{4} 2[u_i - a_1 - a_2 t_i - a_3 t_i^2 - a_4 t_i^3]\, t_i^2 = 0 \\ \sum_{i=1}^{4} 2[u_i - a_1 + a_2 t_i + a_3 t_i^2 + a_4 t_i^3]\, t_i^3 = 0 \end{cases} \quad (16)$$

From here we get the system:

$$\begin{cases} 4a_1 + a_2\sum_{i=1}^{4} t_i + a_3\sum_{i=1}^{4} t_i^2 + a_4\sum_{i=1}^{4} t_i^3 = \sum_{i=1}^{4} u_i \\ a_1\sum_{i=1}^{4} t_i + a_2\sum_{i=1}^{4} t_i^2 + a_3\sum_{i=1}^{4} t_i^3 + a_4\sum_{i=1}^{4} t_i^4 = \sum_{i=1}^{4} t_i u_i \\ a_1\sum_{i=1}^{4} t_i^2 + a_2\sum_{i=1}^{4} t_i^3 + a_3\sum_{i=1}^{4} t_i^4 + a_4\sum_{i=1}^{4} t_i^5 = \sum_{i=1}^{4} t_i^2 u_i \\ a_1\sum_{i=1}^{4} t_i^3 + a_2\sum_{i=1}^{4} t_i^4 + a_3\sum_{i=1}^{4} t_i^5 + a_{k+1}\sum_{i=1}^{4} t_i^6 = \sum_{i=1}^{n} t_i^3 u_i \end{cases} \quad (17)$$

System (17) in matrix form can be written as:

$$\begin{pmatrix} 4 & 440 & 50400 & 5984000 \\ 440 & 50400 & 5984000 & 73248\cdot 10^4 \\ 50400 & 5984000 & 73248\cdot 10^4 & 919424\cdot 10^5 \\ 5984000 & 73248\cdot 10^4 & 919424\cdot 10^5 & 11777664\cdot 10^6 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} = \begin{pmatrix} 60{,}6 \\ 6696 \\ 764480 \\ 89836800 \end{pmatrix}$$

Having solved system (13), we determine the dependence parameters $a_1 = 556{,}8; a_2 = -16{,}51167; a_3 = 0{,}163; a_4 = -0{,}000520834$ and function $f = 556{,}8 - 16{,}51167x + 0{,}163x^2 - 0{,}000520834x^3$.

Now, using the program Maple18, we construct a graph of this function and a diagram of the results (Fig.4).

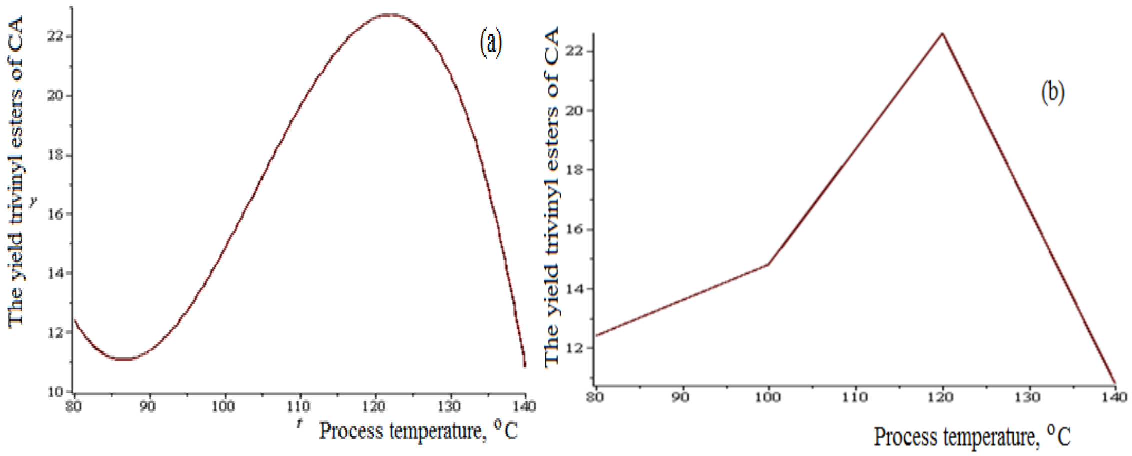

Fig.4. The effect of temperature on the yield of three vinyl esters of cyanuric acid; (a) experimentally; (b) the results of mathematical processing:

t_i	80	100	120	140
ϑ_i	4,48	5,33	8,15	3,89
u_i	12.4	14.8	22.6	10,8

$$S(a_1, a_2, \dots, a_k) = \sum_{i=1}^{4}[u_i - U_i]^2 = \sum_{i=1}^{4}[u_i - f(t_i, \vartheta_i, a_1, a_2, a_3, a_4)]^2 \rightarrow min$$

$$f(t_i, \vartheta_i, a_1, a_2, a_3, a_4) = a_1 t_i + a_2 t_i^2 + a_3 t_i \vartheta_i + a_4 \vartheta_i^2$$

From (2) system (18) from 4 linear equations with 4 unknowns will be obtained.

$$\begin{cases} \sum_{i=1}^{4} 2[u_i - (a_1 t_i + a_2 t_i^2 + a_3 t_i\vartheta_i + a_4\vartheta_i^2)]t_i = 0 \\ \sum_{i=1}^{4} 2[u_i - (a_1 t_i + a_2 t_i^2 + a_3 t_i\vartheta_i + a_4\vartheta_i^2)]\, t_i^2 = 0 \\ \sum_{i=1}^{4} 2[u_i - (a_1 t_i + a_2 t_i^2 + a_3 t_i\vartheta_i + a_4\vartheta_i^2)]\, t_i\vartheta_i = 0 \\ \sum_{i=1}^{4} 2[u_i - (a_1 t_i + a_2 t_i^2 + a_3 t_i\vartheta_i + a_4\vartheta_i^2)]\, \vartheta_i^2 = 0 \end{cases} \quad (18)$$

From here we get the system:

$$\begin{cases} a_1\sum_{i=1}^{4} t_i^2 + a_2\sum_{i=1}^{4} t_i^3 + a_3\sum_{i=1}^{4} t_i^2\vartheta_i + a_4\sum_{i=1}^{4} t_i\vartheta_i^2 = \sum_{i=1}^{4} u_i t_i \\ a_1\sum_{i=1}^{4} t_i^3 + a_2\sum_{i=1}^{4} t_i^4 + a_3\sum_{i=1}^{4} t_i^3\vartheta_i + a_4\sum_{i=1}^{4} t_i^2\vartheta_i^2 = \sum_{i=1}^{4} u_i t_i^2 \\ a_1\sum_{i=1}^{4} t_i^2\vartheta_i + a_2\sum_{i=1}^{4} t_i^3\vartheta_i + a_3\sum_{i=1}^{4} t_i^2\vartheta_i^2 + a_4\sum_{i=1}^{4} t_i\vartheta_i^3 = \sum_{i=1}^{4} u_i t_i\vartheta_i \\ a_1\sum_{i=1}^{4} t_i\vartheta_i^2 + a_2\sum_{i=1}^{4} t_i^2\vartheta_i^2 + a_3\sum_{i=1}^{4} t_i\vartheta_i^3 + a_{k+1}\sum_{i=1}^{4} \vartheta_i^4 = \sum_{i=1}^{n} u_i\vartheta_i^2 \end{cases} \quad (19)$$

System (19) can be written in matrix form:

$$\begin{pmatrix} 50400 & 5984000 & 275576 & 14535,716 \\ 5984000 & 73248\cdot 10^4 & 32381120 & 1665612,72 \\ 275576 & 32381120 & 1665612,72 & 95537,32172 \\ 14535,716 & 1665612,72 & 95537,32172 & 5850,815511 \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} = \begin{pmatrix} 6696 \\ 764480 \\ 40317,04 \\ 23333,89986 \end{pmatrix}$$

Having solved system (19), we determine parameters of the dependence $a_1 = 0,15863913854156$; $a_2 = -8,94907004671319 \cdot 10^{-4}$; $a_3 = 0,00740573017296242$; $a_4 = 0,138615079939314$ and function $f(t_i, \vartheta_i, a_1, a_2, a_3, a_4) = 0,15863913854156 t_i - 8,94907004671319 \cdot 10^{-4} t_i^2 + 0,00740573017296242 t_i \vartheta_i + 0,138615079939314 \vartheta_i^2$.

CONCLUSION

After analyzation of kinetic parameters of the synthesis of cyanuric acid vinyl esters, the average reaction rate was determined and it's activation energy was calculated. Using mathematical modeling, analysis of graphs of analytical functions and diagrams of kinetic parameters of synthesis it is possible to establishe that at a reaction time of 6 hours and a temperature of 120 ° C the yields of vinyl esters have reached a maximum values: mono- vinyl 18.2%, di-vinyl 21.8%, and tri-vinyl - 22.6%.

REFERENCES

1. M.J.Mayor-Lopez, J.Weber, H.P.Luthi, K.Hegetschweiler. SCO Trimers as high-energy materials? A density functional study. J. Mol. Model. **6**, 55 (2000). DOI: https://doi.org/10.1007/PL00010734

2. L.P.Manríquez, A.Cabrera, L.E.Sansores, R.Salcedo. Aromaticity in cyanuric acid. J.Mol.Model. **Vol. 17**, p. 1311–1315 (2011). DOI: https://doi.org/10.1007/s00894-010-0825-2

3. H. Zhu, K.Kannan. Occurrence and distribution of melamine and its derivatives in surface water, drinking water, precipitation, wastewater, and swimming pool water. *Environmental Pollution* **2020,** *258*, 113743. DOI: 10.1016/j.envpol.2019.113743.

4. Falk, Blatchley, Kuechler, Meyer, Pickens, Suppes. Assessing the Impact of Cyanuric Acid on Bather's Risk of Gastrointestinal Illness at Swimming Pools. *Water* **2019,** *11* (6), 1314. DOI: 10.3390/w11061314.

5. David G. Wahman, Matthew T. Alexander, Alison G. Dugan. Chlorinated cyanurates in drinking water: Measurement bias, stability, and disinfectant byproduct formation. *AWWA Water Science* **2019,** *1* (2), 1133. DOI: 10.1002/aws2.1133.

6. K.Damodaran, G.J.Sanjayan, P.R.Rajamohanan, S.Ganapathy, K.N.Ganesh. Conformational modulation of *Ant–Pro* oligomers using chirality alteration of proline residues. Org. Lett. Vol. 3, p. 1921–1924 (2001). DOI: https://doi.org/10.1039/C2OB26132D

7. A.G.Bielejewska, C.E.Marjo, L.J.Prins, P.Timmerman, F.de Jong, D.N. Reinhoudt. Thermodynamic Stabilities of Linear and Crinkled Tapes and Cyclic Rosettes in Melamine−Cyanurate Assemblies: A Model Description. J. Am. Chem. Soc. 123, p. 7518 – 7533 (2001). DOI: https://doi.org/10.1021/ja010664.

8. X.C.Gao, D.C.Zou, K.Fujita, T.Tsutsui. Switchable organic electroluminescence Appl. Phys. Lett. 81, 4508 (2002); DOI: https://doi.org/10.1063/1.1528738.

9. D.L.Flamm, O.Auciello. Plasma deposition, treatment, and etching of polymers the treatment and etching of polymers. New York, Elsevier-2012. P. 42-47.

10. S.P.Patil, D.A.Padmanabhan. Facile preparation of (2,4,6-[14]C)-cyanuric acid under solvent-free conditions. J. Label Compd. Radiophar. 2002, 45, P. 539–542. DOI: http://dx.doi.org/10.1002/jlcr.579

11. Y.F.Zeng. The application of cyanuric acid in chemical industry. Fine Chem. Ind.1987,*2*, P. 42–47.

12. G.F.Janna, G.Klapotke, M.K.Thomas, Z.Naturforsch, K.Burkhard. Synthesis, properties and dimerization study of isocyanic acid. B Chem. Sci. - 2002, № 57, P. 19–24. **DOI:** https://doi.org/10.1515/znb-2002-0103

13. A.B.Parmanov, S.E.Nurmanov, Beata Kolesinsko, Tomash Maniecki, O.E.Ziyadullayev. Homogeneous vinylation of 2-hydroxy-2-phenylethanical acid. Azerbaijan chemical journal. - Azerbaijan, -2019, № 4. P. 32-34. DOI: https://doi.org/10.32737/0005-2531-2019-4-32-34.

14. Parmanov A.B., Nurmonov S.E., Abdugafurov I.A., Ziyadullaev O.E., Mirkhamitova D.X. Synthesis of vinyl ester of lactic acid. Eurasian Union of Scientists. Russia. № 7 (64) / 2019 P. 51-56. DOI: https://doi.org/10.31618/ESU.2413-9335.2019.2.64.227

15. Parmanov A.B., Nurmanov S.E., Phayzullaeva M.Ph., Abdullaev J.U., Soliev M.I. Synthesis of vinyl esters of some carbonic acids. Austrian journal technical and natural science. Vienna, Austria. -2017, -№ 1-2. -P. 129-132. DOI: http://dx.doi.org/10.20534/AJT-17-1.2-129-132

16. А.Э.Зиядуллаев, С.Э. Нурманов, Д.Х.Мирхамитова, Роль высоко-основных систем при винилировании азотсодержащих гетероциклических соединений. Химия и химическая технология. Научно-технический журнал. Тошкент-2018. № 4, Ст. 24-28.

17. Дикусар Е.А., Поткин В.И., Козлов Н.Г., Петевич С.К., Рудаков Д.А. Применение простых и сложных эфиров: Современные аспекты молекулярного дизайна–от душистых веществ и биологически активных соединений до применения а медицинских нанотехнологиях. Журнал Химия растительного сырья, 2014, № 3. – Ст. 61-84. DOI: http://dx.doi.org/10.14258/jcprm.1403061

18. J.L.Murphy, M.J.Arrowood, Xin Lu, M.C.Hlavsa, M.J.Beach, V.R.Hill. Effect of Cyanuric

Acid on the Inactivation of *Cryptosporidium parvum* under Hyperchlorination Conditions. *Environ. Sci. Technol.* 2015, 49, 12, p. 7348-7355. DOI: https://doi.org/10.1021/acs.est.5b00962

19. Н.В.Ушева, О.Е. Мойзес, О.Е. Митянина, Е.А. Кузьменко. Математическое моделирование химико-технологических процессов: учебное пособие. Томск: Изд-во Томского политехнического университета, 2014. – Ст. 135.

20. А.Э.Зиядуллаев, С.Э.Нурманов, У.У.Жумартова, А.Б.Парманов. Теоретические основы реакции гомогенного каталитического винилирования циануровой кислоты. Журнал Евразийский союз ученых, Россия № 9 (66) 2019, 2 часть. Ст. 37-41. DOI: http://dx.doi.org/10.31618/ESU.2413-9335.2019.2.66.304

UDC 541.123.6

Usmonov Muhammadsalim Bozorovich
PhD, Associate Professor
Tajik State Pedagogical University

PHASE EQUILIBRIA IN THE NA, CA// SO_4, F– H_2O SYSTEM AT 75°C

Abstract. The phase equilibria in the Na, Ca //SO_4, F – H_2O system at 75°C were investigated by the translation method. The closed phase diagram for the system was constructed based on the obtained data.

Keywords: translation method – phase equilibria – component –geometric images.

Knowledge of the laws of phase equilibria of the Na, Ca // SO_4, F – H_2O system is necessary to establish optimal conditions for the separation of sulfate and fluoride salts of sodium and calcium from natural and technological solutions containing these salts.

As an analysis of the literature [1] shows, this system has not been investigated so far. We studied it using the translation method, which follows from the principle of compatibility of structural elements n and (n + 1) component systems in one diagram [2]. According to the translation method, structural elements of the diagrams of n-component systems increase their dimension by one unit and translated to the (n + 1) component composition in a transformed form when the next component is added to them (at constant temperature and pressure),. For example, in this case, invariant points of n - component systems at the (n + 1) component level turn into monovariant curves, and monovariant curves into divariant fields, etc. Transformed geometric images, according to their topological properties, at the level of (n + 1) component composition, intersecting each other (observing the Gibbs phase rule) form geometric images of the system at this component level. Thus, the translation method will make it possible to predict the possible phase equilibria of multicomponent systems (when moving from the n-component level to the (n + 1) component level) and theoretically construct their closed phase diagrams. A more detailed application of the translation method for predicting the structure of the phase equilibrium diagram in multicomponent water – salt systems was considered in literature [3-4].

The studied four-component system includes the following three-component systems: Na_2SO_4 – $CaSO_4$ – H_2O, NaF – CaF_2 – H_2O, NaF – Na_2SO_4 – H_2O and CaF_2 – $CaSO_4$ – H_2O.

There are 3, 1, 2 and 1 invaraint points in the Na_2SO_4 – $CaSO_4$ – H_2O, NaF – CaF_2 – H_2O, NaF – Na_2SO_4 – H_2O and CaF_2 – $CaSO_4$ – H_2O systems at 75ºC respectively according to literature [5]. Table 1 gives the list and equilibrium solid phases at the ternary invariant points of the listed systems.

Table 1

Phase equilibria in the invariant points of the Na, Ca// SO_4,F–H_2O system at 75°C at the level of three-component composition

Invariant point	Solid phase composition	Invariant point	Solid phase composition
Na_2SO_4 – NaF –H_2O system		NaF – CaF_2 – H_2O system	
E_1^3	Wo+Shr	E_4^3	Wo+Fo
E_2^3	Shr+Te	Na_2SO_4 – $CaSO_4$ – H_2O system	
CaF_2 – $CaSO_4$–H_2O system		E_5^3	Te+Gb
E_3^3	Fo+ Gp	E_6^3	Gb+ 5Ca·Na·3
		E_7^3	5Ca·Na·3+ Gp

Letter E in Table 1 and further denotes an invariant point with an superscript indicating the multiplicity of the point (system complexity) and subscript indicating the serial number of the point. Following notations were used: Te-tenarditis Na_2SO_4, Gb – glauberite $Na_2SO_4 \cdot CaSO_4$, Gp – gypsum $CaSO_4 \cdot 2H_2O$, Wo – willomite NaF, Fo – fluorite CaF_2, Shr – sheireritis $Na_2SO_4 \cdot NaF$, 5Ca·Na·3 - $5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$.

Figure 1 shows phase equilibria diagram of the Na, Ca//SO_4, F – H_2O system at 75° C. Unfolded pyramid