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KINETICS OF DIRECT AMIDATION OF STEARIC ACID WITH ETHANOLAMINES: EXPERIMENTAL STUDIES AND MATHEMATICAL MODELING

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Abstract

This paper presents the results of the study of kinetics of stearic acid direct amidation with mono- and diethanolamines in a closed thermodynamic system. The rate constants of stearic acid ethanolamides synthesis at different temperatures and the activation energy values of these reactions were determined experimentally. It has been demonstrated that the reaction of stearic acid amidation with ethanolamine in a closed system is run until the equilibrium acid–amide, which is shifted towards the reaction products, and the equilibrium constants of this reaction have been determined. Also, it has been shown that the reaction of stearic acid with diethanolamine has a more complicated kinetic behavior than that with monoethanolamine, and it does not end at the stage of diethanolamide formation as far as a number of side reactions take place. A mathematical model for the process of stearic acid amidation, which takes into consideration contributions both of the main reaction and of the number of side-reactions, has been developed. The model adequacy is supported with high correlation between predicted values and experimental ones. Using this model the reaction rate constants and their activation energy values have been calculated

Keywords

Direct amidation, kinetic study, ethanolamides, alcanolamides, stearic acid

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Introduction. Fatty acid ethanolamides (alkanolamides) are a highly important and industrially significant class of nitrogen-containing nonionic surfactants. Such products are widely used as detergent components, foam softeners and stabilizers in makeup preparations, as wetting and antistatic agents in textile industry, as dispersants and corrosion inhibitors etc. [1–4]. Low HLB values (about 2 or 3 units) for ethanolamides make possible their application as efficient stabilizers for inverted emulsions used in oil and gas wells drilling [5–8], in oil recovery methods [9, 10], in manufacture of emulsion explosives [11], cutting lubricants etc. Besides, fatty acid ethanolamides are a key stock material for production of other classes of surfactants, e.g. oxyethylated ethanolamides (*Amadol* and *Ethomid*, *Akzo Nobel*; *Lutensol FSA*, *BASF* etc.) [2, 3]; sulfoesters [12], also used in different economy branches.

Main industrially significant methods of ethanolamides synthesis are: fatty acid esters (including triglycerides) ammonolysis with ethanolamines [1, 2, 13–17] and fatty acids direct amidation with ethanolamines [1, 2, 4, 16, 18, 19]. The former method at the present time is more widely used. This could be explained by the fact that the reaction conditions for ammonolysis are soft, the instrumentation is quite simple, and the starting material is easily accessible. As far as the reaction is practically irreversible, the most complete conversion and the highest product yields could be achieved. This method has an incontestable advantage in case the target products are vegetable oil ethanolamides, which are used as components of detergents or makeup.

Fatty acids direct amidation requires hard conditions, the presence of a catalyst, and some special techniques to remove by-produced water (vacuuming, purging with inert gases etc.). Despite this, the method is highly significant for industrial production as far as it allows using such easily available stock material like fatty acids of tall oil or synthetic fatty acids.

One more method, acylation of ethanolamines with halogen substituted anhydrides of the fatty acids [20], is of limited application due to high expensiveness of the starting halogen substituted anhydrides.

For historical reasons, the researchers’ most acute attention was paid at esterification of carboxylic acids with alcohols. Nowadays this group of reactions is most completely studied in kinetic aspect, including their mechanisms, the influence of each component’s nature on their reactivity, the effect of catalyst on the rate of reaction; the kinetic parameters for a wide range of acids and alcohols have been determined experimentally. On the other hand, the data on amidation kinetics are relatively poor. If we consider the direct synthesis of ethanolamides, those few papers in that field e.g., [21, 22], were devoted to the study of amidation in partially open systems, when water was being permanently removed from the reaction system. Those studies were, as a rule, of exceptionally applied character, and the kinetic relationships obtained could not be regarded as unequivocally candid, because they did not take into consideration the rate of water removal and a number of some other factors. Meanwhile, the direct amidation of carboxylic acids involves rather important reaction group widely used in chemical processes [23]. Thus, gaining new knowledge on mechanism, kinetics, and thermodynamics of amidation reaction will create a theoretical foundation necessary for development and improvement of synthesis technology of this class of compounds.

It is believed that formation of amides from carboxylic acids as well as formation of esters is a reaction of nucleophilic substitution at a trigonal carbon atom, so called “tetrahedral mechanism” [24, 25]. Such reactions, as a rule, are described with a second order kinetic equation, in which the concentration of acid and that of amine are the first power.

The principal task of this work was the study of fatty acids direct amidation kinetics, the reaction of stearic acid with mono- and diethanolamine in a closed thermodynamic system being chosen as an object of study. To solve the problem, it was necessary to experimentally determine the kinetic parameters of the process and create a mathematical model of the reaction of stearic acid with diethanolamine, taking into account the contribution of the reverse reaction and some side reactions. The rate of change in stearic acid concentration was chosen as the main criterion for studying the kinetics of amidation. Recording changes in amine concentration over time is a laborious task due to the presence of a large number of products containing a free amino group in the reaction mixture.

Stearic acid as the most widely spread saturated fatty acid was used as a model substrate. A number of assumptions had been accepted in this work: 1) the reaction system is considered as homogenous; 2) the process is regarded as isochoric and isothermal; 3) other physical parameters of the system do not change during the reaction. The process of amidation was run without solvent, catalyst, or any other auxiliary reagent. The reaction systems contained the acid and the amine in equimolar quantities.

Experimental. *Chemicals and reagents.* Stearic acid (**SA**) of reagent grade was used, without a preliminary purification. Monoethanolamine (**MEA**) and diethanolamine (**DEA**) of technical grade having 99.3 and 99.2 per cent purity respectively, had been purchased from “OKA Synthesis Co. Ltd.”, preliminarily dried using an azeothropic distillation: the mixture of the amine and benzene was boiled in a flask supplied with a Dean-Stark trap. After a water condensate had been removed, the benzene residue was removed using a vacuum rotary evaporator.

Kinetic study. The mixture of **SA** and ethanolamine in molar ratio 1 : 1 (± 0.1 per cent) was prepared. The mixture was vigorously stirred at 80 to 90 °C till a complete homogeneity. The experimental part of the kinetic study was run in 10 ml stainless steel ampoules supplied with screw caps. Per 8 to 9 g of a preliminarily prepared reaction mixture was loaded in ampoules and hermetically sealed. Then the ampoules were placed in a preliminarily heated thermostated oil bath. The temperature accuracy was ± 1 °C. Through the scheduled periods of time a pair of ampoules were taken out of the bath and rapidly cooled in cold water, the reaction mass then was analyzed.

Stearic acid content in samples was determined by titration with an alcoholic potassium hydroxide solution in presence of phenolphthalein as an indicator. A reaction mixture weighing 0.5 to 1 g (0.0001 g accuracy) was dissolved in alcohol at 50 to 60 °C while stirring, and 2 or 3 drops of a 1 per cent phenolphthalein solution where added. The solution obtained was then titrated with an alcoholic potassium hydroxide solution until a slightly pink color was stable for 30 s. The concentration of **SA** was calculated according to the formula below

$$c(\mathbf{SA}) = \frac{c(\mathrm{KOH})V(\mathrm{KOH})\gamma}{1000\,m}, \qquad (1)$$

where c(KOH) is the concentration of KOH solution, mol/L; V(KOH) — the volume of KOH solution spent, cm^3; γ — reaction, g/dm^3, for the system **SA–MEA** $\gamma = 877$ g/L, for **SA–DEA** $\gamma = 860$ g/L; m — weighing, g. An average value of not less than three parallel measurements with difference between them no more than 2 per cent was taken as a result.

Mathematical modeling was performed using a software package *Maple 18*™ (Waterloo Maple Inc.).

Results and discussion. *Reaction of stearic acid with monoethanolamine.* The process of monoethanolamide formation starting with **SA** and **MEA** could be presented as a complex set of chemical reactions (Fig. 1).

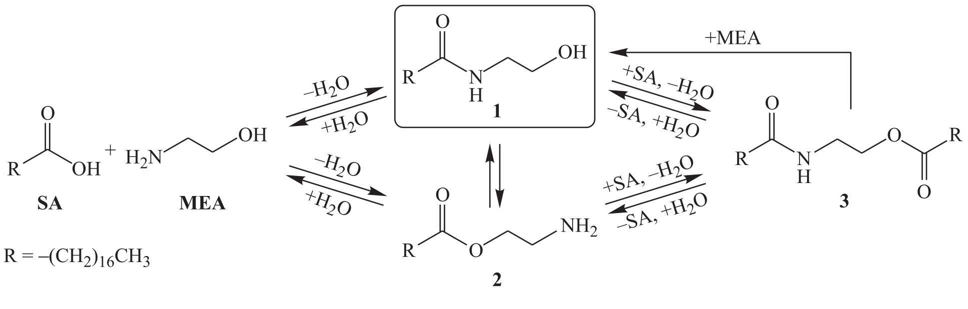


Fig. 1. Monoethanolamide synthesis starting with **SA** and **MEA**

Monoethanolamine, being a binucleophilic reagent containing both an amino and a hydroxy functional group, when reacting with carboxylic acids, can form two kinds of products: amides **1** and esters **2**, depending on what nucleophilic group of **MEA** is reacting. Taking into account the fact that the nucleophilicity of amino group is much stronger than that of hydroxy group, the reaction producing amide **1** predominates [4]. On the other hand, we should not exclude an alternative way that leads to monoethanolamide **1** through its ester **2** by the ammonolysis of the latter with **MEA**.

Stoichiometrically, this reaction is a rearrangement of ester **2** to amide **1**, as far as the **MEA** balance is equal to zero in the end. The equilibrium of this reaction is strongly shifted towards amide **1** formation. Moreover, there is some probability of a diacylated product formation (amidoester **3**), the quantity of the latter amongst the reaction products being changing simbatly with the change of the molar ratio **SA** : **MEA**. In the equimolar mixture of reagents the formation of product **3** unavoidably leads to a redundant accumulation of **MEA**, the increase of its concentration being promoting amidoester **3** ammonolysis giving amide **1**. As far as all the experiments in this work were performed using equimolar reagent mixtures, that reaction may be ignored.

Thus, regardless of what reaction predominates, monoethanolamide **1** to be the basic product, as confirmed experimentally.

When studying amidation kinetics, we supposed that the change of **SA** concentration during the reaction to be the basic criterion. Based on that data the main parameters of the process were being determined. So, dealing with amidation kinetic parameters, such as a rate constant or an activation energy value, we assume those values are “effective”, i.e., they include contributions of all presumptive reactions resulting in the final product formation.

The kinetic curves obtained for the reaction of **SA** with **MEA** at different temperature are given in Fig. 2; t (s), reaction time is in x-direction, stearic acid concentration (**SA**) is in y-direction (mol/dm^3). According to the data obtained, the reaction can be described with a typical kinetic curve of a reversible reaction; this is confirmed by the fact that **SA** concentration after it had reached a definite value stops changing. This observation, in principle, does not contradict the existing knowledge about the mechanism of such reactions [24].

The chart shown in Fig. 2 demonstrates that the equilibrium can be reached in 120 to 150 min at 200 °C, in 400 to 480 min at 170 °C, and it can not be reached at all at lower temperatures.

The data obtained for the temperature ranges mentioned makes possible the equilibrium concentration of **SA**, corresponding to the average value of the

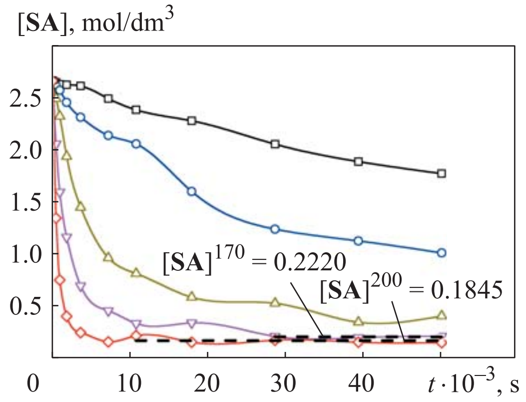


Fig. 2. Kinetic curves of **SA** with **MEA** reaction at temperatures 110 (□), 130 (○), 150 (△), 170 (▽), and 200 °C (◇)

last five points at 200 °C and of the last three points at 170 °C to be determined: $[\overline{\mathbf{SA}}]^{200}$ and $[\overline{\mathbf{SA}}]^{170}$ (see Fig. 2).

When the equilibrium concentration of stearic acid $[\overline{\mathbf{SA}}]$ and the initial one $c_0(\mathbf{SA})$ are known, the equilibrium constants at the corresponding temperatures were calculated according to the formula below:

$$K_c = \frac{\left(c_0(\mathbf{SA}) - [\overline{\mathbf{SA}}]\right)^2}{[\overline{\mathbf{SA}}]^2}. \qquad (2)$$

Also, a maximum conversion degree of **SA**, X(**SA**) was found, as a ratio of the reacted acid quantity to its initial amount.

The reaction order and rate constants were determined graphically. Taking into account that amide **1** formation is a reversible reaction and its equilibrium is shifted towards reaction products, as confirmed with high K_c values, to correctly find kinetic parameters of the forward reaction, the starting sections of kinetic curves, i.e., those time points were used, when the starting components concentrations are high and, therefore, the forward reaction rate is maximal. The reverse reaction at those time periods can be neglected.

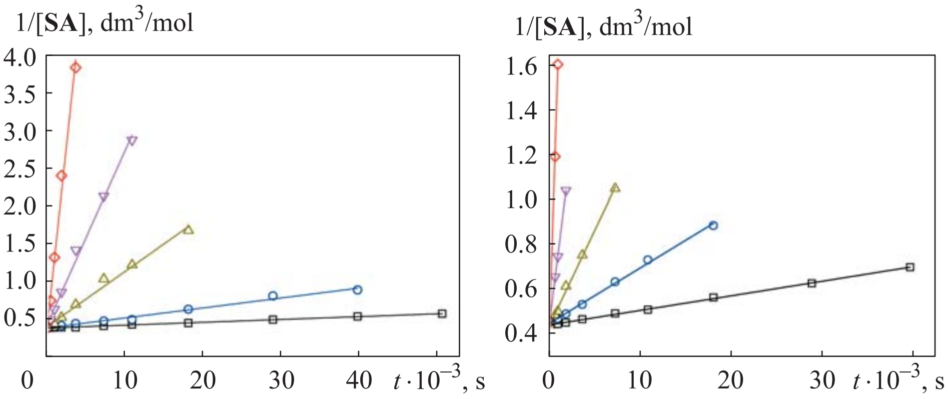
We have found that a linear regression occurred in a coordinate system 1/[**SA**] – t (Fig. 3) that unequivocally indicates the reaction possess a second order with respect to **SA**. Because the experiments were run using equimolar mixtures of **SA** and **MEA**, it can be supposed that the kinetic equation for the forward reaction will be as follows:

$$-\frac{d[\mathbf{SA}]}{dt} = k_1[\mathbf{SA}]^2 = k_1[\mathbf{SA}][\text{amine}]. \qquad (3)$$

Using a second order kinetic equation, which should be written in this case as follows:

$$\frac{1}{[\mathbf{SA}]} = k_1 t + \frac{1}{c_0(\mathbf{SA})}, \tag{4}$$

the rate constants k_1 for the forward reaction were determined as slope coefficients of the approximate lines.



a *b*

Fig. 3. Graphical determination of the rate constants k_1 for monoethanolamide **1** synthesis reaction at temperatures 110 (□), 130 (○), 150 (△), 170 (▽), and 200 °C (◇)

Then the activation energy value E_a for the forward reaction was calculated. To do this, a $\ln k_1 – 1/T$ chart was plotted. The values obtained can be described with a linear function, which is an integrated Arrhenius equation:

$$\ln k_1 = -\frac{E_a}{R}\frac{1}{T} + B, \tag{5}$$

where R is a universal gas constant; B is integration constants, the slope tangent is equal to the value $–E_a/R$. The data obtained and the calculated value of E_a are given in Table 1.

Besides, knowing the values of k_1 и K_c, the rate constant for the reverse reactions k_{-1} at 170 and 200 °C were calculated using the ratio:

$$k_{-1} = \frac{k_1}{K_c}. \tag{6}$$

Reaction of stearic acid with diethanolamine. Diethanolamide synthesis reaction can be observed from the same point of view as that of monoethanolamide (Fig. 4). In that case the basic product is amide **4**, and, similarly, ester **5**, can be formed, the latter then being rearranged to amide **4**. Also, there is a possibility of a diacylated amidoester **7** and its conversion back to ethanolamide **4** after reaction with **DEA**. Besides, some more reactions could theoretically be run, for instance, the formation of **DEA** derivative where all NH_2- и OH-groups are substituted with stearyls. However, those reactions will not be discussed in this paper because of their negligible contribution to the total process.

Table 1

Calculated values of kinetic parameters

T, °C (T, K)	$1/T$, K^{-1}	SA–MEA		SA–DEA	
		k_1, $dm^3/(mol \cdot s)$	$\ln k_1$	k_1, $dm^3/(mol \cdot s)$	$\ln k_1$
110 (383)	0.002611	$3.775\cdot10^{-6}$	−12.4858	$6.532\cdot10^{-6}$	−11.9388
130 (403)	0.002481	$1.330\cdot10^{-5}$	−11.2277	$2.485\cdot10^{-5}$	−10.6027
150 (423)	0.002364	$7.361\cdot10^{-5}$	−9.5167	$8.552\cdot10^{-5}$	−9.3668
170 (443)	0.002257	$2.319\cdot10^{-4}$	−8.3694	$3.216\cdot10^{-4}$	−8.0422
200 (473)	0.002114	$9.773\cdot10^{-4}$	−6.9307	$1.269\cdot10^{-3}$	−6.6695
		E_a = 95.17 kJ/mol $\chi^2 = -0.99770$ Adj. $R^2 = 0.99386$		E_a = 89.28 kJ/mol $\chi^2 = -0.99938$ Adj. $R^2 = 0.99836$	

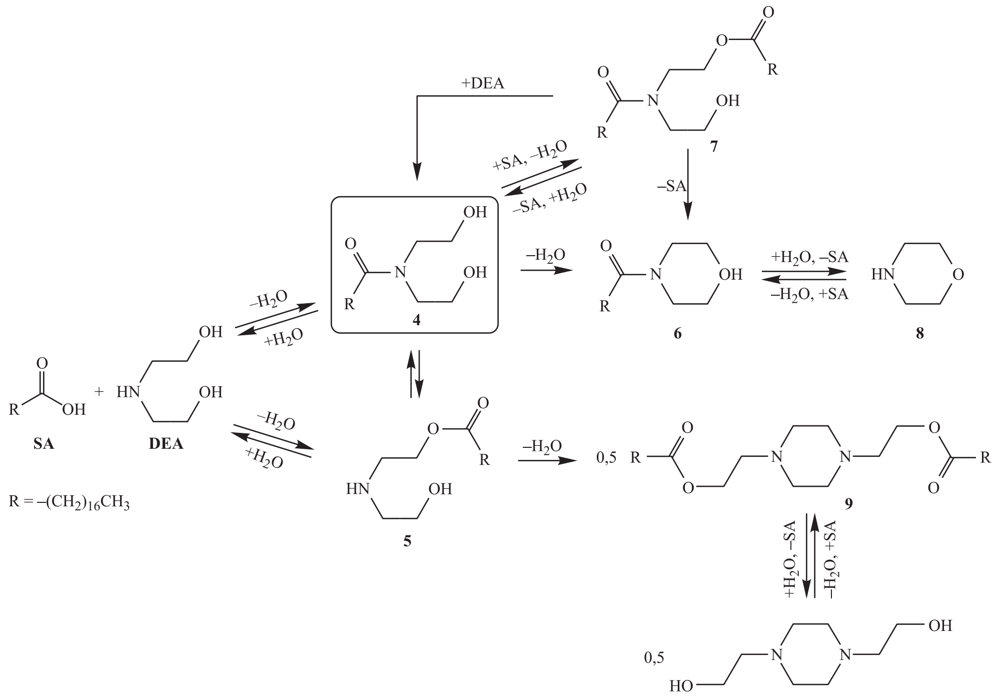


Fig. 4. Reaction of **SA** with **DEA**

Kinetic curves for the reaction of **SA** with **DEA** at different temperatures are given in Fig. 5. Comparison of kinetic curves for the reaction of **SA** with **MEA** and that of **SA** with **DEA** indicates that the processes have principal differences, the main one being the fact that **SA** concentration, decreasing during the starting periods, once it had reached a certain value, begins to smoothly increase. Thus, unlike the reaction of **SA** with **MEA**, in this case kinetic curves have strongly pronounced minimums. This effect becomes more evident at higher temperatures. So, at 110 and at 130 °C during the period being studied only decrease of **SA** concentration can be observed. When the temperature rose up to 150 °C and higher, after SA concentration had reached a concentration of 0.60 to 0.81 mol/dm^3 that corresponds to about 64–73 per cent conversion, then the content **SA** in the reaction system begins to rise again, the higher the reaction temperature, the quicker a minimum point is achieved, and the lower **SA** concentration at that point.

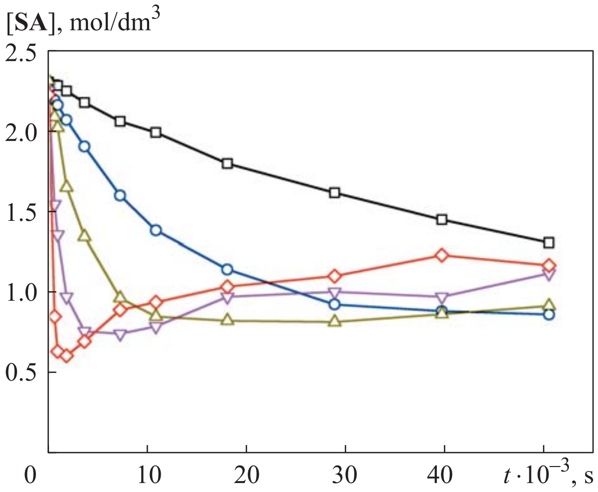


Fig. 5. Kinetic curves for the reaction of **SA** with **DEA** at temperatures 110 (□), 130 (○), 150 (△), 170 (▽), and 200 °C (◇)

The dependencies observed indicate that the processes occurred in the reaction system **SA**–**DEA**, have a more complicated character than that in the reaction system **SA**–**MEA**. According to the literary data [16–26] the reaction of carboxylic acids comes with a number of side reactions, most important of them being inter- and intramolecular cyclizations involving a diethanolamine moiety that is part of the primary reaction products, amide **4** and ester **5** (see Fig. 4).

In the [18] when we studied acid-catalyzed amidation of fatty acids with **DEA** with azeothropic water removal, we had demonstrated that the reaction is not completed at the stage of diethanolamides formation. Resuming the process under the same conditions will result in additional water formation that exceeds its stoichiometric quantity, corresponding to a complete conversion of fatty acids to diethanolamides. It had been shown that the extra quantity of water was formed as a result of cyclization, involving diethanolamide hydroxyethyl groups, as was confirmed with the product hydroxyl value decrement. Thus, the main difference between amidation of fatty acids with **DEA** and that with **MEA** consists in a possibility of further transformation of diethanolamides.

Near the starting point of the process the concentrations of **SA** и **DEA** are high and, therefore, the rate of diethanolamide **4** and other **DEA** acylation products is maximal. As the content of amide **4** begins to rise, the tare of its dehydration (leading, e.g. to morpholinylamide **6** with some additional quantity of water formation) also increases, and we have good reasons to consider that reaction to be practically irreversible. If in the system **SA–MEA** the water that forms as a result of amidation (or esterification) only affect the equilibrium, but in the system **SA–DEA** one more water-formation source (mentioned above dehydration) appears. The increase of water content that occurs in a closed system unavoidably leads to a shift of amide **4** formation equilibrium towards the starting compounds (**SA** и **DEA**), and initiates the hydrolysis of morpholinamide **6** itself that results in a molecule of SA and a molecule of morpholine **8** formation. Thus, as we believe, it is the dehydration reaction that can explain the presence of the sectors on kinetic curves where **SA** concentration increases.

Besides intermolecular cyclization of diethanolamide **4** to morpholinylamide **6**, also a possibility of an irreversible intermolecular cyclization of ester **5**, producing a mole of water, to a piperazine derivative **9**, the latter, in its turn, reacting with water, can hydrolyze, giving **SA** and 1,4-*bis*(*2*-hydroxyethyl)piperazine **10**, thus composing an alternative reaction route. It is easy to notice that in terms of stoichiometry and kinetics those two routes are quite similar and only have difference in intermediate products structure. Both routes have a reversible stage of a monoacylated **DEA** (amide **4** or ester **5**) formation that comes with one mole of water formation; an irreversible cyclization stage that comes with one mole of water formation (products: **6** or **9**), and a stage of a cyclic product hydrolysis producing **SA**. Thus, for this reaction system, as for the system **SA–MEA**, we can only speak about “effective” kinetic parameters of the process.

The order and rate constants of the forward reactions of diethanolamide **4** formation were estimated like those for monoethanolamide **1**, graphically, using starting sections of kinetic curves, those sections being considered to correspond only to the forward reaction of amide **4** formation, the reverse reaction and side reactions being neglected.

Like in the case of the reaction of **SA** with **MEA**, we had demonstrated that a linear correlation can only be observed in 1/[**SA**]–*t* coordinate system (Fig. 3, *b*). Thus, it could be confirmed that the forward reaction of **SA** with **MEA** has also the second order and can be described with a kinetic equation similar to (3).

Activation energy value E_a for **SA** with **DEA** reaction was estimated as described above.

The comparison of the kinetic parameters for the two reactions (see Table 1), which have difference only in chemical structure of one component, made possible to draw a number of conclusions. First, the rate constants of **SA** amidation with diethanolamine at the same temperature are always higher than those with monoethanolamine. Second, the activation energy value for monoethanolamide **1** is about 5.9 kJ/mol greater than that for diethanolamide **4**. The facts observed can easily be explained using the modern views on organic reactions mechanism. According to the theory, in the processes of bimolecular nucleophilic substitution to which, particularly, the amidation reaction belongs, one of the key factors that affect the reaction rate, is the reagent nucleophilicity. While being complicatedly described quantitatively, nevertheless, qualitatively this parameter is considered a reliable instrument for the estimation of the reactivity of compounds that possess a nucleophilic behavior [24]. In our case, the amino group of **DEA** is a stronger nucleophile as far as it contains two alkyl substituents while a molecule of **MEA** has only one. And, therefore, the reactions of carboxylic acids with **DEA** should progress faster than that with **MEA**. Thus, the results of the present research are one more time confirming the correlation between the structure of amine and its reactivity.

Mathematical model of the reaction of stearic acid with diethanolamine. To develop the mathematical model, we have chosen the two reactions as being the most probable: the forward (1) and the reverse (2) diethanolamide **4** synthesis reactions; cyclization of amide **4** to morpholinylamide **6** (3); hydrolysis of amide **6** (4), and the reverse reaction (5). The scheme of the reactions mentioned and their mass balances for equal initial concentrations of starting compounds is given below:

$$1,2)\quad \underset{c_0-x+z}{\mathbf{SA}} + \underset{c_0-x}{\mathbf{DEA}} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \underset{x-y}{\mathbf{4}} + \underset{x+y-z}{H_2O}$$

$$3)\quad \underset{x-y}{\mathbf{4}} \xrightarrow{k_3} \underset{y-z}{\mathbf{6}} + \underset{x+y-z}{H_2O}$$

$$4,5)\quad \underset{y-z}{\mathbf{6}} + \underset{x+y-z}{H_2O} \underset{k_5}{\overset{k_4}{\rightleftarrows}} \underset{z}{\mathbf{8}} + \underset{c_0-x+z}{\mathbf{SA}}$$

Having assumed all the stages of this mechanism to be elementary, then we used the mass action law the principle of independence of the reactions progress to describe the kinetics of those reactions using a differential equation system. For the present system the number of independent equations is equal to three. It is convenient to transform the system through differentials of auxiliary variables x, y, z, the physical meaning of which is clear from the scheme below:

$$\begin{aligned}
\frac{dx}{dt} &= k_1(c_0 - x + z)(c_0 - x) - k_2(x - y)(x + y - z),\\
\frac{dy}{dt} &= k_3(x - y),\\
\frac{dz}{dt} &= k_4(x - z)(x + y - z) - k_5(c_0 - x + z)z.
\end{aligned} \tag{7}$$

Further, we solve the equation numerically using the mathematical software package Maple. The input data are: starting compounds initial concentration and the pre-estimated values of k_1 and the first stage activation energy. To do this, we should select the values of rate constants for all stages to fit the **SA** concentration change curve into a characteristic shape starting from the highest temperature (200 °C), then optimizing the rate constant values until the best match of a model curve with the experimental points. This operation was repeated for every case the process was run at a higher temperature. Then the activation energy values for each stage were estimated, and the final results (rate constants obtained) were adjusted until the experimental kinetic curves match satisfactorily with a model dependence (Fig. 6) provided that the Arrhenius equation is true for the rate constants of all stages, i.e. there is a linear correlation between $\ln k_1$ and $1/T$ for each stage.

The optimal values of the rate constants k_i obtained using the model, at different temperatures are given in Table 2.

Besides **SA** concentration values, the suggested mathematical model allows to predict a concentration change for all the components of interest in the reaction system during the process. The calculated concentration dynamics for all principal reactants is given in Fig. 7.

The calculations demonstrate that diethanolamide **4** concentration has a maximum, the position and an absolute value of which depends on a temperature level: the higher the temperature, the faster the maximum **4** concentration is reached, and the higher its value. This can be explained by the fact that the activation energy of diethanolamide **4** formation is higher than that of its con-

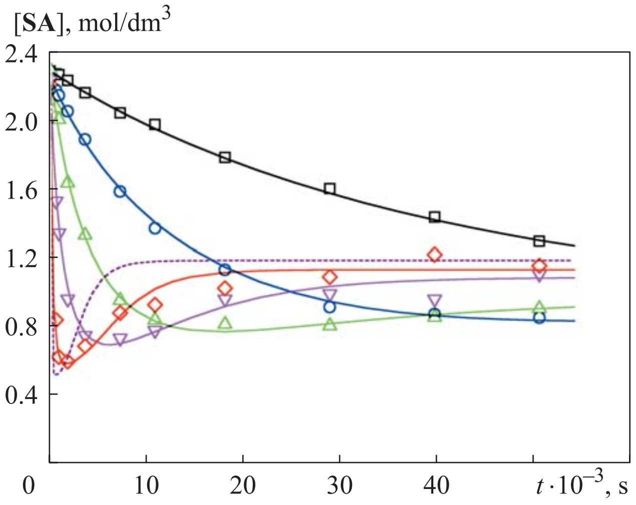


Fig. 6. Experimental and model curves of **SA** change after optimization of the rate constants of the individual stages of the mechanism described by the equation system (7) at temperatures 110 (□), 130 (○), 150 (△), 170 (▽), 200 (◇), and 230 °C (-----)

version to amide **6** or diester **9**, it follows from this that the influence of temperature on product **4** formation is stronger than on the rate of its conversion. For instance, the data in Table 2 show that when a temperature is raised from 110 to 120 °C, k_1 increases by 250 times, but k_3 only by 40 times.

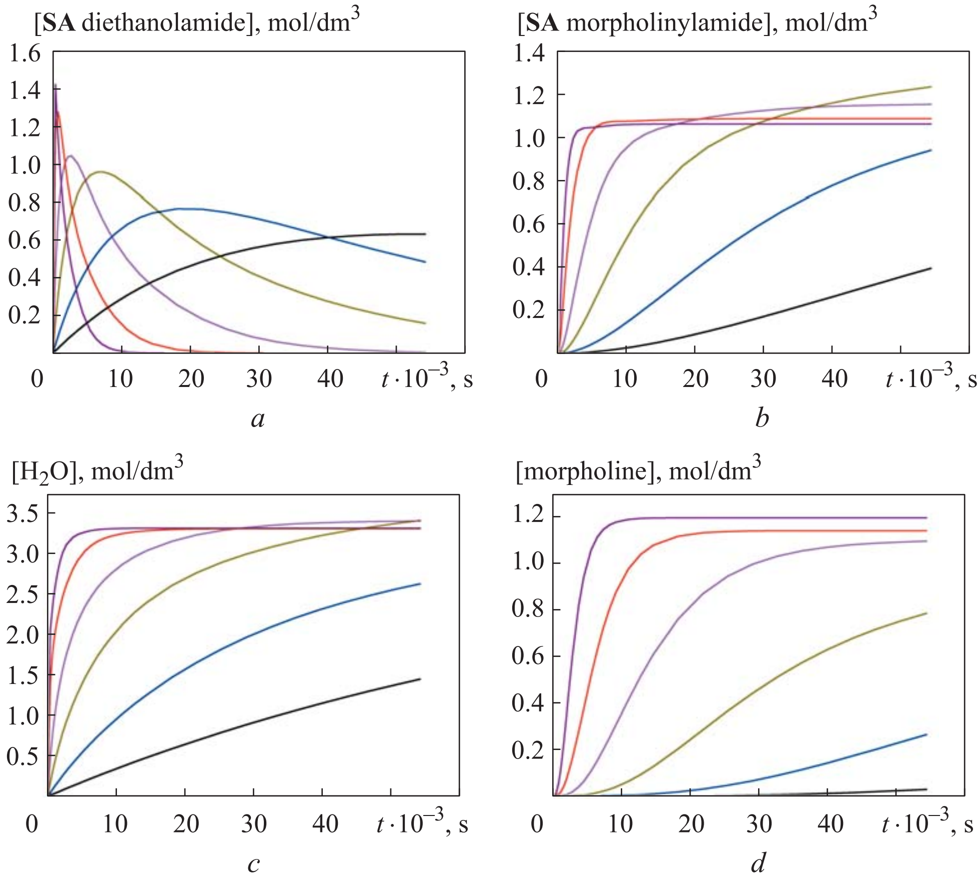
Table 2

Rate constant values, dm³/(mol · s)

T, °C	k_1	k_2	k_3	k_4	k_5	Correlation coefficient
110	$6.944 \cdot 10^{-6}$	$8.333 \cdot 10^{-7}$	$1.667 \cdot 10^{-5}$	$4.1667 \cdot 10^{-6}$	$2.361 \cdot 10^{-5}$	0.99949
130	$2.5 \cdot 10^{-5}$	$2.361 \cdot 10^{-6}$	$3.611 \cdot 10^{-5}$	$7.5 \cdot 10^{-6}$	$4.444 \cdot 10^{-5}$	0.99946
150	$9.167 \cdot 10^{-5}$	$1.111 \cdot 10^{-5}$	$7.5 \cdot 10^{-5}$	$1.528 \cdot 10^{-5}$	$7.778 \cdot 10^{-5}$	0.99823
170	$3.056 \cdot 10^{-4}$	$3.611 \cdot 10^{-5}$	$1.667 \cdot 10^{-4}$	$3.333 \cdot 10^{-5}$	$1.083 \cdot 10^{-4}$	0.99459
200	$1.75 \cdot 10^{-3}$	$1.944 \cdot 10^{-4}$	$3.611 \cdot 10^{-4}$	$6.111 \cdot 10^{-5}$	$1.694 \cdot 10^{-4}$	0.99276
230*	$7.056 \cdot 10^{-3}$	$5.778 \cdot 10^{-4}$	$6.778 \cdot 10^{-4}$	$1.339 \cdot 10^{-4}$	$3.306 \cdot 10^{-4}$	–

* Predicted values.

Close to each other activation energy values of the first and of the second stages make their ratio practically constant, while the temperature changes. This makes possible to estimate a maximum theoretical yield of the end product about 75 per cent, in case side reactions run is neglected. The decrease of the activation energy of the subsequent stages leads us to a conclusion that a maximum yield of the end product (diethanolamide) can be achieved applying a high temperature that makes its conversion during the subsequent stages lower, regarding to the first one. However, the calculation of diethanolamide theoretical yield at 230 °C (Fig. 7, *a*) does not show any significant increase.



a *b* *c* *d*

Fig. 7. Concentration dynamics for the components of the system **SA–DEA** at temperatures 110 (—), 130 (—), 150 (—), 170 (—), 200 (—), 230 °C (—) and (model results):

a) **SA** diethanolamide; *b*) **SA** morpholinylamide; *c*) H_2O; *d*) morpholine

The large duration of the process makes amide **4** concentration tends to zero, i.e., this compound is not a final product of the reaction. The reason is that, as mentioned above, the product irreversible conversion into cyclic products **6** and **9**. Thus, during the late stages the composition of the reaction system is entirely defined by reactions (4) and (5) equilibrium, i.e., by k_4 and k_5 ratio. The obtained regularities were independently confirmed by GC/MS data, according to which in the reaction system **SA–DEA** at 200 °C after 6 hours of reaction amide **4** and ester **5** were not detected, but **SA** and some other products, such as **6**, **8**, **10**, were present.

It is easy to notice that the activation energy values for the reactions (1) and (5) are significantly different. Обращает на себя внимание существенное различие в энергиях активаций для реакций (1) и (5). Despite that at the first sight both of these reactions are amidation of **SA** with similar-structure amines, their activation energy values differ almost three times. Furthermore, while the reaction of **DEA** with **SA** is run practically without a thermal effect: E_a (1) ≈ E_a (2), the reaction of morpholine with **SA** is an explicitly exothermic one: E_a (5) < E_a (4). This fact can be explained that, as mentioned before, the reaction of **SA** amidation with morpholine (5) consists of the two parallel reaction: amidation of **SA** with morpholine **8** and esterification of **SA** with diol **10** (see Fig. 2). Thus, the obtained values of E_a (5) and E_a (4) represent some average values for these two processes, the contribution of each being unknown. It follows from this that the reverse reaction, morpholinylamide **6**/diester **9** hydrolysis, has a total endothermic effect, and, due to this, a raised temperature the equilibrium of this reaction is shifted rightwards, towards morpholinylamide **6**/diester **9**, towards morpholine **8**/diol **10** and **SA**, the equilibrium concentrations of which, as shown in Fig. 7, are increasing, while the concentrations of water and morpholinylamide **6**/diester **9** are decreasing.

Thus, the suggested model can be used as a reliable instrument for prediction of the behavior of fatty acids amidation with **DEA** at different temperatures and different process duration, those features can be useful, e.g. in the synthesis of that class of compounds.

Conclusion. In the present work the study of kinetics of stearic acid direct amidation with mono- and diethanolamines in a closed thermodynamic system, without any and without a catalyst, solvent has been performed. The rate constants of stearic acid ethanolamides synthesis at different temperatures and the activation energy values of these reactions were determined experimentally. It has been shown that the amidation with diethanolamine in a closed system proceeds until the equilibrium acid – amide is reached, which is strongly shifted towards the reaction products, the equilibrium constants of that reaction at 170 and 200 °C also were being determined. The process of amidation with diethanolamine has a more complicated kinetic behavior than that with monoethanolamine, this becomes apparent in a compound shape of stearic acid kinetic curves, passing through a concentration minimum, and can be explained by the presence of a number of side reactions. A mathematical model for the pro-

cess of stearic acid amidation, which takes into consideration contributions both of the main reaction and of the number of side-reactions, has been developed. The model adequacy is supported with high correlation between calculated kinetic curves and experimental ones. Using this model, the reaction rate constants and their activation energy values at different temperatures have been calculated. The results obtained in this research have a significant importance both for theoretical organic chemistry and surface-active compounds process technology.

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