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KINETIC RESEARCH AND MODELING OF BENZOIC ACID ESTERIFICATION PROCESS

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Abstract

The kinetic regularities of benzoic acid esterification with 1-butyl alcohol catalyzed by p-toluenesulfonic acid under stationary conditions have been studied. The study shows that the reaction has the first order with respect to benzoic acid. It is proposed a method for calculating the forward and reverse reaction constants, and the equilibrium constant using the determined effective rate constant of the esterification reaction. The preexponential factors and activation energies of the forward and reverse reactions as well as the thermal effect and the entropy change of the esterification reaction have been calculated. In particular, the thermal effect of benzoic acid esterification reaction with 1-butyl alcohol at a temperature of 365.2–389.4 K is 622 $J\cdot mol^{-1}$, and the activation energies of the forward and reverse reactions are 58.40 and 57.70 $kJ\cdot mol^{-1}$, respectively. The calculated kinetic characteristics of the esterification reaction were used in mathematical modeling of the butyl benzoate obtaining process under nonstationary conditions. Taking into account the kinetic characteristics of the reactions and the stages peculiarities of the butyl benzoate obtaining process the calculation of the change in the benzoic acid conversion over time was performed. The study shows that under optimal conditions the benzoic acid conversion in 120 min reaches 92 %. The use of the experimental results and the created mathematical model of benzoic acid esterification process with 1-butyl alcohol makes it possible to calculate of kinetic curves of the reagent consumption under nonstationary conditions. The experimentals can be used to improve the technological process of butyl benzoate manufacture in the industry.

Keywords: benzoic acid; 1-butyl alcohol; butyl benzoate; esterification; kinetic; p-toluenesulfonic acid; modeling.

КІНЕТИЧНІ ДОСЛІДЖЕННЯ ТА МОДЕЛЮВАННЯ ПРОЦЕСУ ЕСТЕРИФІКАЦІЇ БЕНЗОЙНОЇ КИСЛОТИ

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Анотація

У стаціонарних умовах досліджено кінетичні закономірності естерифікації бензойної кислоти бутан-1-олом в присутності п-толуенсульфонової кислоти. Показано, що реакція має перший порядок за бензойною кислотою. Запропоновано методику розрахунку констант прямої та зворотної реакцій і константи рівноваги за визначеною ефективною константою швидкості реакції естерифікації. Розраховано преекспоненційні множники та енергії активації прямої та зворотної реакцій, а також тепловий ефект і зміну ентропії реакції естерифікації. Зокрема тепловий ефект реакції естерифікації бензойної кислоти бутан-1-олом за температури 365.2–389.4 К становить 622 $Дж\cdot моль^{-1}$, а енергія активації прямої та зворотної реакцій 58.40 та 57.70 $кДж\cdot моль^{-1}$, відповідно. Одержані кінетичні характеристики реакції естерифікації використані для математичного моделювання періодичного процесу одержання бутилбензоату в нестаціонарних умовах. З врахуванням кінетичних характеристик реакцій та стадій процесу одержання бутилбензоату виконано розрахунок зміни ступеня перетворення бензойної кислоти з часом. Показано, що за оптимальних умов конверсія бензойної кислоти за 120 хв реакції досягає 92 %. Використання одержаних експериментальних результатів і створеної математичної моделі процесу естерифікації бензойної кислоти бутан-1-олом дало змогу отримати кінетичні криві витрати реагентів у нестаціонарних умовах. Одержані результати можуть бути використані для вдосконалення технологічного процесу одержання бутилбензоату в промисловості.

Ключові слова: бензойна кислота; бутан-1-ол; бутилбензоат; естерифікація; кінетика; п-толуенсульфонова кислота; моделювання.

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КІНЕТИЧЕСКИЕ ИССЛЕДОВАНИЯ И МОДЕЛИРОВАНИЕ ПРОЦЕССА ЭТЕРИФИКАЦИИ БЕНЗОЙНОЙ КИСЛОТЫ

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Аннотация

В стационарных условиях исследованы кинетические закономерности этерификации бензойной кислоты *н*-бутиловым спиртом в присутствии *п*-толуолсульфоновой кислоты. Показано, что реакция имеет первый порядок по бензойной кислоте. Предложена методика расчета констант прямой и обратной реакций и константы равновесия по определенной эффективной константе скорости реакции этерификации. Рассчитаны предэкспоненциальные множители и энергии активации прямой и обратной реакций, а также тепловой эффект и изменение энтропии реакции этерификации. В частности, тепловой эффект реакции этерификации бензойной кислоты *н*-бутиловым спиртом при температуре 365.2–389.4 К составляет 622 Дж·моль$^{-1}$, а энергия активации прямой и обратной реакций 58.40 и 57.70 кДж·моль$^{-1}$, соответственно. Полученные кинетические характеристики реакции этерификации использованы для математического моделирования периодического процесса получения бутилбензоата в нестационарных условиях. С учетом кинетических характеристик реакций и стадий процесса получения бутилбензоата выполнен расчет изменения степени превращения бензойной кислоты во времени. Показано, что при оптимальных условиях конверсия бензойной кислоты за 120 мин реакции достигает 92 %. Использование полученных экспериментальных результатов и созданной математической модели процесса этерификации бензойной кислоты н-бутиловым спиртом позволило получить кинетические кривые расхода реагентов в нестационарных условиях. Полученные результаты могут быть использованы для совершенствования технологического процесса получения бутилбензоата в промышленности.

Ключевые слова: бензойная кислота; н-бутиловый спирт; бутилбензоат; этерификация; кинетика; п-толуолсульфоновая кислота; моделлирование.

Introduction

Esters are an important substance in the industry as components of pesticides [1], food additives and cosmetics [2], biodiesel [3], plasticizers [4], etc.

The benzoic acid (BAc) esterification process is investigated both in batch and continuous conditions. In particular, it has been shown that the process in a continuous flow microwave reactor takes less time to provide a high yield of butyl benzoate than a batch process. At the same time, the esterification process in a continuous flow microwave reactor requires temperatures above 140 °C and high pressure, respectively [5].

The use of catalysts makes it possible the reaction temperature reducing and provides high specific productivity of the process. Today it is known about the use of a wide range of substances that accelerate the esters manufacture. Usually these are homogeneous and heterogeneous catalysts [6].

The advantage of using homogeneous catalysts is their high activity and, accordingly, high conversion degree of carboxylic acid and alcohol. Such properties are possessed by mineral acids and organic sulfonic acids [7; 8], a number of metal salts [9; 10], N-bromosuccinimide [11], enzymes [12], etc.

Ionic liquids also are homogeneous esterification catalysts. It was found that in the benzoic acid esterification reaction with different alcohols catalyzed by ionic liquids in 3 h high degrees of the acid conversion are reached [13]. In particular, the yield of the corresponding esters is from 83 to 98 % in the benzoic acid esterification reaction with methyl, butyl, cyclohexyl, benzenemethyl and lauryl alcohols catalysed by $[C_3SO_3Hmim]HSO_4$.

Heterogeneous catalysts of an esterification process are easily isolated from the reaction products. They are often suitable for repeated use, and also they are characterized by better environmental performance. It is known to use of ion exchange resins [14], heteropolyacids [15], Zirconium based double salts [16], metal salts [17], iron oxide nanoparticles supported on mesoporous materials (FeNP@SBA-15) [18], etc. to accelerate esterification reactions.

It should be noted that today a study of the regularities of benzoic acid esters manufacture is carried out using all the above catalysts. A significant number of publications also present kinetic study results of the esterification reactions. The experimental make it possible to predict the chemical process intensity and the reaction mixture composition [19].

In particular, sulfuric acid and Amberlyst-15 ion exchange resin were used as esterification catalysts. The determined preexponential factor and activation energy of the reaction catalysed by sulfuric acid are $1.48\pm0.02\cdot10^{8}\cdot l\cdot mol^{-1}\cdot s^{-1}$ and 80.5 ± 0.5 kJ·mol^{-1}, respectively. The authors also declare that the reaction kinetic equation has a second order with respect to benzoic acid for both catalysts. They also proposed a mathematical model describing temperature profiles and predicting the benzoic acid conversion in a microwave reactor [20].

Ionic liquid (1-butyl-3-methylimidazole chloride), deep eutectic solvent, and ion exchange resin were used as the catalysts of benzoic acid esterification with ethyl, butyl, and hexyl alcohols [21]. p-Toluenesulfonic acid (pTSA) was used as a hydrogen donor, and benzyltriethylammonium chloride was used as an acceptor for the deep-eutectic solvent. The deep-eutectic solvent provided the highest catalytic activity among three different catalysts. The benzoic acid conversion in the reaction with ethyl, butyl, and hexyl alcohols is 88.3, 87.8, and 67.5 %, respectively. The molar ratio of BAc : alcohol was 1 : 10, and the catalyst content in the reaction mixture was 10 wt. %. It is shown that the benzoic acid conversion increases from 43.39 to 87.87 % with temperature increasing from 55 to 75 °C in the reaction catalysed by deep-eutectic solvent.

A high yield of methyl benzoate was also achieved in the benzoic acid esterification with methyl alcohol in toluene over the H_2SO_4/SiO_2 catalyst [22]. Benzyl benzoate was also synthesized using H_2SO_4 and SiO_2-SO_3H as a catalysts [23]. These catalysts promote the benzyl benzoate and/or benzyl ether accumulating in different amounts according to the process conditions.

Silica gel silanized with (3-mercaptopropyl)trimethoxysilane in toluene first heated under reflux (S1), and then at room temperature (S3), and oxidized with H_2O_2 and methanesulfonic acid was used in the benzoic acid esterification reaction with methyl alcohol [24]. The activation energies determined for catalysts S1 and S3 were 65.9±0.7 and 44.9±0.6 $kJ \cdot mol^{-1}$, and the preexponential factors were $(17.58 \pm 0.19) \cdot 10^8$ and $(6.00 \pm 0.10) \cdot 10^5$ h^{-1}, respectively. The authors emphasize that the determined activation energies correlate well with the corresponding activation energies for other heterogeneous catalysts of benzoic acid esterification with ethyl alcohol such as SO_4^{2-}/Ti_3AlC_2 (42.65 $kJ \cdot mol^{-1}$) [25], Amberlyst-15 (69.1 $kJ\ mol^{-1}$) [20], and Amberlyst-39 [26]. At the same time, the ceramic catalyst SO_4^{2-}/Ti_3AlC_2 provides an acid conversion of 80.4 % and selectivity of ester over 99 % in the benzoic acid esterification reaction with ethyl alcohol at a temperature of 120 °C in 34 h [25]. The authors also point to the first reaction order with respect to benzoic acid.

It is obvious that today the improving the process of benzoic acid esters obtaining remains relevant, and kinetic studies of the esterification reaction are the basis for optimizing the technological parameters of this process.

Accordingly, the purpose of this study is to determine the kinetic characteristics of the esterification reaction benzoic acid with 1-butyl alcohol (BA) catalysed by p-toluenesulfonic acid, as well as to create a mathematical model and to establish an optimal condition of the butyl benzoate obtaining process.

Materials and methods

Benzoic acid (reagent grade, ≥99,5 %, Merck), and 1-butyl alcohol (reagent grade, ≥99,5 %, Panreac Química SLU, Spain) were used in the studies. p-Toluenesulfonic acid (monohydrate, reagent grade, ≥98 %, Merck) was used as the catalyst. The 1-butyl alcohol for kinetic studies was further purified by distillation for kinetic research. Benzoic acid and p-toluenesulfonic acid were purified by recrystallization from a hot aqueous solution. p-Toluenesulfonic acid was isolated from an aqueous solution by adding hydrochloric acid.

Kinetic studies were performed in stationary conditions in a glass flask equipped with a thermometer and reflux. A silicone oil bath was used to heat the reaction mixture. The temperature fluctuations in the reactor did not exceed ±0.2 K. The reaction medium was stirred using a magnetic glass stirrer with a speed of 400 rpm^{-1}. Benzoic acid and 1-butyl alcohol were charged to the flask, heated to the reaction temperature, and a catalyst was added. At certain time intervals samples of the reaction mixture were taken to determine the acid number.

The benzoic acid esterification process with 1-butyl alcohol was investigated in nonstationary conditions in the glass flask equipped with a Dean-Stark trap and reflux, and placed in a bath with silicone oil. The reaction temperature was measured using a thermometer placed in the flask. The reaction medium was stirred both by using a magnetic glass stirrer and by boiling the mixture in the reactor.

The reaction product's acid number was determined according to the procedure described in [29].

Since the kinetic regularities of benzoic acid esterification reaction were studied under significant 1-butyl alcohol excess, the rate of this reaction is described by the kinetic equation of the first order with respect to acid and zero with respect to alcohol:

$$\frac{dC_{BAc}}{d\tau} = -k_{ef} C_{BAc}, \qquad (1)$$

where $k_{ef} = kC_{pTSA}C_{BA}$ is an effective constant of reaction rate, s^{-1};
k is the effective constant of esterification reaction rate without taking into account the catalyst and 1-butyl alcohol concentrations, l^2·mol^{-2}·s^{-1};
C_{pTSA} is the catalyst concentration, mol·l^{-1};
C_{BA} is 1-butyl alcohol concentration, mol·l^{-1}.

The values of the reaction rate effective constant were calculated using linearizing the kinetic curves of benzoic acid consumption in the lnC_{BAc} - time coordinates.

The esterification process of benzoic acid with 1-butyl alcohol is based on the equilibrium reaction

$$C_6H_5COOH + C_4H_9OH \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} C_6H_5COOC_4H_9 + H_2O$$

The equilibrium constant of this reaction is expressed by the equation:

$$K = \frac{k_1}{k_{-1}}, \qquad (2)$$

where k_1 is the forward reaction rate constant, л^2·моль$^{-2}$·с$^{-1}$ l^2·mol^{-2}·s^{-1};
k_{-1} is the reverse reaction rate constant, л^2·моль$^{-2}$·с$^{-1}$ l^2·mol^{-2}·s^{-1}.

The kinetic equations for the reagents consumption and products formations are as follows:

– benzoic acid and 1-butyl alcohol:

$$\frac{dC_{BAc}}{d\tau} = \frac{dC_{BA}}{d\tau} = -k_1 C_{pTSA} C_{BAc} C_{BA} + k_{-1} C_{pTSA} C_{BB} C_{H_2O}; \qquad (3)$$

– butyl benzoate and water:

$$\frac{dC_{BB}}{d\tau} = \frac{dC_{H_2O}}{d\tau} = k_1 C_{pTSA} C_{BAc} C_{BA} - k_{-1} C_{pTSA} C_{BB} C_{H_2O}. \qquad (4)$$

The reagents and product concentrations can be expressed through the benzoic acid conversion degree X_{BAc}:

$$C_{BAc} = C_{BAc,0}(1 - X_{BAc}), \qquad (5)$$

$$C_{BA} = C_{BAc,0}(\beta - X_{BAc}), \qquad (6)$$

where $\beta = \frac{C_{BA,0}}{C_{BAc,0}}$ is an alcohol excess ratio

$$C_{BB} = C_{H_2O} = C_{BAc,0} X_{BAc} \qquad (7)$$

Then the kinetic equation of benzoic acid consumption is:

$$\frac{d\left(C_{BAc,0}(1 - X_{BAc})\right)}{d\tau} = -k_1 C_{pTSA} C_{BAc,0}(1 - X_{BAc}) C_{BAc,0}(\beta - X_{BAc}) + k_{-1} C_{pTSA} C_{BAc,0}^2 X_{BAc}^2 \qquad (8)$$

and finally

$$\frac{dX_{BAc}}{k_1(1 - X_{BAc})(\beta - X_{BAc}) - k_{-1} X_{BAc}^2} = C_{BAc,0} C_{pTSA} d\tau. \qquad (9)$$

This equation solution when changing of benzoic acid conversion degree from 0 to X_{Bac} and time from 0 to τ is:

$$\ln\left|\frac{2(k_1 - k_{-1})X_{BAc} - k_1(\beta + 1) - \sqrt{k_1^2(\beta + 1)^2 - 4(k_1 - k_{-1})k_1\beta}}{2(k_1 - k_{-1})X_{BAc} - k_1(\beta + 1) + \sqrt{k_1^2(\beta + 1)^2 - 4(k_1 - k_{-1})k_1\beta}}\right| - \\ - \ln\left|\frac{-k_1(\beta + 1) - \sqrt{k_1^2(\beta + 1)^2 - 4(k_1 - k_{-1})k_1\beta}}{-k_1(\beta + 1) + \sqrt{k_1^2(\beta + 1)^2 - 4(k_1 - k_{-1})k_1\beta}}\right| = \sqrt{k_1^2(\beta + 1)^2 - 4(k_1 - k_{-1})k_1\beta}\, C_{BAc,0} C_{pTSA} \tau \qquad (10)$$

To determine the value of k_1 we written the equation

$$k = k_1 - \Delta k. \qquad (11)$$

Respectively

$$k_1 = k + \Delta k. \qquad (12)$$

Taking into account the equilibrium constant of the esterification reaction (2):

$$k_{-1} = \frac{k + \Delta k}{K} \qquad (13)$$

After substituting equations (11) and (12) into equation (10):

$$\ln\left|\frac{2\left(k+\Delta k-\dfrac{k+\Delta k}{K}\right)X_{BAc}-(k+\Delta k)(\beta+1)-\sqrt{(k+\Delta k)^2(\beta+1)^2-4\left(k+\Delta k-\dfrac{k+\Delta k}{K}\right)(k+\Delta k)\beta}}{2\left(k+\Delta k-\dfrac{k+\Delta k}{K}\right)X_{BAc}-(k+\Delta k)(\beta+1)+\sqrt{(k+\Delta k)^2(\beta+1)^2-4\left(k+\Delta k-\dfrac{k+\Delta k}{K}\right)(k+\Delta k)\beta}}\right|-$$

$$-\ln\left|\frac{-(k+\Delta k)(\beta+1)-\sqrt{(k+\Delta k)^2(\beta+1)^2-4\left(k+\Delta k-\dfrac{k+\Delta k}{K}\right)(k+\Delta k)\beta}}{-(k+\Delta k)(\beta+1)+\sqrt{(k+\Delta k)^2(\beta+1)^2-4\left(k+\Delta k-\dfrac{k+\Delta k}{K}\right)(k+\Delta k)\beta}}\right|=$$

$$=\sqrt{(k+\Delta k)^2(\beta+1)^2-4\left(k+\Delta k-\dfrac{k+\Delta k}{K}\right)(k+\Delta k)\beta}\,C_{BAc,0}C_{pTSA}\tau \qquad (14)$$

and after the series of transformations is completed we got:

$$\frac{\ln\left|\dfrac{2\left(1-\dfrac{1}{K}\right)X_{BAc}-(\beta+1)-\sqrt{(\beta-1)^2+\dfrac{4\beta}{K}}}{2\left(1-\dfrac{1}{K}\right)X_{BAc}-(\beta+1)+\sqrt{(\beta-1)^2+\dfrac{4\beta}{K}}}\right|-\ln\left|\dfrac{-(\beta+1)-\sqrt{(\beta-1)^2+\dfrac{4\beta}{K}}}{-(\beta+1)+\sqrt{(\beta-1)^2+\dfrac{4\beta}{K}}}\right|}{C_{BAc,0}C_{pTSA}\tau\sqrt{(\beta-1)^2+\dfrac{4\beta}{K}}}-k=\Delta k\,. \qquad (15)$$

From equation (15) we calculated the values of Δk and K. When the value of K changes from 2 to 30, the value of Δk will change minimally, in particular at a temperature of 389.4 K it is $(3.8438–3.6120)\cdot10^5$ $l^2\cdot mol^{-2}\cdot s^{-1}$, at 381.0 K it is $(3.4129–3.3610)\cdot10^5$ $l^2\cdot mol^{-2}\cdot s^{-1}$and at 365.2 K it is $(2.8284–2.8232)\cdot10^5$ $l^2\cdot mol^{-2}\cdot s^{-1}$, respectively.

The value of K and then the value of Δk were calculated from equation (15). In particular the value of K is valid when Δk is equal to zero. The calculated value of K is the equilibrium constant of the benzoic acid esterification reaction with 1-butyl alcohol.

The determined value of Δk was used to calculate the value of the forward reaction rate constant k_1. Using the value of k_1 and the equilibrium constant K, the reverse reaction rate constant k_{-1} was calculated.

Results and discussion

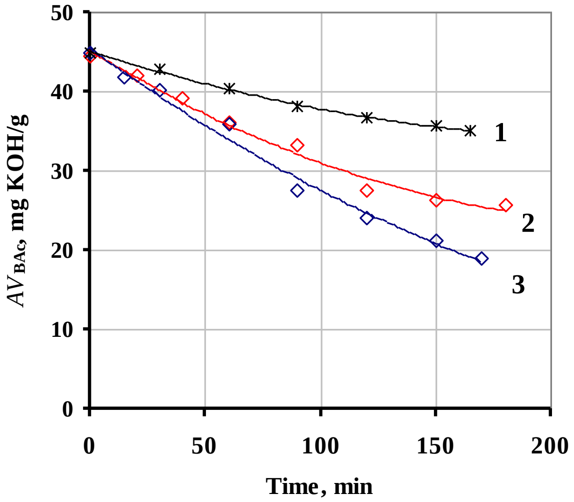
The kinetic regularities of benzoic acid esterification with 1-butyl alcohol catalysed by p-toluenesulfonic acid were investigated in the temperature range from 365.2 to 389.4 K in batch reaction. The catalyst concentration was $1.8\cdot10^{-2}$ $mol\cdot l^{-1}$. Because benzoic acid is limitedly soluble in 1-butyl alcohol, a significant excess of alcohol was used in the kinetic studies. In particular, the molar ratio of BA : BAc was (15.6-15.7) : 1.

A significant excess of alcohol makes it possible to consider the reaction as almost nonequilibrium.

Fig. 1 shows the change of the reaction mixture acid number over time, and Fig. 2 shows kinetic curves of benzoic acid consumption. Obviously, the reaction intensity increases with temperature.

Fig. 3 shows the logarithmic dependence of benzoic acid concentration on time at different reaction temperature. The linear character of the curves points on the reaction first order with respect to benzoic acid. These results were used to calculate the reaction rate effective constants k at the corresponding temperature (Table 1).

The calculated high values of the equilibrium constant of benzoic acid esterification reaction with 1-butyl alcohol correlate well with the results obtained using a phosphotungstic acid as a catalyst. In particular, the benzoic acid yield in the batch reaction catalysed by phosphotungstic acid at 1.5-fold alcohol excess was very high, and it was 88 % at a temperature of 110 °C, and 91 % at a temperature of 120 °C [27].



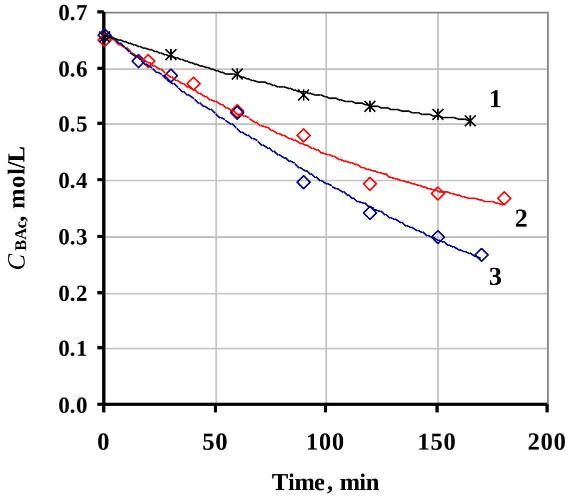
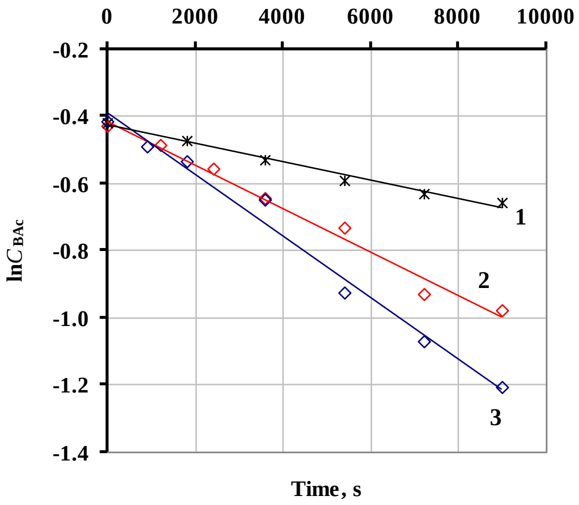


Fig. 1. Dependence of the reaction mixture acid number on time at different reaction temperatures (K): 1 – 365.2; 2 – 381.0; 3 – 389.4

Fig. 2. Dependence of benzoic acid concentration on time at different reaction temperatures (K): 1 – 365.2; 2 – 381.0; 3 – 389.4

According to the determined rate constants of the forward and reverse reactions, the benzoic acid conversion degree was calculated, and the curves of it depending on time at the studied reaction temperatures were plotted. They are in good agreement with the obtained experimental results (Fig. 4).



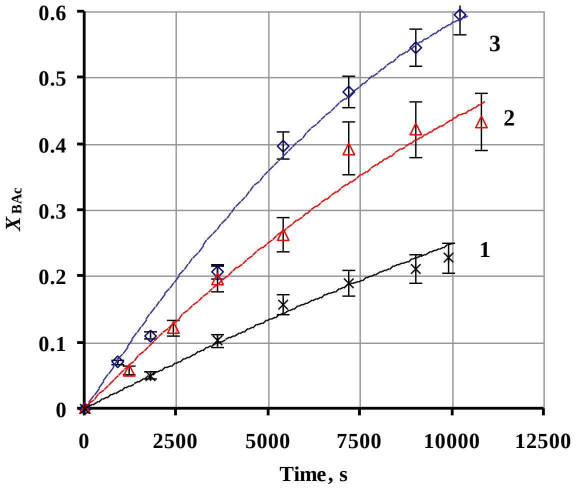


Fig. 3. Logarithmic dependence of benzoic acid concentration on time at different reaction temperatures (K): 1 – 365.2; 2 – 381.0; 3 – 389.4

Fig. 4. Dependence of benzoic acid conversion degree on time at different temperatures (K) of benzoic acid esterification reaction with 1-butyl alcohol: 1 – 365.2; 2 – 381.0; 3 – 389.4. Points are experimental results. Lines are plotted using calculated constants. Error levels are 10%

Fig. 5 shows the dependence of $\ln k_i$ on the reaction temperature. According to this dependence, the effective activation energies and activation energy of forward and reverse esterification reactions, as well as preexponential factors of the Arrhenius equation, were calculated (Table 2).

Table 1

The effective rate constant (*k*), the rate constants of forward (k_1) and reverse (k_{-1}) reaction, and the equilibrium constant (*K*) of benzoic acid esterification reaction with 1-butyl alcohol at different temperatures

Temperature, K	The constant of reaction rate, $l^2 \cdot mol^{-2} \cdot s^{-1}$			The equilibrium constant *K*
	$k \cdot 10^4$	$k_1 \cdot 10^4$	$k_{-1} \cdot 10^5$	
389.4	4.57	4.93	3.24	15.2
381.0	2.92	3.26	2.16	15.1
365.2	1.20	1.48	0.99	15.0

Table 2

Activation energies and preexponential factors of benzoic acid esterification reaction with 1-butyl alcohol catalysed by p-toluenesulfonic acid

Indicator	effective	forward reaction	reverse reaction
E_A, J·mol^{-1}	65090	58400	57770
$k_{0,i}$, l^2·mol^{-2}·s^{-1}	2.5·10^5	3.4·10^4	1.8·10^3

The changes in the standard enthalpy and standard entropy of benzoic acid esterification reaction with 1-butyl alcohol, which are 622 J·mol^{-1} and 24.2 J·mol^{-1}·K^{-1}, respectively, were calculated from the dependence of the determined equilibrium constant on temperature (Fig. 6). The calculated thermal effect and the reaction entropy change correlate with the data obtained by the study of the reaction between benzoic acid and isoamyl alcohol [28].

It is known that the equilibrium constant dependence on temperature describes the equation:

$$\ln K = -\frac{\Delta G_T^o}{RT} = -\frac{\Delta H_T^o}{RT} + \frac{\Delta S_T^o}{R}$$

To model the benzoic acid esterification process with 1-butyl alcohol, we assumed that the process occurs in several stages:

i – the reagents heating from a temperature of 293 K to the reaction mixture boiling point: at low water content in the reaction mixture the beginning of boiling corresponds to the 1-butyl alcohol evaporation temperature, and at high water content the boiling temperature is higher than the azeotrope evaporation temperature of water and 1-butyl alcohol, and it is below the boiling temperature of 1-butyl alcohol;

ii – the water and 1-butyl alcohol evaporation, subsequent condensation, and separation of the aqueous and organic layers until the water separator is completely filled;

iii – the returning of butyl alcohol to the reactor after filling the water separator in the amount corresponding to the volume of distilled water. The third stage lasts until the esterification process is complete.

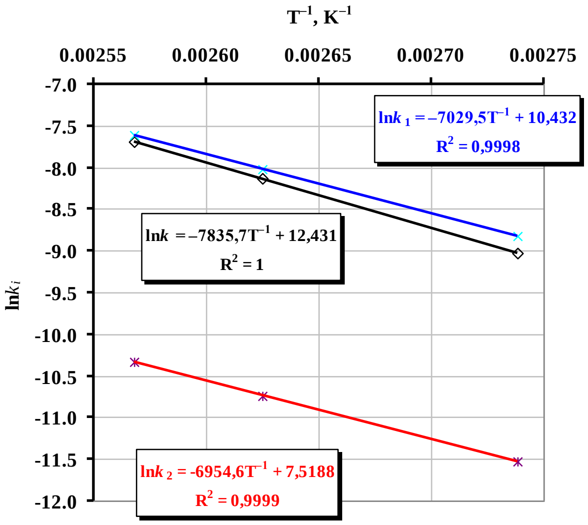


Fig. 5. Arrhenius plot of benzoic acid esterification reaction with 1-butyl alcohol catalysed by p-toluenesulfonic acid

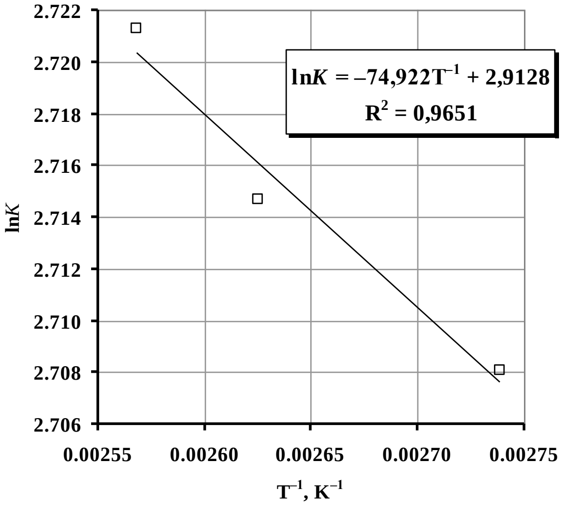


Fig. 6. Dependence of the equilibrium constant of benzoic acid esterification reaction with 1-butyl alcohol catalysed by p-toluenesulfonic acid on the reaction temperature

The first stage of butyl benzoate obtaining is described by a kinetic equation (15) using a determined effective constant of reaction rate:

$$\frac{dX_{BAc}}{d\tau} = kC_{pTSA}C_{BAc,0}\left(1 - X_{BAc}\right)\left(\beta - X_{BAc}\right), \qquad (15)$$

where $k = 2.5\cdot10^5\exp\left(65090/RT\right)$, l^2·mol^{-2}·s^{-1}.

By sufficiently and intensive removal of water the conversion degree change of benzoic acid at the second stage is described by an equation (16) containing the forward reaction rate constant:

$$\frac{dX_{BAc}}{d\tau} = k_1 C_{pTSA} C_{BAc,0} (1 - X_{BAc})(\beta - X_{BAc}), \qquad (16)$$

where $k_1 = 3.4 \cdot 10^4 \exp(58400/RT)$, $\text{l}^2\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$.

The mathematical model describing the second stage of the esterification process should additionally contain the equation of alcohol and water concentration change:

$$\frac{dC_{BA}}{d\tau} = -k_1 C_{pTSA} C_{BAc} C_{BA} - W_{BA} C'_{BA}, \qquad (17)$$

where W_{BA} is the volumetric flow rate of alcohol evaporating from the reactor, $\text{l}\cdot\text{s}^{-1}$;

C'_{BA} is 1-butyl alcohol concentration in the flow evaporating from the reactor, $\text{mol}\cdot\text{l}^{1}$;

$$\frac{dC_{H_2O}}{d\tau} = k_1 C_{pTSA} C_{BAc} C_{BA} - W_{H_2O} C'_{H_2O}, \qquad (18)$$

where W_{H_2O} is the volumetric flow rate of water evaporating from the reactor, $\text{l}\cdot\text{s}^{-1}$;

C'_{H_2O} is water concentration in the flow evaporating from the reactor, $\text{mol}\cdot\text{l}^{-1}$.

Equation (16) also describes the change of benzoic acid conversion degree over time at the second stage of the esterification process.

The mathematical model describing the third stage of the process esterification should additionally contain the equation of alcohol and water concentration change (19): the distilled water displaces the equivalent volume of alcohol into the reactor, taking into account the molecular weights of water (18) and alcohol (74):

$$\frac{dX_{BA}}{d\tau} = k_1 C_{pTSA} C_{BAc,0} (1 - X_{BAc})(\beta - X_{BAc}) + \frac{W_{H_2O} C'_{H_2O} \cdot 18}{74}. \qquad (19)$$

Equation (18) also describes the change of water concentration over time at the third stage of the esterification process.

To determine the regularity of reaction temperature changes over time the experiments with different excess alcohol, in particular, at a ratio of BA : BAc - 1.2 : 1 and 3.0 : 1 were performed. The concentration of p-toluenesulfonic acid as catalyst was $2\cdot10^{-2}$ $\text{mol}\cdot\text{l}^{-1}$.

It is established that the reaction temperature depends on the initial alcohol content in the reaction mixture: the lower it is the higher is the final reaction temperature, which asymptomatically approaches the heater temperature with increasing benzoic acid conversion. The volumetric flow rate of water and 1-butyl alcohol, which accumulates in the water separator, was also calculated using these experiments. We also assumed that the alcohol and water molar concentration in the flow evaporating from the reactor corresponded to the molar concentration of pure substances C'_{BA} = 10.9 $\text{mol}\cdot\text{l}^{-1}$ and C'_{H_2O} = 55.6 $\text{mol}\cdot\text{l}^{-1}$, respectively.

The obtained results were used to optimize the esterification process of benzoic acid with 1-butyl alcohol in nonstationary conditions. Fig. 7 shows the dependence of the reaction mixture acid number on time at the estimated optimal ratio of BA : BAc - 2.9 : 1 (mol.) and the catalyst concentration $5.2\cdot10^{-2}$ $\text{mol}\cdot\text{l}^{-1}$. Using these data the benzoic acid conversion degree was calculated (Fig. 8). Also, using the mathematical model of the esterification process, the graphical dependence of the benzoic acid conversion degree on time under the reaction conditions was plotted (Fig. 8). It is obvious (Fig. 8) that the determined preexponential factors and activation energies as well as the proposed esterification process model adequately describe the process of butyl benzoate obtaining.

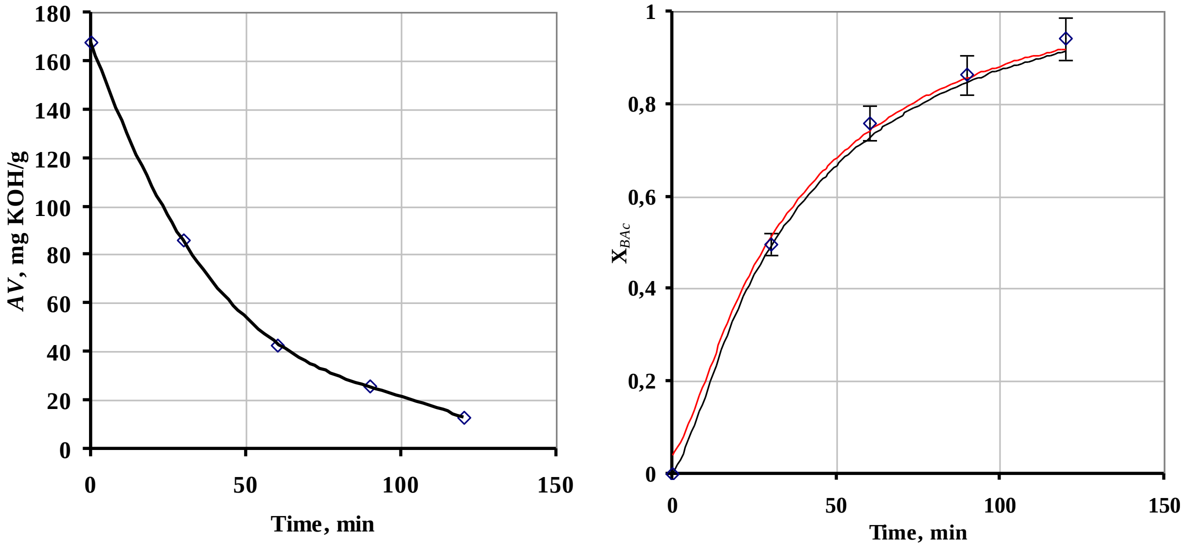


Fig. 7. Dependence of the reaction mixture acid number on time. The ratio of BA : BAc is 2.9 : 1 (mol.). The p-toluenesulfonic acid concentration is $5.2\cdot10^{-2}$ mol·l^{-1}

Fig. 8. Dependence of the calculated (black dots are without taking into account the first stage of the process; red dots are taking into account the first stage of the process X_{BA} = 4 %) and the experimentally determined (dots) BAc conversion degree on time. Error levels are 5%. The ratio of BA : BAc is 2.9: 1 (mol.). The pTSC concentration is $5.2\cdot10^{-2}$ mol·l^{-1}

Using the mathematical model of the butyl benzoate obtaining process the dependence of reagent concentrations on time was determined (Fig. 9). It is obvious that under the process conditions of butyl benzoate obtaining a part of the water remains in the reactor. These data correlate well with experimental results, according to which the aqueous layer volume per 120 min consists 33 % of the water volume that should have been formed during the reaction.

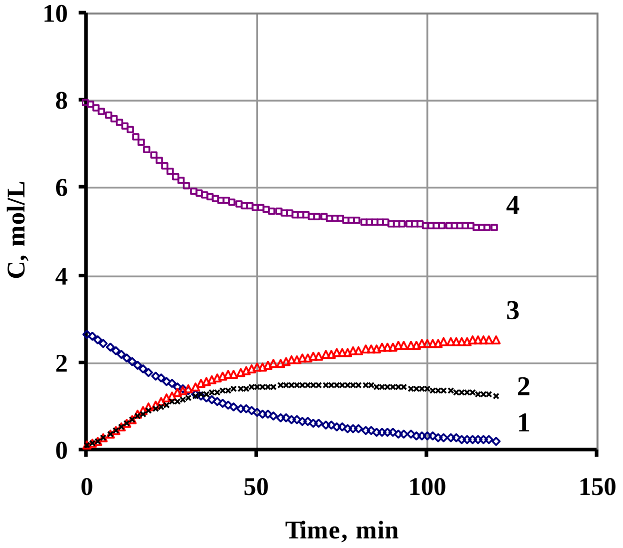


Fig. 9. Dependence of reagents concentration on time in the butyl benzoate obtaining process. The ratio of BA : BAc is 2.9: 1 (mol.). The pTSC concentration is $5.2\cdot10^{-2}$ mol·l^{-1}

Since in the esterification process a part of the water remains in the reaction mixture, it is more correct to create a mathematical model of the second and the third stages of the process using preexponential factor and activation energy calculated for effective rate constant *k*. At the same time, the recalculation of the benzoic acid conversion degree according to this assumption does not show a significant difference between the calculated curves.

Conclusions

The kinetic regularities of benzoic acid esterification reaction with 1-butyl alcohol at different temperatures were investigated and the effective rate constant and rate constants of the forward and reverse reactions were determined. The calculated preexponential factors and activation energies of the reactions are $2.5 \cdot 10^5$, $3.4 \cdot 10^4$, and $1.8 \cdot 10^3$ $l^2 \cdot mol^{-2} \cdot s^{-1}$ and 65.09, 58.40, and 57.77 $kJ \cdot mol^{-1}$, respectively.

It was shown that the equilibrium constant of benzoic acid esterification reaction with 1-butyl alcohol varies from 15.0 to 15.2 at a temperature range from 365.2 to 389.4 K. These results correspond to the change of the reaction enthalpy and entropy of 622 $J \cdot mol^{-1}$ and 24.2 $J \cdot mol^{-1} \cdot K^{-1}$ respectively.

The proposed mathematical model of nonstationary process of butyl benzoate obtaining adequately describes the reaction course using determined kinetic parameters.

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