

KINETIC ASPECTS OF CATALYTIC INTERACTIONS INVOLVING  
PENTYL ACETATE AND ETHANOLAMINEStepan Melnyk<sup>1,✉</sup>, Yurii Melnyk<sup>1</sup>, Halyna Mahorivska<sup>1</sup>, Olena Fuchyla<sup>1</sup><https://doi.org/10.23939/chcht17.04.820>

**Abstract.** A conversion scheme for pentyl acetate, ethanolamine, and the products resulting from their interaction through aminolysis, transesterification, and O-N-acyl migration reactions catalyzed by homogeneous and heterogeneous Brønsted-Lowry bases and acids is proposed. It has been determined that acid and base catalysts significantly enhance the aminolysis reaction of esters with amino alcohols when compared to the non-catalytic process. The impact of the catalyst on each reaction has been assessed.

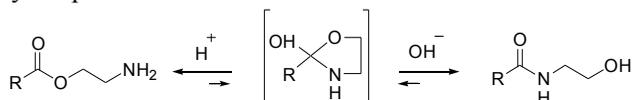
**Keywords:** aminolysis, transesterification, O-N-acyl migration, kinetics, acid and base Brønsted-Lowry catalysts.

## 1. Introduction

Reactions between esters and ethanolamines serve mainly for obtaining alkanolamides, as well as aminoesters of carboxylic acids, which are raw materials for producing detergents and cosmetics, pharmaceutical products, fungicides, dyes, corrosion inhibitors, *etc.*<sup>1-4</sup> Carboxylic acids also show high reactivity with ethanolamines.<sup>5-6</sup>

It is believed, that the main reaction that occurs during the interaction of an ester and amino alcohol is transesterification. Then, the formed ester undergoes further intermolecular transformation (N-O-acyl migration) producing ester amide. Such a conversion scheme was proposed for obtaining hydroxyalkyl amides in the methanol solution of sodium carbonate.<sup>7</sup>

O- and N-acyl migration occurs via an intermediate cyclic product:



Its direction depends on the medium pH. In particular, acid treatment of N-arachidonoyl ethanolamine causes its rearrangement into O-arachidonoyl ethanolamine, and

during the base treatment of O-arachidonoyl ethanolamine or O-palmitoyl ethanolamine, their N-amides are formed.<sup>8</sup>

Temperature also affects the reaction between esters and ethanolamines. It has been particularly revealed that the increase in temperature of the reaction of methyl laurate with monoethanolamine and diethanolamine catalyzed by sodium methoxide increases the yield of ester amide.<sup>9</sup> The temperature increase over 200 °C also leads to the formation of the oxazoline derivative.<sup>10</sup>

It was also determined that in the reaction of methyl linoleate and ethanolamine catalyzed by sodium methoxide the excess of ethanolamine provides a higher yield of linoleoyl ethanolamide compared with other solvents (hexane and methylene chloride). Ethanolamine can also show catalytic properties. At the same time, the authors demonstrate that the temperature does not significantly affect the reaction.<sup>11</sup>

Alkanolamides and amino esters of carboxylic acids are produced in the absence of a catalyst, as well as in its presence.

It is proposed to produce N-(2-hydroxyethyl)acetamide via the reaction of ethyl acetate and ethanolamine by boiling the reaction mixture in the absence of the catalyst. The molar ratio ethanolamine: ethyl acetate is 3 : (4-5). The reaction time is 3-4 hours. The yield of the N-(2-hydroxyethyl)acetamide is 92-95 %.<sup>1</sup>

The most widespread industrial catalysts of the reactions between esters and ethanolamines are hydroxides and alcoholates of alkaline metals. In particular, a high yield of alkanolamides is achieved in the reactions of methyl esters of aliphatic acids (C<sub>7</sub>-C<sub>21</sub>) and ethanolamines catalyzed by hydroxides and alcoholates of alkaline metals. The reaction temperature is 90-150 °C, the molar ratio of alkanolamide to ester is in the range of 1–1.3 and the reaction time is 1-6 hours. Under these conditions, the content of ester amide in the reaction product does not exceed 3 %.<sup>12</sup>

In addition to hydroxides and alcoholates of alkaline metals, potassium tert-butoxide, 1,8-diazabicyclo(5.4.0)undec-7-ene, Cs<sub>2</sub>CO<sub>3</sub>, NaH, 2-tert-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine, N,N-bis(mesylylimidazolium chloride, magnesium/

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aluminum layered double hydroxide (Mg/Al LDH), Merrifield resin-bound azidoproazaphosphatane  $N_3=P(MeNCH_2CH_2)_3N$  were also investigated as catalysts for the reactions of esters and amino alcohols.<sup>13-16</sup>

The use of heterogeneous catalysts has the advantage that they can be separated from the reaction mixture by filtration. It is known that among these catalysts the ion-exchange resins show high activity in the transesterification reactions.<sup>17</sup> Therefore, the investigations of their influence on the interaction between esters and ethanolamines are quite promising.

The established aspects of product accumulation during the interaction of pentyl acetate with ethanolamine catalyzed by both homogeneous and heterogeneous Brønsted-Lowry bases and acids correlate quite well with the concepts presented above regarding this process.<sup>18</sup> According to the kinetic studies, the authors also proposed the conversion scheme of pentyl acetate, ethanolamine, and the products of their interaction catalyzed by H-cation exchange resin.<sup>19</sup> However, the information regarding the catalytic influence of Brønsted-Lowry bases and acids on individual reactions involving esters and ethanolamines is rather limited.

This research aimed to determine the kinetics of the reactions involving pentyl acetate, ethanolamine, and the products of their interaction, catalyzed by Brønsted-Lowry bases and acids. Additionally, the goal was to compare the rate constants of these reactions with those of non-catalytic reactions and assess the adequacy of the proposed kinetic scheme for the interconversion of the mentioned substances.

## 2. Experimental

Ethanolamine (EA, the 93.8 wt.% content, the rest was water), pentyl acetate (PAC, the content of 76.0 wt.%, the rest was pentyl alcohol (PA, 21.8 wt.%), and acetic acid (2.2 wt.%) were used as the raw materials. Cation exchange resin KY-2-8 (I grade, total static exchange capacity was  $1.8 \text{ mmol}\cdot\text{eq}\cdot\text{g}^{-1}$ ), OH-anion exchange resin AB-17-2 (high-purity grade, total static exchange capacity was  $1.9 \text{ mmol}\cdot\text{eq}\cdot\text{g}^{-1}$ ), p-toluenesulfonic acid (pTSA, monohydrate, high-purity grade), and potassium hydroxide (KOH, reagent grade) were used as catalysts. Isopropyl alcohol (analytical grade) was used as the solvent while carrying out chromatographic analysis.

A round-bottom flask with a reflux was used as the reactor. The reaction mixture was stirred using a magnetic stirrer with an intensity of  $400 \text{ rpm}^{-1}$ . The reaction temperature was 393 K.

The reaction between pentyl acetate and ethanolamine (in the presence of pentyl alcohol) was investigated using H-cation exchange resin, p-toluenesulfonic acid, OH-anion exchange resin, potassium hydroxide, and

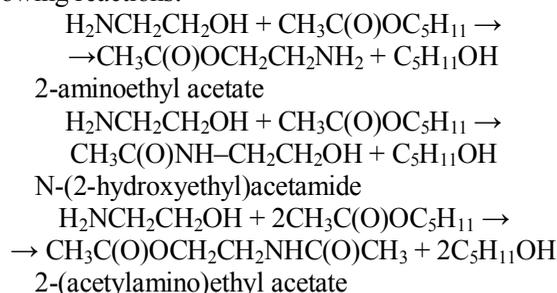
without the catalyst. The mass fraction of H-cation and OH-anion exchange resins as the catalyst was 2.5 wt.% of the reaction mixture. This corresponded to the concentration of  $H^+$  or  $OH^-$  ions in the solution equal to  $4.2\cdot 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ . The same concentration of pTSA and KOH in the reaction mixture was observed when they were used as catalysts. The molar ratio PAC: EA was 1: 1.5.

A LKhM-80 chromatograph equipped with a thermal conductivity detector was used to determine the fractions of pentyl alcohol and ethanolamine in the reaction mixture. These substances were separated using a 1 m long, 3 mm diameter metal column filled with Polysorb-1. Helium was used as a carrier gas. Its consumption was  $3 \text{ L}\cdot\text{h}^{-1}$ . The vaporizer temperature was 463 K, the detector temperature was 473 K, and the column temperature was 393 K. The error of chromatographic analysis did not exceed 4.3 rel. %. The mass fraction of the pentyl acetate and ethanolamine was determined by the absolute calibration method using the graph drawn according to the solution of these substances in isopropyl alcohol. Current concentrations  $C_{EA}$  and  $C_{PA}$  were calculated using the results of the chromatographic analysis.

The amine number (AN) of the reaction mixture was determined by conductometric titration with a 0.1M solution of HCl. For measuring the electric conduction, an ELWRO N5721M conductometer was used.

A method for calculating the concentrations of individual substances, namely 2-aminoethyl acetate, N-(2-hydroxyethyl)acetamide, and 2-(acetylamino)ethyl acetate, as described in the paper,<sup>20</sup> has been developed.

It is assumed that 2-aminoethyl acetate (AEA), N-(2-hydroxyethyl)acetamide (HEA), and 2-(acetylamino)ethyl acetate (AAEA) are formed according to the following reactions:



It is evident that the concentration of pentyl acetate spent on the reaction is equal to the quantity of produced alcohol:

$$C_{PAC,0} - C_{PAC} = C_{PA} - C_{PA,0} \quad (1)$$

Then, the current concentration of pentyl acetate is:

$$C_{PAC} = C_{PA,0} - C_{PA} + C_{PAC,0} \quad (2)$$

The cumulative current concentration of amines characterizing the total content of ethanolamine and 2-aminoethyl acetate in the reaction mixture is:

$$C_{AN} = C_{EA} + C_{AEA} \quad (3)$$

It is related to the amine number of the reaction mixture:

$$C_{AN} = \frac{AN \cdot m}{36.5V} \quad (4)$$

where AN is the amine number of the reaction mixture, mg HCl·g<sup>-1</sup>; m is the weight of the reaction mixture, g; V is the volume of the reaction mixture, mL; 36.5 is a molar weight of hydrochloric acid, g·mol<sup>-1</sup>.

Then, the concentration of 2-aminoethyl acetate is:

$$C_{AEA} = C_{AN} - C_{EA} \quad (5)$$

Taking into account that

$$C_{PA} - C_{PA,0} = C_{AEA} + C_{HEA} + 2C_{AAEA} \quad (6)$$

and

$$C_{EA,0} - C_{EA} = C_{AEA} + C_{HEA} + C_{AAEA}, \quad (7)$$

current concentration of 2-(acetylamino)ethyl acetate is:

$$C_{AAEA} = (C_{PA} - C_{PA,0}) - (C_{EA,0} - C_{EA}), \quad (8)$$

and current concentration of N-(2-hydroxyethyl)acetamide is:

$$C_{HEA} = (C_{PA} - C_{PA,0}) - 2C_{AAEA} - C_{AEA} \quad (9)$$

The value of true reaction rate constant  $k'_i$  (L<sup>2</sup>·mol<sup>-2</sup>·s<sup>-1</sup> or L·mol<sup>-1</sup>·s<sup>-1</sup>) was determined similarly to our previous work<sup>21</sup> by dividing the efficient reaction rate constant value  $k_i$  (L·mol<sup>-1</sup>·s<sup>-1</sup> or s<sup>-1</sup>) by the catalyst ions concentration in terms of mol·L<sup>-1</sup>.

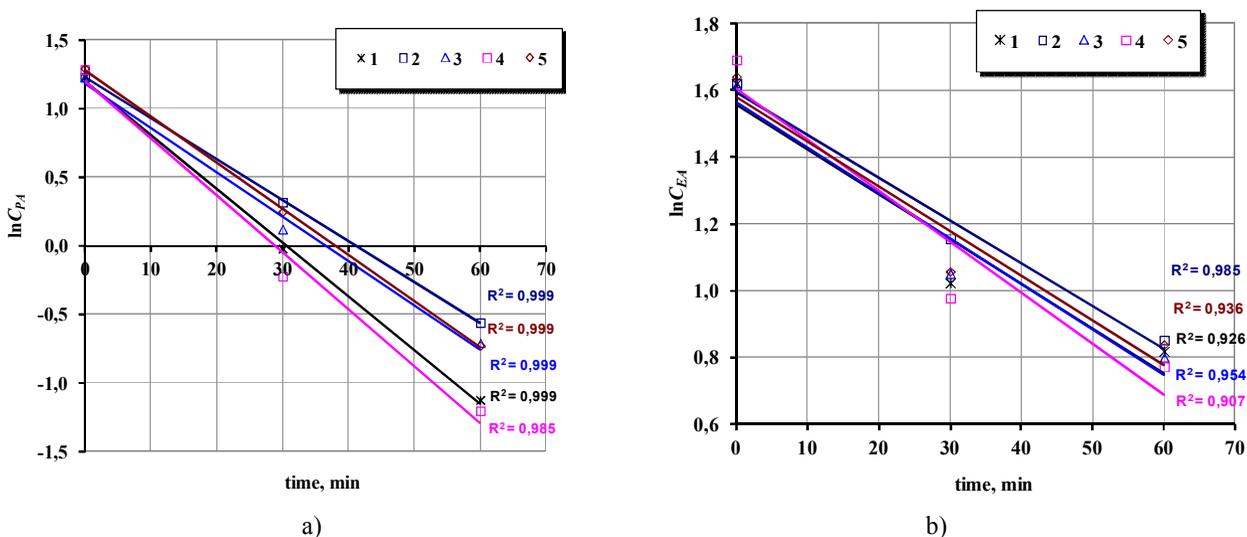
### 3. Results and Discussion

To create the conversion scheme of pentyl acetate, ethanolamine, and the products of their interaction in both non-catalytic and catalyst-assisted reactions, we incorporated the assumptions proposed by Glavan *et al.*<sup>22</sup> In parti-

cular, it was stated that the transesterification reactions, which take place during the interaction between pentyl acetate and ethanolamine, are inverse as opposed to aminolysis reactions. O-N-Acyl migration of 2-aminoethyl acetate into N-(2-hydroxyethyl)acetamide was also taken into account.

As shown in Fig. 1, the semi-logarithmic transformations of the concentration changes of pentyl acetate and ethanolamine over time, with a high degree of correlation, indicate first-order kinetics for these reactants. However, for the system involving consecutive, parallel, reversible, and irreversible reactions, it was not possible to determine the kinetics order with respect to 2-aminoethyl acetate, N-(2-hydroxyethyl)acetamide, and 2-(acetylamino)ethyl acetate by interacting with one of the three reactive functional groups. Therefore, to simplify the calculations, we assumed first-order kinetics for each of the reactants and the catalyst.

It was found that the increase in the stirring intensity over 300 min<sup>-1</sup> while keeping other conditions constant does not affect the concentrations of substances. Since the reaction occurs under steady-state conditions, it can be assumed that the temperature of the exchange resin particles and the liquid medium is the same. Therefore, there is no resistance to mass and heat transfer to the surface and within the internal matrix of the catalyst. Accordingly, we considered the reactor contents as a homogeneous continuous medium, and the reactions involving the heterogeneous catalyst as quasi-homogeneous. This assumption allowed us to utilize constants related to the concentration of H<sup>+</sup> ions and OH<sup>-</sup> ions on the heterogeneous catalyst.



**Fig. 1.** Semi-logarithmic transformations of the concentration changes of pentyl acetate (a) and ethanolamine (b) over time. Temperature is 393 K, ratio EA: PAc is 1.5: 1 (mol). Catalyst: 1 – p-toluenesulfonic acid; 2 – H-cation exchange resin; 3 – KOH; 4 – OH-anion exchange resin; 5 – without a catalyst

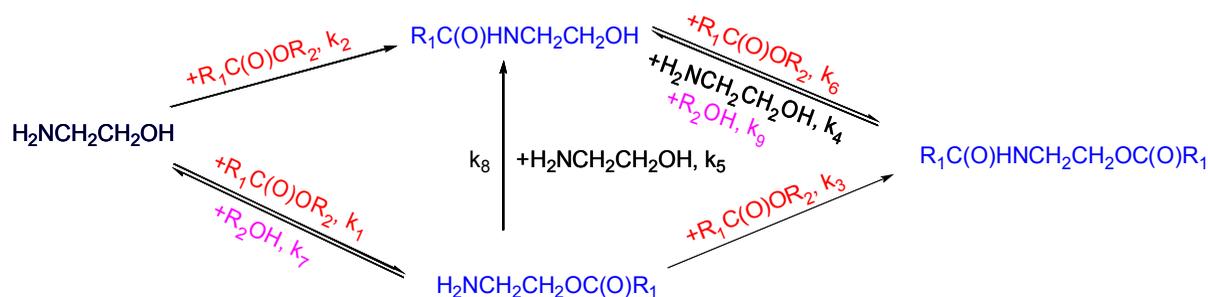


Fig. 2. Interaction scheme involving pentyl acetate, ethanolamine, and the products of their interaction

The scheme of conversions (Fig. 2) between pentyl acetate, ethanolamine, and the products of their interaction was proposed.<sup>19</sup>

According to this scheme, taking into account the assumptions outlined above, the consumption of reagents and the formation of products are described by kinetic equations:

$$\begin{aligned} \frac{dC_{EA}}{d\tau} &= -k_1 C_{EA} C_{PAC} - k_2 C_{EA} C_{PAC} - \\ &- k_4 C_{EA} C_{AAEA} - k_5 C_{EA} C_{AEA} + k_7 C_{AEA} C_{PA} , \\ \frac{dC_{PAC}}{d\tau} &= -k_1 C_{EA} C_{PAC} - k_2 C_{EA} C_{PAC} - \\ &- k_3 C_{AEA} C_{PAC} - k_6 C_{HEA} C_{PAC} + k_7 C_{AEA} C_{PA} \\ \frac{dC_{AEA}}{d\tau} &= k_1 C_{EA} C_{PAC} - k_3 C_{AEA} C_{PAC} - \\ &- k_5 C_{EA} C_{AEA} - k_7 C_{AEA} C_{PA} - k_8 C_{AEA} , \\ \frac{dC_{HEA}}{d\tau} &= k_2 C_{EA} C_{PAC} + k_5 C_{EA} C_{AEA} + \\ &+ 2k_4 C_{EA} C_{AAEA} - k_6 C_{HEA} C_{PAC} + k_8 C_{AEA} + k_9 C_{AAEA} C_{PA} , \\ \frac{dC_{AAEA}}{d\tau} &= k_3 C_{AEA} C_{PAC} - k_4 C_{EA} C_{AAEA} + \\ &+ k_6 C_{HEA} C_{PAC} - k_9 C_{AAEA} C_{PA} , \\ \frac{dC_{PA}}{d\tau} &= k_1 C_{EA} C_{PAC} + k_2 C_{EA} C_{PAC} + k_3 C_{AEA} C_{PAC} + \\ &+ k_6 C_{HEA} C_{PAC} - k_7 C_{AEA} C_{PA} - k_9 C_{AAEA} C_{PA} , \end{aligned}$$

where  $k_i = k'_i C_{\text{H}^+/\text{OH}^-}$ ,  $k'_i$  is the true reaction rate constant,  $\text{L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$  or  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ;  $k_i$  is the effective reaction rate constant,  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  or  $\text{s}^{-1}$ ;  $C_{\text{H}^+/\text{OH}^-}$  is the concentration of  $\text{H}^+$  or  $\text{OH}^-$  ions of catalyst,  $\text{mol} \cdot \text{L}^{-1}$ .

The system of these equations contains nine unknowns being the reaction rate constants. Therefore, its

solution was found by numerical integration using the Euler method, particularly by adjusting the corresponding constant values considering experimentally determined and calculated substance concentrations.

The value of the reaction rate constant was considered acceptable if the value  $\delta$  calculated by the formula was minimal

$$\delta = \frac{100}{N} \sum_{i=1}^N \left| \frac{C_{i,\text{exp}} - C_{i,\text{calc}}}{C_{i,\text{exp}}} \right| \quad (10)$$

where  $C_{i,\text{exp}}$  and  $C_{i,\text{calc}}$  are the experimentally determined and calculated values of concentration,  $\text{mol} \cdot \text{L}^{-1}$ ;  $N$  is the number of determinations.<sup>22</sup>

The calculated value  $\delta$  varied from 7.6 to 23.6%.

Each reaction rate constant used in the kinetic equations is inherently a product of the true rate constant and the catalyst concentration. Specifically, the concentration of  $\text{H}^+$  or  $\text{OH}^-$  in the ion exchange resin is determined based on its total static exchange capacity. Therefore, the values of the true rate constants were calculated similarly to those described elsewhere.<sup>21</sup> The values of the true rate constants of investigated reactions are provided in Tables 1-2.

Selectivity of HEA, AEA i AAEA in terms of PAC (in %) was calculated by the following equation:

$$S_i^{\text{PAC}} = \frac{v_{\text{PAC},i} C_i \cdot 100}{v_i (C_{\text{PAC},0} - C_{\text{PAC}})} \quad (11)$$

where  $C_i$  is the current concentration of the  $i$ -th reaction product (HEA, AEA, AAEA),  $\text{mol} \cdot \text{L}^{-1}$ ;  $v_{\text{PAC},i}$  and  $v_i$  are the stoichiometric coefficients for PAC in the reaction of formation from it the  $i$ -th product and for the  $i$ -th product, respectively;  $(C_{\text{PAC},0} - C_{\text{PAC}})$  is the concentration of reacted PAC,  $\text{mol} \cdot \text{L}^{-1}$ .

The values of calculated effective reaction rate constants, which are the product of the true reaction rate constant and catalyst concentration, as well as true reaction rate constants themselves, are provided in Tables 1-2. The ratio of the effective rate constants for catalytic reactions to the rate constants of the respective non-catalytic reactions clearly demonstrates the significant impact of the catalyst on the reactions between pentyl acetate, ethanolamine, and the products of their interaction (Table 1).

First of all, it should be noted that in the presence of OH-anion exchange resin and pTSA the effective rate constant ( $k_{2,eff}$ ) for the aminolysis reaction of pentyl acetate and ethanolamine to form N-(2-hydroxyethyl)acetamide is 123 times higher than in the non-catalytic process. When catalyzed by H-cation exchange resin and KOH it is 37-39 times higher. The effective rate constants for the catalytic aminolysis reaction of 2-aminoethyl acetate and ethanolamine ( $k_{5,eff}$ ) are 13-20 times higher than the rate constant of the non-catalytic reaction. In the presence of the mentioned catalysts, the ratio of these constants increases to a lesser extent for the aminolysis reaction of 2-aminoethyl acetate and pentyl acetate ( $k_{3,eff}$ ) and for the transesterification reaction of 2-aminoethyl acetate and pentyl alcohol ( $k_{7,eff}$ ) by factors of 1.5-4 and 1.3-3.3, respectively. Simultaneously, in the presence of all catalysts, the ratio of effective rate constants for the transesterification reaction of pentyl acetate and ethanolamine to form 2-aminoethyl acetate ( $k_{1,eff}$ ) is 2.0-4.3 times lower than the non-catalytic process. Similarly, the ratio of effective rate constants for the transesterification reaction of N-(2-hydroxyethyl)acetamide and pentyl acetate resulting in the formation of 2-(acetylamino)ethyl acetate ( $k_{6,eff}$ ) is 2.7-20 times lower. Additionally, for the transesterification reaction of 2-(acetylamino)ethyl acetate and pentyl alcohol ( $k_{9,eff}$ ), the ratio of effective rate constants is 1.3-1.6 times lower. The effective rate constant for the reaction of O-N-acyl migration catalyzed by H-cation exchange resin is 3.4 times higher than the rate constant of the non-catalytic reaction ( $k_{8,eff}$ ). However, in the presence of this catalyst, unlike other catalysts, the ratio between these constants is 3.3 times lower for the aminolysis reaction of 2-(acetylamino)ethyl acetate and ethanolamine ( $k_{4,eff}$ ), compared to the non-catalytic process. The effective rate constant for the O-N-acyl migration reaction

catalyzed by pTSA, OH-anion exchange resin, and KOH is approximately 20 times lower than the rate constant of non-catalytic reaction. However, for the aminolysis reaction of 2-(acetylamino)ethyl acetate and ethanolamine catalyzed by pTSA, OH-anion exchange resin, and KOH the effective rate constant is 1.1-1.6 times higher compared to the non-catalytic reaction (Table 1).

However, the values of true rate constants of all catalytic reactions of pentyl acetate, ethanolamine, and products of their interaction are higher than the rate constants of non-catalytic reactions (Table 2).

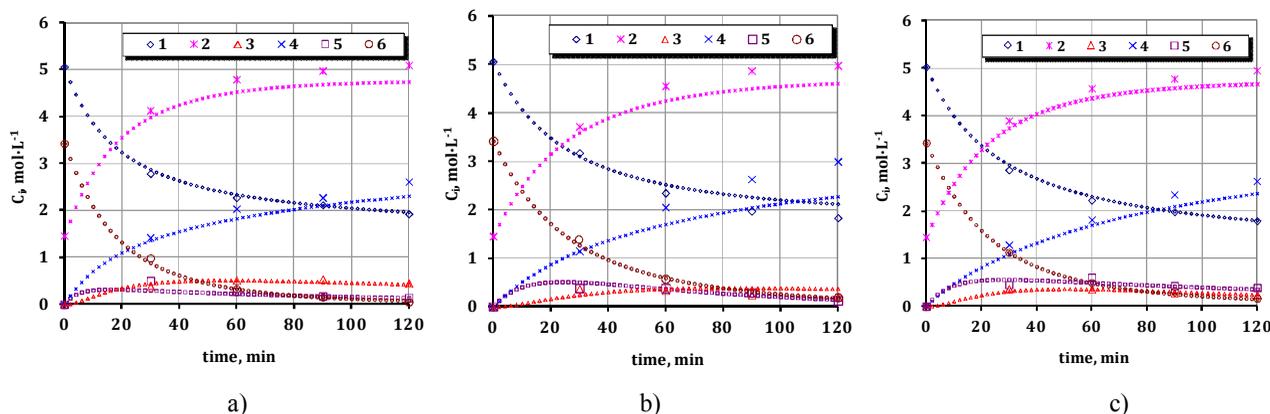
First and foremost, it should be noted that the use of a catalyst significantly increases the rate constant of the aminolysis reaction of pentyl acetate and ethanolamine ( $k_2$ ) to form N-(2-hydroxyethyl)acetamide, compared to the non-catalytic process. Specifically, the application of OH-anion exchange resin increases the rate constant of this reaction by over 3000 times, while pTSA enhances it by nearly 1400 times. Similarly, the use of H-cation exchange resin and potassium hydroxide substantially accelerates the aminolysis reaction of pentyl acetate by ethanolamine, with the rate constant being approximately 950 times higher for H-cation exchange resin and over 800 times higher for potassium hydroxide than the rate of the corresponding non-catalytic process. The investigated catalysts also considerably increase the rate of another aminolysis reaction. Specifically, the rate constant of the reaction between ethanolamine and 2-aminoethyl acetate increases by 321–828 times. The rate constants of the remaining catalytic reactions involving pentyl acetate, ethanolamine, and the products of their interaction increase to a lesser extent, ranging from 1.1 to 201 times. The maximum value of the ratio of these constants also refers to the aminolysis reaction, particularly the reaction of pentyl acetate and 2-aminoethyl acetate.

**Table 1.** The effective rate constants of the reactions between pentyl acetate, ethanolamine, and products of their interaction. Temperature is 393 K. EA: Pac molar ratio is 1.5:1

Indicator	Rate constants, $k_{eff,i} = k_i C_{cat}$								
	$L^2 \cdot mol^{-2} \cdot s^{-1}$							$L \cdot mol^{-1} \cdot s^{-1}$	$L^2 \cdot mol^{-2} \cdot s^{-1}$
Catalyst	$k_{1,eff} 10^5$	$k_{2,eff} 10^4$	$k_{3,eff} 10^4$	$k_{4,eff} 10^5$	$k_{5,eff} 10^5$	$k_{6,eff} 10^5$	$k_{7,eff} 10^5$	$k_{8,eff} 10^4$	$k_{9,eff} 10^6$
Without catalyst	9.5	0.01	0.47	5.9	0.1	5.9	0.3	0.56	8.0
pTSA	4.5	1.2	0.69	9.5	1.3	0.4	0.4	0.03	6.0
Cation exchange resin	4.2	0.39	0.95	1.5	1.4	2.2	1.0	1.9	6.0
KOH	4.8	0.37	1.9	6.3	2.0	0.3	0.6	0.03	5.0
Anion exchange resin	2.2	1.2	0.69	9.5	1.3	0.4	0.4	0.03	6.0
Indicator	Ratio of $k_{eff,i}/k_{(without catalyst)}$								
Catalyst	$k_{1,eff}$	$k_{2,eff}$	$k_{3,eff}$	$k_{4,eff}$	$k_{5,eff}$	$k_{6,eff}$	$k_{7,eff}$	$k_{8,eff}$	$k_{9,eff}$
pTSA	0.47	123	1.5	1.6	13	0.07	1.3	0.05	0.75
Cation exchange resin	0.44	39	2.0	0.3	14	0.37	3.3	3.4	0.75
KOH	0.51	37	4.0	1.1	20	0.05	2.0	0.05	0.63
Anion exchange resin	0.23	123	1.5	1.6	13	0.07	1.3	0.05	0.75

**Table 2.** The rate constants of the reactions between pentyl acetate, ethanolamine, and products of their interaction. Temperature is 393 K. EA: PAc molar ratio is 1.5:1

Indicator		Rate constants, $k_i$								
		$L \cdot mol^{-1} \cdot s^{-1}$						$s^{-1}$	$L \cdot mol^{-1} \cdot s^{-1}$	
Catalyst		$k_1 \cdot 10^3$	$k_2 \cdot 10^3$	$k_3 \cdot 10^3$	$k_4 \cdot 10^3$	$k_5 \cdot 10^4$	$k_6 \cdot 10^4$	$k_7 \cdot 10^4$	$k_8 \cdot 10^3$	$k_9 \cdot 10^4$
Without catalyst		0.095	0.001	0.047	0.059	0.01	0.59	0.03	0.056	0.08
pTSA		1.1	1.4	9.5	0.54	8.3	0.71	1.4	0.24	0.71
Cation exchange resin		1.0	0.95	2.3	0.36	3.4	5.3	2.4	4.6	1.5
KOH		1.1	0.81	4.2	1.4	4.4	0.66	1.3	0.66	1.1
Anion exchange resin		0.54	3.0	1.7	2.3	3.2	0.99	0.99	7.4	1.5
Indicator		Ratio of $k_i/k_{i(\text{without catalyst})}$								
		$k_1$	$k_2$	$k_3$	$k_4$	$k_5$	$k_6$	$k_7$	$k_8$	$k_9$
pTSA		11.2	1396	201	9,2	828	1.2	47	4,2	8.9
Cation exchange resin		10.7	946	49	6,2	364	9.0	81	82	18.2
KOH		11.1	812	89	23	439	1.1	44	1.2	13.7
Anion exchange resin		5.7	3036	36	40	321	1.7	33	1.3	18.5

**Fig. 3.** The experimental points and graphical representations (dashed points) of the kinetic model for the reactions between pentyl acetate, ethanolamine, and their interaction products:

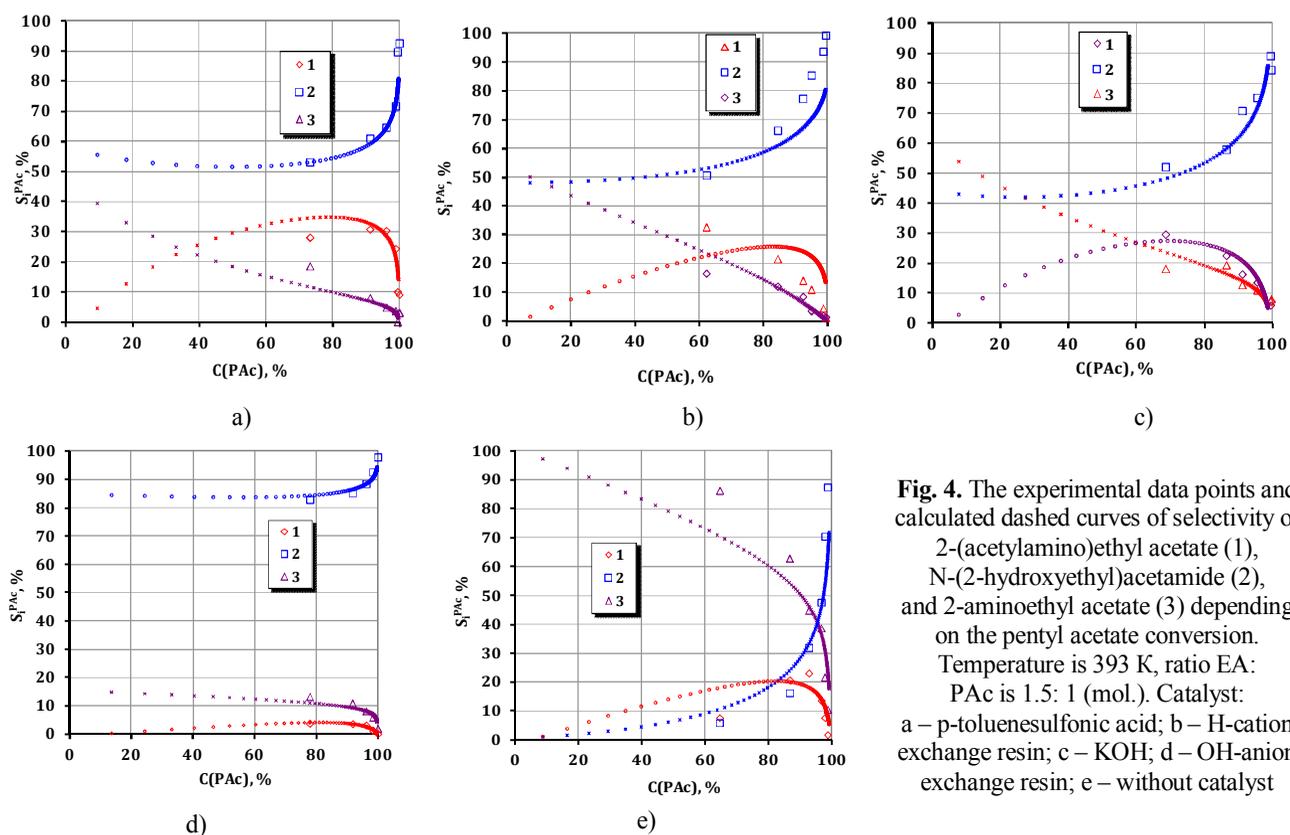
1 – ethanolamine; 2 – pentyl alcohol;  
 3 – 2-(acetylamino)ethyl acetate;  
 4 – N-(2-hydroxyethyl)acetamide;  
 5 – 2-aminoethyl acetate; 6 – pentyl acetate. Temperature is 393 K, ratio EA: PAc is 1.5: 1 (mol.). Catalyst: a – p-toluenesulfonic acid; b – H-cation exchange resin; c – KOH; d – OH-anion exchange resin; e – without catalyst

Graphical representations of the kinetic model of reactions involving pentyl acetate, ethanolamine, and their interaction products were constructed based on the determined rate constants (Fig. 3). The graphical representations demonstrate a good agreement between experimental data and calculations.

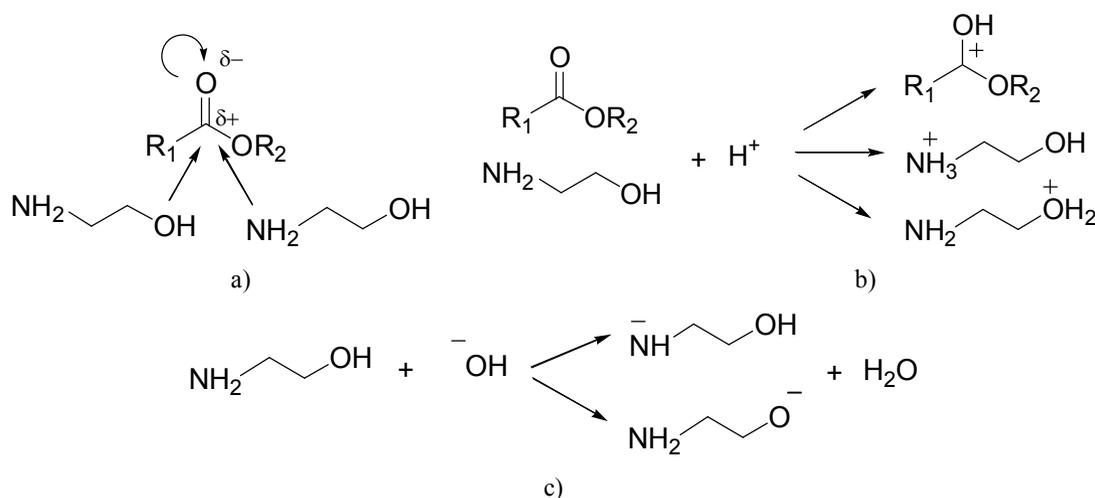
The proposed conversion scheme and the calculated reaction rate constants are validated by the fact that the error in the calculated concentrations of the components in the reaction mixture determined using Eq. (11) has a minimum value of 6.0% for catalysis with OH-anion exchange resin and a maximum value of 16.2% for catalysis with H-cation exchange resin.

Fig. 4 shows the experimental data points and calculated dashed curves of selectivity of 2-(acetylamino)ethyl acetate (1), N-(2-hydroxyethyl)acetamide (2), and 2-aminoethyl acetate (3) depending on the pentyl acetate conversion at a temperature of 393 K and a molar

ratio of PAc to EA from 1 to 1.5. These curves also demonstrate the agreement between the experimental and calculated results, indicating the adequacy of the proposed kinetic scheme for the reaction of pentyl acetate and ethanolamine.



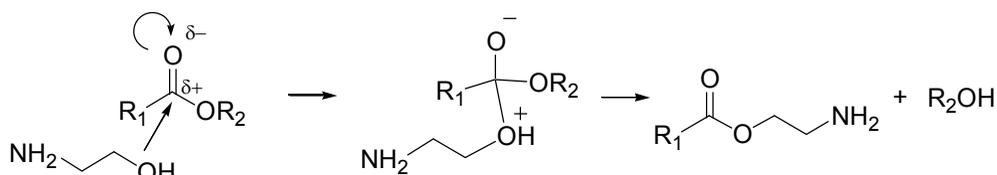
**Fig. 4.** The experimental data points and calculated dashed curves of selectivity of 2-(acetylamino)ethyl acetate (1), N-(2-hydroxyethyl)acetamide (2), and 2-aminoethyl acetate (3) depending on the pentyl acetate conversion. Temperature is 393 K, ratio EA: PAc is 1.5: 1 (mol.). Catalyst: a – p-toluenesulfonic acid; b – H-cation exchange resin; c – KOH; d – OH-anion exchange resin; e – without catalyst



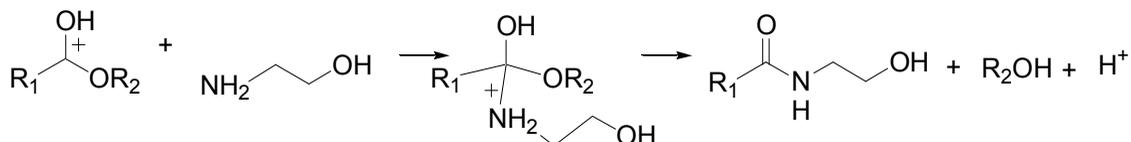
**Fig. 5.** Possible variants of reagent molecule activation in non-catalytic (a) and catalyzed by H<sup>+</sup> (b) and OH<sup>-</sup> (c) ions reactions between pentyl acetate and ethanolamine

In Fig. 5, we can observe the potential modes of activation for the reagents in non-catalytic reactions (a), as well as in reactions of pentyl acetate and ethanolamine catalyzed by  $H^+$  and  $OH^-$  ions.

It is evident that the interaction between ester and amino alcohol in the non-catalytic reaction is determined by the competition between the oxygen or nitrogen atom in the ethanolamine molecule for the carbonyl carbon atom (Fig. 5a).



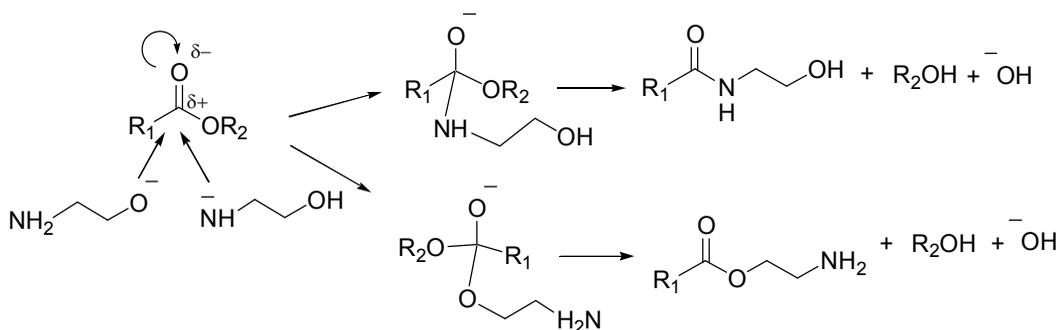
In the presence of acidic catalysts, the attachment of a proton can form onium intermediates (Fig. 5b). Protonation of the carbonyl oxygen with the transfer of a positive



charge to the carbonyl carbon atom significantly reduces its electron density, thereby accelerating the transesterification and aminolysis reactions of the ester, in particular:

Protonation of the nitrogen atom (which is more probable) or the oxygen atom of ethanolamine reduces its nucleophilicity and facilitates the attachment of the amino alcohol to the carbonyl carbon atom of the ester via the corresponding opposite oxygen or nitrogen atom.

During the basic catalysis of the reaction of pentyl acetate and ethanolamine, a hydrogen bond is



It is obvious, that first of all, the studied catalysts accelerate aminolysis reactions ( $k_2$ ,  $k_3$ ,  $k_4$ ,  $k_5$ ) which are characterized by corresponding higher values of ratios between rate constants of catalytic and non-catalytic reactions (Table 2).

## 4. Conclusions

The catalytic effect of homogenous and heterogeneous Brønsted-Lowry acids and bases on the reactions of pentyl acetate, ethanolamine, and the products of their

interaction was determined. It has been shown that the values of true rate constants of all catalytic reactions between pentyl acetate, ethanolamine, and products of their interaction are higher than the rate constants of non-catalytic reactions.

On the basis of the calculated rate constants for the proposed reagent conversion scheme, it was found that in comparison with the non-catalytic process, where the main reactions are the transesterification of esters with amino alcohols followed by the migration of O-N-acyl hydroxyalkylamides, acid and base catalysts significantly

likely formed between the hydrogen of the amino group or hydroxyl group, which leads to its detachment and an increase in electron density or the emergence of a negative charge on the nitrogen or oxygen atom, respectively (Fig. 5c). This promotes the acceleration of the aminolysis or transesterification reaction, in particular:

It is obvious from Table 2 that the rate constant of the non-catalytic transesterification reaction of pentyl acetate and ethanolamine  $k_2$  to form N-(2-hydroxyethyl)acetamide is nearly two orders of magnitude lower than the corresponding rate constant of the aminolysis reaction  $k_1$  resulting in the formation of 2-aminoethyl acetate. This confirms the much higher probability that the transesterification reaction occurs in a non-catalytic process:

It is obvious from Table 2 that the rate constant of the non-catalytic transesterification reaction of pentyl acetate and ethanolamine  $k_2$  to form N-(2-hydroxyethyl)acetamide is nearly two orders of magnitude lower than the corresponding rate constant of the aminolysis reaction  $k_1$  resulting in the formation of 2-aminoethyl acetate. This confirms the much higher probability that the transesterification reaction occurs in a non-catalytic process:

accelerate the aminolysis of esters with alcohols and amino alcohols. It was assumed that the main reason for the increase in the reaction rate catalyzed by homogeneous and heterogeneous bases and Brønsted-Lowry acids is primarily the ionization of the ethanolamine molecule with  $H^+$  and  $OH^-$  ions.

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## КІНЕТИЧНІ АСПЕКТИ КАТАЛІТИЧНОЇ ВЗАЄМОДІЇ АМІЛАЦЕТАТУ Й ЕТАНОЛАМІНУ

**Анотація.** Запропоновано схему перетворень амілацетату, етаноламіну та продуктів їхньої взаємодії за реакціями амінолізу, трансестерифікації та O-N-ацил міграції, каталізованих гомогенними і гетерогенними основами і кислотами Бренстеда-Лоурі. Встановлено, що порівняно з некаталітичним процесом кислотні та основні каталізатори істотно прискорюють реакції амінолізу естерів аміноспиртами. Оцінено вплив каталізаторів на кожну з реакцій.

**Ключові слова:** аміноліз, трансестерифікація, O-N-ацил міграція, кінетика, каталізатори кислоти й основи Бренстеда-Лоурі.