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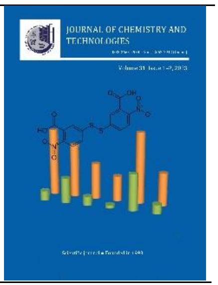

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ETHANOLAMINE AND PENTYL ACETATE INTERACTION CATALYZED BY CATION EXCHANGE RESIN: KINETIC INSIGHT

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Abstract

We report the scheme of ethanolamine, pentyl acetate, and their interaction products in transesterification, aminolysis, and *O*-*N*-acyl migration reactions catalyzed by H-cation exchange resin. The routes of *N*-(2-hydroxyethyl)acetamide, 2-aminoethyl acetate, and 2-(acetylamino)ethyl acetate formation indicate that *N*-(2-hydroxyethyl)acetamide is the final product. The determined rate constant values for the proposed quasi-homogeneous reaction model indicate the significant role of aminolysis reaction by ethanolamine and pentyl acetate interaction catalyzed by H-cation exchange resin. In particular, high values of the rate constant of aminolysis reactions indicate a high rate of amide formation during the interaction of ethanolamine and pentyl acetate, 2-aminoethyl acetate, or 2-(acetylamino)ethyl acetate. The proposed kinetic model adequately describes the *N*-(2-hydroxyethyl)acetamide obtaining process from ethanolamine and pentyl acetate. The values of the considered reactions' pre-exponential factors, rate constants, energy activation, entropy and enthalpy activation were calculated. In particular, the reaction of *N*-(2-hydroxyethyl)acetamide formation by aminolysis of pentyl acetate with ethanolamine has the lowest activation energy (15.8 $kJ\cdot mol^{-1}$), and the reaction of 2-(acetylamino)ethyl acetate formation by N-(2-hydroxyethyl)acetamide with pentyl acetate transesterification has the highest activation energy (89.1 $kJ\cdot mol^{-1}$). A linear relationship was revealed between the pre-exponential factor logarithms of reaction rate constants and activation energies and between the enthalpy and entropy activation. We assume the compensatory effect and the absence of an isokinetic relationship for the entire set of reactions. The study results are the basis for modeling the N-(2-hydroxyethyl)acetamide obtaining process from ethanolamine and pentyl acetate.

Keywords: ethanolamine; pentyl acetate; *N*-(2-hydroxyethyl)acetamide; 2-aminoethyl acetate; 2-(acetylamino)ethyl acetate; kinetic; aminolysis; transesterification; cation exchange resin.

ВЗАЄМОДІЯ МІЖ ЕТАНОЛАМІНОМ І АМІЛАЦЕТАТОМ: АСПЕКТИ КІНЕТИКИ

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Анотація

Запропоновано схему перетворень за участю етаноламіну, *н*-амілацетату та продуктів їх взаємодії в реакціях трансестерифікації, амінолізу та *O*-*N*-ацил міграції в присутності каталізатора – Н-катіоніту. Встановлений характер накопичення *N*-(2-гідроксіетил)ацетаміду, 2-аміноетилацетату та 2-(ацетиламіно)етилацетату показав, що кінцевим продуктом перетворень є *N*-(2-гідроксіетил)ацетамід. Значення констант швидкості, визначені для квазігомогенної моделі реакції, вказують на суттєву роль реакцій амінолізу під час взаємодії етаноламіну і *н*-амілацетату в присутності Н-катіоніту. Зокрема на перебіг з високою швидкістю реакцій утворення амідів взаємодією етаноламіну і *н*-амілацетату, 2-аміноетилацетату, або 2-(ацетиламіно)етилацетату вказують високі значення констант швидкостей цих реакцій. Показано, що запропонована кінетична модель адекватно описує процес одержання *N*-(2-гідроксіетил)ацетаміду з етаноламіну і *н*-амілацетату. Розраховано значення преекспонент констант швидкості, енергії, ентропії та ентальпії активації вказаних реакцій. Встановлено, зокрема, що найнижча енергія активації (15.8 $кДж\cdot моль^{-1}$) властива для реакції утворення *N*-(2-гідроксіетил)ацетаміду амінолізом *н*-амілацетату етаноламіном, а найвища (89.1 $кДж\cdot моль^{-1}$) – для реакції утворення 2-(ацетиламіно)етилацетату взаємодією N-(2-гідроксіетил)ацетаміду та *н*-амілацетату. Виявлено лінійну залежність між логарифмами преекспонент констант швидкості реакцій та їхніми енергіями активації, а також між ентальпією і ентропією активації. Зроблено припущення про наявність компенсаційного ефекту та відсутність ізокінетичного ефекту для всієї сукупності реакцій. Результати дослідження є основою для математичного моделювання технологічного процесу одержання *N*-(2-гідроксиетил)ацетаміду з етаноламіну та *н*-амілацетату.

Ключові слова: етаноламін; амілацетат; *N*-(2-гідроксиетил)ацетамід; 2-аміноетилацетат; 2-(ацетиламіно)етилацетат; кінетика; аміноліз; трансестерифікація; катіонообмінна смола.

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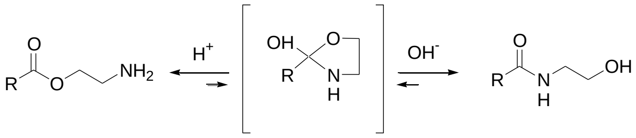
Introduction

Alkanolamides and ester amines feature wide applications in industry. They are used to manufacture nonionic surfactants, detergents, cosmetics, pharmaceuticals, fungicides, dyes, corrosion inhibitors, etc. [1–4].

Mainly alkanolamides and ester amines are obtained by reactions between amino alcohols and esters or free fatty acids. Alkanolamides are also formed during the interaction of amino alcohols and carboxylic acid chlorides [5–7]. However, esters are believed to be better acyl donors than free fatty acids [8].

The amino alcohol and ester interaction is considered transesterification and further intramolecular rearrangement of ester amine (*N*-*O*-acyl migration) with the sequential amide formation. Such a mechanism is proposed for hydroxyalkyl amides formation under mild conditions in a methanolic solution of sodium carbonate [9].

Markey *et al.* [10] showed that the direction of rearrangement of *O*- and *N*-acyl (palmitoyl- or arachidonoyl-) ethanolamines depends on the pH. In particular, during alkaline treatment, *O*-arachidonoylethanolamine or *O*-palmitoylethanol-amine migrates to their *N*-amides. Acid treatment of *N*-arachidonoylethanolamine causes rearrangement to *O*-arachidonoylethanolamine. The rearrangement proceeds through a cyclic intermediate:



It is also established that temperature increasing (over 100 °C) by methyl laurate and monoethanolamine or diethanolamine interaction catalyzed by sodium methoxide or potassium hydroxide leads to a higher concentration of ester amide in the products [11].

Considering the products' composition, the authors claim that the amidation reaction is dominant over the transesterification reaction in the interaction between ethanolamine and methyl linoleate catalyzed by sodium methoxide [8]. An excess of ethanolamine provides a higher yield of ester amide than other solvents (hexane and dichloromethane). Also, the authors note that ethanolamines can act as a catalyst and positively affect the aminolysis reaction. The temperature is reported to have no significant effect on the reaction.

The excessive temperature (over 200 °C) leads to product degradation with an oxazoline derivative formation [12].

The alkanolamides and ester amines obtaining processes occur both in the absence and in the presence of a catalyst.

N-(2-Hydroxyethyl)acetamide is obtained by reacting ethanolamine and ethyl acetate without a catalyst while boiling the reaction mixture and refluxing ethyl acetate. The *N*-(2-hydroxyethyl)acetamide yield is 92–95 %. The molar ratio of ethanolamine: ethyl acetate is 3 : (4–5). The duration of the reaction is 3–4 h [13].

However, most alkanolamides and ester amines obtaining processes are catalytic, and basic catalysts are preferred.

The most available and most common industrial catalysts are alkali metal hydroxides and alcoholates.

In particular, the use of hydroxides and alcoholates of alkali metals in the reactions of methyl esters of aliphatic acids (C_7–C_{21}) with alkanolamines provides a high yield of alkanolamide. Under these conditions, the ester amide content in the reaction mixture does not exceed 3 %. The reaction temperature is 90–150 °C, the molar ratio of alkanolamide to fatty acid ester is from 1 to 1.3, and the reaction time is 1-6 h [14].

Using sodium methoxide as a catalyst and methanol as a solvent at a temperature of 30 °C and a molar ratio of ethanolamine : methyl linoleate – 10 : 1 provides a linoleoyl ethanolamide yield of 95.9–97.2 % [8]. The yield of linoleoyl ethanolamine in 1.5 hours of reaction is 1.6 % and 2.5% in 5 hours.

In addition to hydroxides and alcoholates of alkali metals, potassium *tert*-butoxide, 1,8-diazabicyclo(5.4.0)undec-7-ene, Cs_2CO_3, NaH, 2-*tert*-butylimino-2-diethylamino-1,3-dimethylper-hydro-1,3,2-diazaphosphorine [15], *N*,*N*-bismesylylimidazolium chloride [16], activated layered double Mg/Al-hydroxide [17], Merrifield resin-bound azidoproazaphosphatrane $N_3 = P(MeNCH_2CH_2)_3N$ [18] are efficient catalysts of esters and aminoalcohols interaction.

The heterogeneous catalysts have an advantage due to their separation from the reaction mixture by filtration. We found that among this type of catalysts, high activity in transesterification reactions is demonstrated by ion exchange resins, the main application of which is water treatment [19; 20].

Previously obtained by our results [21] indicate that the kinetics of the products' formation of ethanolamine and pentyl acetate interaction can be largely explained by the above ideas about this process. However, creating a kinetic model and calculating the kinetic indicators of reactions is helpful both for its better understanding and for the results used to model the process.

The study aimed to develop a kinetic scheme of ethanolamine (**1**), pentyl acetate (**5**), and their interaction products and determine the reactions' kinetic indicators.

Materials and methods

Ethanolamine (EA, the 93.8 %wt. content, the rest was water) and 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. A cation exchange resin named KU-2-8 (I grade, static exchange capacity was 1.8 mmol-eq·g^{-1}) was used as the catalyst. Analytical grade propyl alcohol was used as the solvent for chromatographic analysis of ethanolamine and pentyl acetate standard mixture.

A round-bottom flask with reflux was used as the reactor. The reaction mixture was stirred using a magnetic stirrer. The reaction medium was stirred using a glass magnetic stirrer with a speed of 400 rpm. The reaction temperature range was from 383 to 403 K.

Samples of the reaction mixture were taken for chromatographic and conductometric analysis.

A chromatograph "LKhM-80" with a thermal conductivity detector was used to determine the ethanolamine and pentyl alcohol (**6**) content in the reaction mixture. These substances were separated using a metal column 1 m long with a diameter of 3 mm, filled with a stationary phase Polysorb-1. Helium was used as a carrier gas. The consumption of helium was 3 l/h. The temperature of the evaporator was 463 K, the detector was 473 K, and the column was 393 K. The error of the chromatographic analysis did not exceed 4.3 %. The EA and PA mass content was determined by the absolute calibration method.

The amine number (AN) of the reaction mixture was determined by conductometric titration with 0.1 M HCl solution. ELWRO N5721M conductometer was used to measure electrical conductivity. The error of the analysis did not exceed 2.8 %.

The current concentrations of C_{EA} and C_{PA} were calculated on the chromatographic analysis results.

The method of concentration calculation of individual substances (2-aminoethyl acetate (AEA, **2**), *N*-(2-hydroxyetyl)acetamide (HEA, **3**), and 2-(acetylamino)ethyl acetate (AAEA, **4**)), according to the paper [22], was developed.

To calculate the material balance, we assumed that AEA, HEA, and AAEA are formed by the reactions:

$$H_2NCH_2CH_2OH + CH_3C(O)OC_5H_{11} \rightarrow \underset{\mathbf{2}}{CH_3C(O)OCH_2CH_2NH_2} + C_5H_{11}OH$$

$$H_2NCH_2CH_2OH + CH_3C(O)OC_5H_{11} \rightarrow \underset{\mathbf{3}}{CH_3C(O)NH{-}CH_2CH_2OH} + C_5H_{11}OH$$

$$H_2NCH_2CH_2OH + 2CH_3C(O)OC_5H_{11} \rightarrow \underset{\mathbf{4}}{CH_3C(O)OCH_2CH_2NHC(O)CH_3} + 2C_5H_{11}OH$$

The pentyl acetate concentration consumed in the reaction is equal to the pentyl alcohol concentration:

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

Then the current pentyl acetate concentration is:

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

The total current amines concentration characterized by the total content of EA and AEA in the reaction mixture can be calculated by the formula:

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

The amines' concentration is related to the amine number of the reaction mixture with equation:

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

where AN is the amine number of the reaction mixture, mg HCl/g;
m is the mass of the reaction mixture, g;
V is the volume of the reaction mixture, cm^3;
36.5 is the molar mass of hydrochloric acid, g/mol.

Then the AEA concentration is:

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

Given that

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

and

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

the current concentration of AAEA is:

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

and the current concentration of HEA is:

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

The value of the reaction rate constant ($l^2\cdot mol^{-2}\cdot s^{-1}$ or $l\cdot mol^{-1}\cdot s^{-1}$) was determined by dividing the value of the effective reaction rate constant k_i ($l\cdot mol^{-1}\cdot s^{-1}$ or s^{-1}) on the catalyst ion concentration (H^+, mol/l).

The activation enthalpy ($J\cdot mol^{-1}$) was calculated according to the equation:

$$\Delta H^{\neq} = E_A - R\overline{T}, \qquad (10)$$

where EA is the reaction activation energy, $J\cdot mol^{-1}$; R is the molar gas constant, $J\cdot K^{-1}\cdot mol^{-1}$; $\overline{T}$ = 393 K is the average reaction temperature, K^{-1}.

Activation entropy ($J\cdot mol^{-1}\cdot K^{-1}$) was calculated according to the equation:

$$\Delta S^{\neq} = \frac{\Delta H^{\neq}}{\overline{T}} - R\ln\frac{k_B}{h} + R\ln\frac{k}{\overline{T}} = R\left(\ln k_0 - \ln\overline{T} - 24{,}76\right), \qquad (11)$$

where k_B is the Boltzmann constant, $J\cdot K^{-1}$; h is the Planck constant, $J\cdot s^{-1}$; k is reaction rate constant, $l^2\cdot mol^{-2}\cdot s^{-1}$ or $l\cdot mol^{-1}\cdot s^{-1}$; k_0 is the pre-exponential factor of the reaction rate constant, $l^2\cdot mol^{-2}\cdot s^{-1}$ or $l\cdot mol^{-1}\cdot s^{-1}$ [23].

The activation free energy ($J\cdot mol^{-1}$) was determined by the equation:

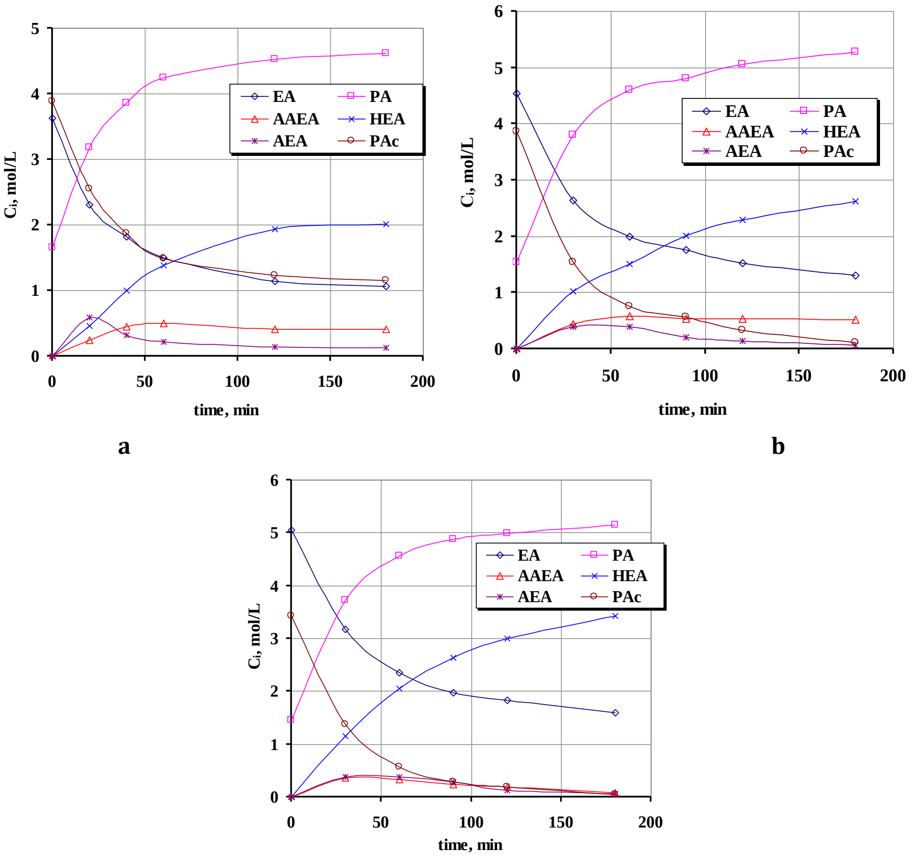
$$\Delta G^{\neq} = \Delta H^{\neq} - \overline{T}\Delta S^{\neq}. \qquad (12)$$

Experimental part

Previously obtained results of the reagents ratio and temperature influence on the indicators of ethanolamine and pentyl acetate interaction catalyzed by cation exchange resin were used to calculate the reactions' kinetic indicators [21].

The content of the catalyst was 2.5 %wt. That corresponded to $4.2\cdot10^{-2}$ mol/l of the H^+-ions concentration. The EA : PAc molar ratio was (0.9–1.5) : 1, and the PA initial content was 14.0–16.2%wt.

Fig. 1 shows the kinetic curves of the reagents' consumption and the reaction products' accumulation at different EA: PAc molar ratios. It is evident that N-(2-hydroxyethyl)acetamide is the final product of the process, and 2-aminoethyl acetate and 2-(acetylamino)ethyl acetate are intermediate products. A decrease in AEA and AAEA concentrations follows their accumulation in the process beginning. It indicates that the AEA formation precedes the AAEA accumulation (Fig. 1 a, b). The EA and PAc consumption is almost the same by the almost equimolar ratio of EA: PAc – 0.9: 1. With a significant excess of EA, the consumption of PA is higher. That indicates, first of all, 2-(acetylamino)ethyl acetate formation by PA and AEA interaction.



a

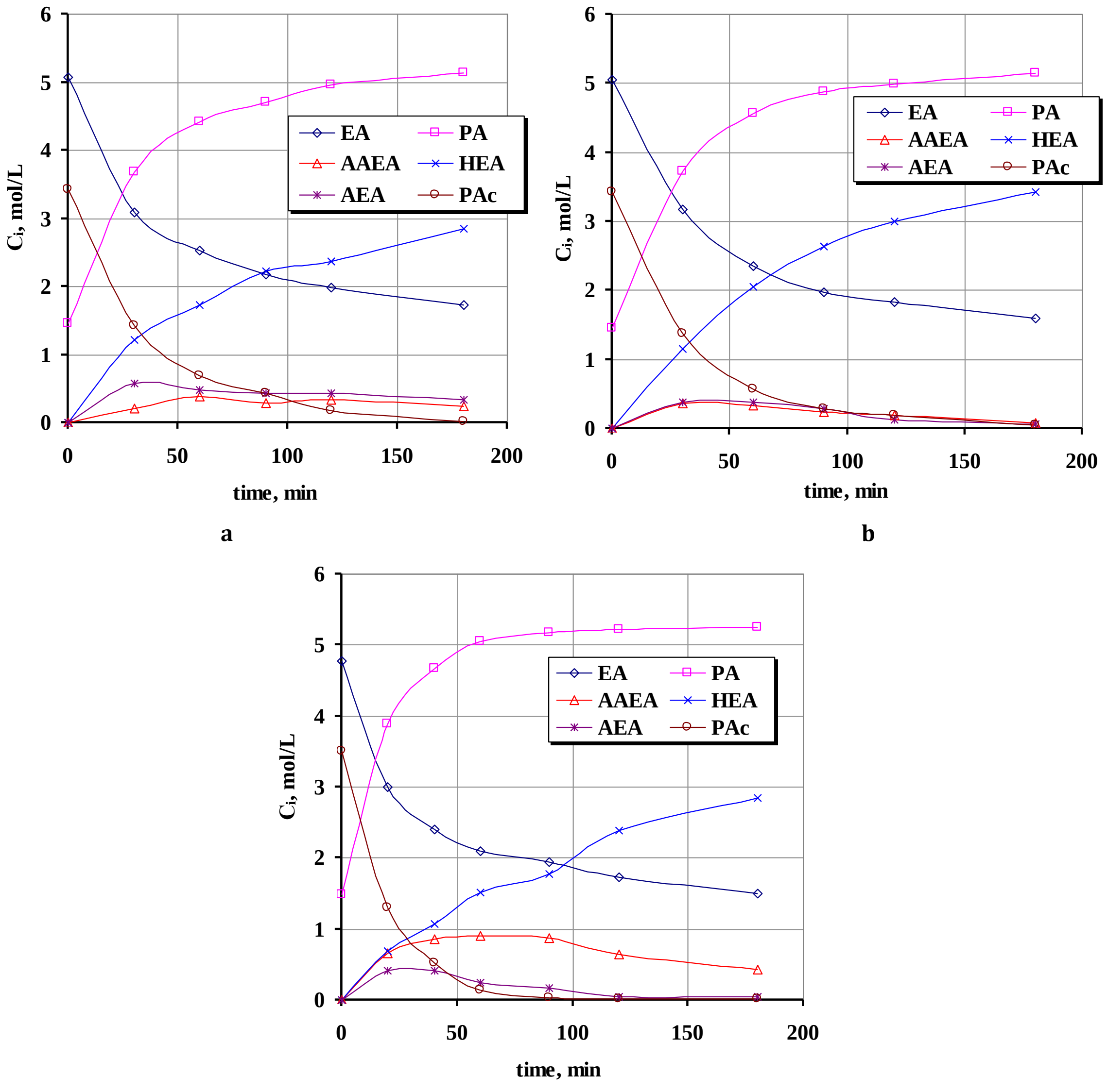
b

c

Fig. 1. Kinetic curves of reagents consumption and reaction products accumulation for different EA : AA ratios: a – 0.9 : 1; b – 1.25 : 1; c – 1.5 : 1. Temperature is 393 K

Another feature of this process is that a much lower AAEA concentration is observed at the highest EA excess. The AAEA concentration also decreases after reaching the maximum. It can be assumed that such changes are due to increased EA and AAEA reaction rate with the HEA formation. The HEA concentration naturally increases with an increase in EA excess.

Similar depends were at different temperatures of the EA and PAc interaction (Fig. 2). That confirms the earlier assumptions. With an increase in temperature at the EA: AA molar ratio of 1.5: 1, the EA and PAc consumption intensity generally increases. Simultaneously, the ester is consumed more intensively. That primarily affects the temporary increase in the intermediate product concentrations, namely 2-aminoethyl acetate and 2-(acetylamino)ethyl acetate. The intensity of HEA accumulation, respectively, is lower. The highest HEA concentration is reached at a temperature of 393 K.



a

b

c

Fig. 2. Kinetic curves of reagents consumption and reaction products accumulation for different temperatures: a – 383 K; b – 393 K; in – 403 K. EA : PAc is 1.5 : 1 (mol.)

The kinetic model was designed to confirm the assumptions about the possible routes of reagents' consumption, and kinetic indicators were calculated.

Results and their discussion

To design the kinetic scheme of ethanolamine, pentyl acetate, and their interaction products, we assumed that the transesterification reactions between EA and PAc are reversible, and the aminolysis reactions are not reversible.

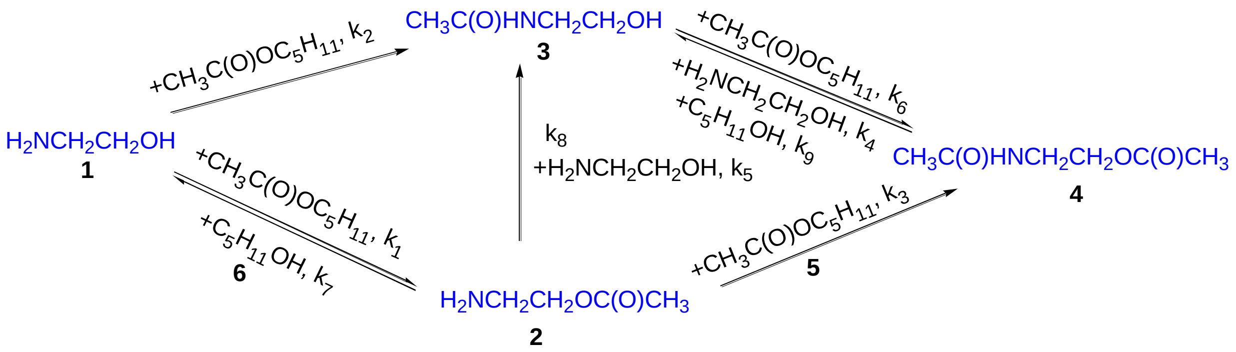
Aminolysis reactions were considered because of the 2-(acetylamino)ethyl acetate formation.

Also, O-N-acyl rearrangement of 2-aminoethyl acetate to N-(2-hydroxyethyl)acetamide through a cyclic intermediate was taken into account [24].

The mixing intensity increase of over 300 rpm does not affect the kinetic curves. Considering that the reaction occurs in stationary conditions, we can assume that the temperature of the cation exchange resin grains and the liquid medium is the same. Therefore is no mass and heat transfer resistance to the surface and to the internal matrix of the catalyst. Thus we considered the reactor contents as a homogeneous continuous medium and the reactions as quasi-homogeneous. This assumption allowed using constants related to the H⁺ ions catalyst concentration.

Unfortunately, we could not establish each reagent order for this system of consecutive, parallel, reversible, and irreversible reactions provided the interaction of three reactive functional groups. Therefore, we accepted the first order for each reagent to simplify calculations. For these same reasons, we accepted the first order of the catalyst.

The following scheme of reactions between ethanolamine, pentyl acetate, and their interaction products was accepted:



Scheme 1. Kinetic scheme of ethanolamine and pentyl acetate interaction

According to this scheme, the reagents' consumption and the products' formation are described by the kinetic equations:

$$\frac{dC_{EA}}{d\tau} = -k_1C_{EA}C_{PAc} - k_2C_{EA}C_{PAc} - k_4C_{EA}C_{AAEA} - k_5C_{EA}C_{AEA} + k_7C_{AEA}C_{PA}, \quad (13)$$

$$\frac{dC_{PAc}}{d\tau} = -k_1C_{EA}C_{PAc} - k_2C_{EA}C_{PAc} - k_3C_{AEA}C_{PAc} - k_6C_{HEA}C_{PAc} + k_7C_{AEA}C_{PA}, \quad (14)$$

$$\frac{dC_{AEA}}{d\tau} = k_1C_{EA}C_{PAc} - k_3C_{AEA}C_{PAc} - k_5C_{EA}C_{AEA} - k_7C_{AEA}C_{PA} - k_8C_{AEA}, \quad (15)$$

$$\frac{dC_{HEA}}{d\tau} = k_2C_{EA}C_{PAc} + k_5C_{EA}C_{AEA} + 2k_4C_{EA}C_{AAEA} - k_6C_{HEA}C_{PAc} + k_8C_{AEA} + k_9C_{AAEA}C_{PA}, \quad (16)$$

$$\frac{dC_{AAEA}}{d\tau} = k_3C_{AEA}C_{PAc} - k_4C_{EA}C_{AAEA} + k_6C_{HEA}C_{PAc} - k_9C_{AAEA}C_{PA}, \quad (17)$$

$$\frac{dC_{PA}}{d\tau} = k_1C_{EA}C_{PAc} + k_2C_{EA}C_{PAc} + k_3C_{AEA}C_{PAc} + k_6C_{HEA}C_{PAc} - k_7C_{AEA}C_{PA} - k_9C_{AAEA}C_{PA}, \quad (18)$$

where $k_i = k_i^{'}C_{H^+}$, $k_i^{'}$ is the rate constant, $l^2\cdot mol^{-2}\cdot s^{-1}$ or $l\cdot mol^{-1}\cdot s^{-1}$; k_i is the effective rate constant; C_{H^+} is a H⁺ ions concentration of the ion exchange resin, mol/l.

The system of these equations contains nine unknown reaction rate constants. Therefore, the solution was found by numerical integration using Euler's method, particularly by selecting appropriate constants values considering the experiments' results.

The values of the reaction rate constants were determined by iteration and considered acceptable if the value of δ calculated by the formula was minimal:

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

where $C_{i,exp}$ and $C_{i,calc}$ are experimentally determined and calculated concentration value, mol/l; N is the number of definitions [25].

The calculated value of δ was 7.7 to 23.6 %.

Each determined effective reaction rate constant used in the kinetic equations is the product of the rate constant and the catalyst concentration. In particular, the H⁺ ion concentration for cation exchange resins is determined by their static exchange capacity value. From this reasoning, the value of the rate constants was calculated similarly to the paper [26]. The constants' values for the different reagents ratios and temperatures are given in table 1–2.

The high values of the rate constants (k_2, k_4, k_5) indicate the H^+ ions catalysis of the aminolysis reaction. This fact confirms the correctness of the assumption made about the aminolysis reactions evidence in the catalytic process.

Table 1

Rate constants of ethanolamine and pentyl acetate interaction for various reagent molar ratios. Confidence level – 95%

Indicator	Rate constants,								
	$l^2 \cdot mol^{-2} \cdot s^{-1}$							$l \cdot mol^{-1} \cdot s^{-1}$	$l^2 \cdot mol^{-2} \cdot s^{-1}$
EA : PAc (mol.)	$k_1 \cdot 10^4$	$k_2 \cdot 10^4$	$k_3 \cdot 10^3$	$k_4 \cdot 10^3$	$k_5 \cdot 10^4$	$k_6 \cdot 10^4$	$k_7 \cdot 10^4$	$k_8 \cdot 10^3$	$k_9 \cdot 10^4$
0.9 : 1	10.2	9.5	2.3	3.6	3.4	5.3	2.4	4.6	1.5
1.25 : 1	9.9	9.1	2.4	3.5	3.1	5.4	2.6	4.7	1.4
1.5 : 1	9.2	8.6	2.0	3.3	3.4	4.9	2.2	4.2	1.3
Average k_i	9.8	9.0	2.2	3.5	3.3	5.2	2.4	4.5	1.4
Relative error,%	16.3	16.7	12.9	17.6	13.8	7.2	0.2	9.5	17.6

Table 2

Rate constants of ethanolamine and pentyl acetate interaction under various temperatures

Indicator	Rate constants								
	$l^2 \cdot mol^{-2} \cdot s^{-1}$							$l \cdot mol^{-1} \cdot s^{-1}$	$l^2 \cdot mol^{-2} \cdot s^{-1}$
T, K	$k_1 \cdot 10^4$	$k_2 \cdot 10^4$	$k_3 \cdot 10^3$	$k_4 \cdot 10^4$	$k_5 \cdot 10^4$	$k_6 \cdot 10^4$	$k_7 \cdot 10^4$	$k_8 \cdot 10^3$	$k_9 \cdot 10^4$
383	8.0	8.4	1.9	3.0	1.8	3.6	1.1	2.3	0.9
393	10.2	9.5	2.3	3.6	3.4	5.3	2.4	4.6	1.5
403	19.4	10.8	3.9	5.9	5.9	14.7	3.4	6.6	2.2

The minimum value of the calculation relative error of the reaction rate constants for different molar ratios of EA : PAs is 0.2% (for k_7), and the maximum value of this error is 17.6% (for k_9) for the confidence level of 95% (table 1).

The calculated constants were used for modeling of the EA and PAc interaction process. An example of the reactant concentrations' change determined experimentally and calculated is shown in fig. 3. The close match of experimental points and kinetic curves testifies to the adequacy of the determined rate constant values for the proposed kinetic model of ethanolamine and pentyl acetate interaction catalyzed by cation exchange resin.

Based on the reaction rate constants determined for the temperature range from 383 to 403 K, the pre-exponential factor and activation energy of the reactions for schema 1 were calculated using the Arrhenius equation (Fig. 4, Table 3).

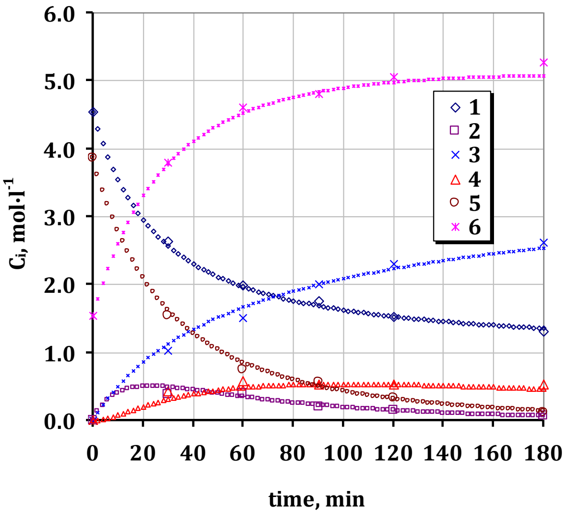


Fig. 3. Experimental points and kinetic curves (lines) of the ethanolamine and pentyl acetate interaction catalyzed by cation exchange resin calculated according to the kinetic constants. The temperature is 383 K, and the EA : PAc ratio is 1.25 : 1 (mol.)

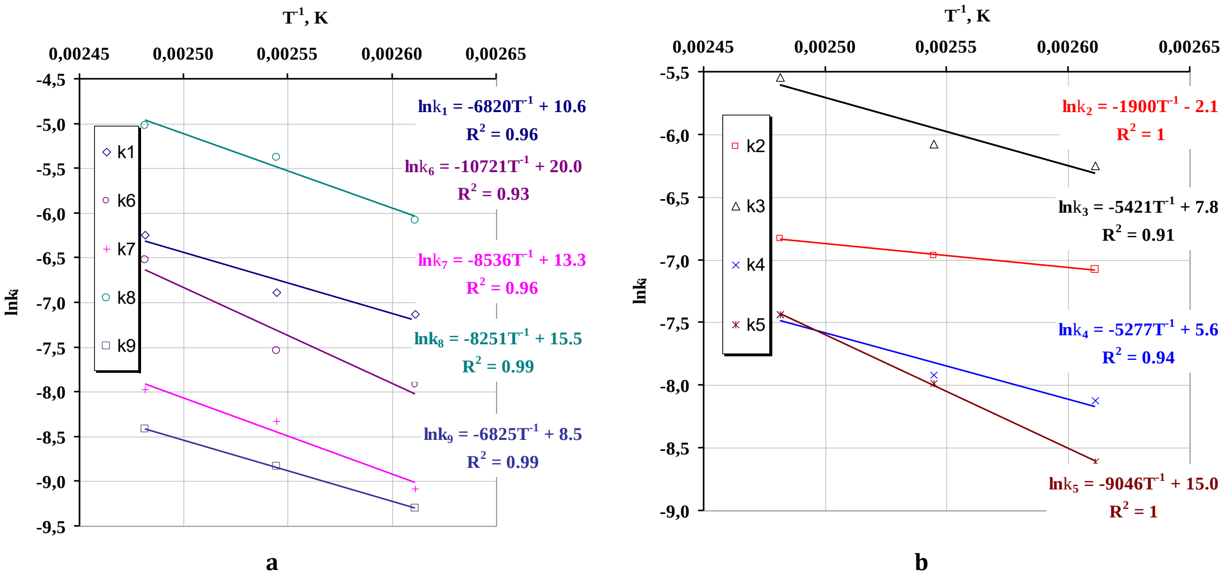


Fig. 4. Arrhenius plot of ethanolamine and pentyl acetate interaction catalyzed by cation exchange resin: a – aminolysis and O-N-acyl migration; b – transesterification

The lowest activation energy (15.8 kJ·mol^{-1}) is for the reaction between the EA and PAc with the N-(2-hydroxyethyl)acetamide formation, and the highest activation energy (89.1 kJ·mol^{-1}) is for the reaction between the HEA and PAc with the 2-(acetylamino)ethyl acetate formation. The activation energies of other reactions are from 43.9 to 75.2 kJ·mol^{-1}.

Also, according to equations (10–12), the activation thermodynamic indicators of reactions that occur by ethanolamine and pentyl acetate interaction catalyzed by cation exchange resin were calculated (Table 3).

Table 3 also shows the absolute and relative errors of energy, enthalpy, entropy, and free activation energy calculations. The higher error of E_i and $\Delta H^{\neq}_i$ for the rate constant k_2 is caused by a much lower values of the energy and enthalpy activation of the reaction between ethanolamine and pentyl acetate formed N-(2-hydroxyethyl)acetamide.

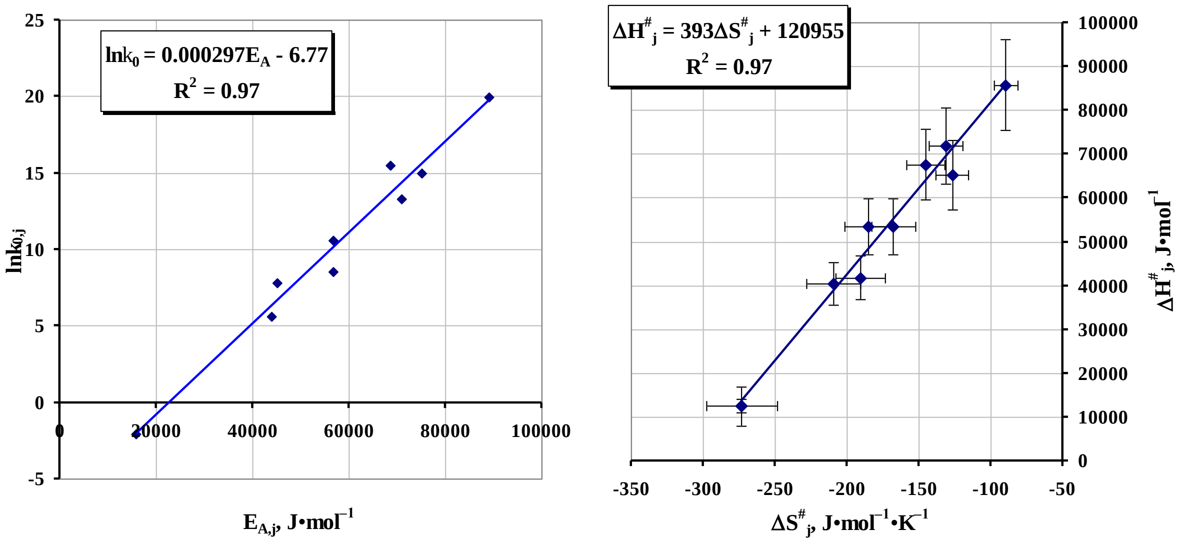
Table 3

Activation and thermodynamic indicators of ethanolamine and pentyl acetate interaction catalyzed by cation exchange resin

Indicator for k_i	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8	k_9
$k_{0,i}$, $l^2 \cdot mol^{-2} \cdot s^{-1}$ or $l \cdot mol^{-1} \cdot s^{-1}$	$4.0 \cdot 10^4$	$1.2 \cdot 10^{-1}$	$2.4 \cdot 10^3$	$2.7 \cdot 10^2$	$3.3 \cdot 10^6$	$4.7 \cdot 10^8$	$5.8 \cdot 10^5$	$5.4 \cdot 10^6$	$5.0 \cdot 10^3$
$E_i \cdot 10^{-3}$, $J \cdot mol^{-1}$	55.9	15.8	45.0	44.0	75.3	89.1	71.0	68.6	56.7
$\Delta H^{\neq}_i \cdot 10^{-3}$, $J \cdot mol^{-1}$	52.7	12.6	41.8	40.8	72.0	85.9	67.7	65.3	53.5
$\Delta S^{\neq}_i$, $J \cdot mol^{-1} \cdot K^{-1}$	-169	-273	-191	-208	-130	-42	-145	-126	-185
$\Delta G^{\neq}_i \cdot 10^{-3}$, $J \cdot mol^{-1}$	119.2	119.8	116.7	122.5	123.1	121.0	124.8	115.1	126.0
$\Delta(E_i) \cdot 10^{-3}$, $\Delta(\Delta H^{\neq}) \cdot 10^{-3}$, $\Delta(\Delta G^{\neq}) \cdot 10^{-3}$, $J \cdot mol^{-1}$	4.5	4.7	4.0	4.7	4.1	3.0	0.4	3.5	4.7
$\delta(E_i)$,%	8.0	28.9	8.9	10.7	5.5	3.4	0.6	5.0	8.3
$\delta(\Delta H^{\neq}_i)$,%	8.5	36.7	9.6	11.6	5.8	3.5	0.7	5.3	8.8
$\delta(\Delta S^{\neq}_i)$,%	6.9	4.3	5.3	5.7	8.1	8.5	0.8	6.9	6.5
$\Delta(\Delta G^{\neq}_i)$,%	3.7	3.7	3.4	3.8	3.3	2.5	0.4	3.0	3.7

Despite the visible compensation for high or low activation energies by corresponding values of pre-exponential factor logarithms (fig. 5 a), we did not find an isokinetic relationship for this set of reactions [11]. It is no single common point of the intersection of the lines in the coordinates $\ln k_i - T^{-1}$ (fig. 4).

Accordingly, we can assume that it is only a compensatory effect for reactions between ethanolamine, pentyl acetate, and their interaction products. This conclusion is confirmed by the plot $\Delta Gi^{\neq}/RT = f(\Delta Hi^{\neq})$ according to Exner [27, 28], as well as the calculation of error bars, the results of which are shown in the diagram of the dependence $\Delta H_i^{\neq} = f(\Delta S_i^{\neq})$ (Fig. 5 b, and 6, Table 3) [29].



a **b**

Fig. 5. The preexponential factor logarithm vs. activation energy (a) and the activation enthalpy vs. activation entropy (b) of ethanolamine and pentyl acetate interaction catalyzed by cation exchange resin

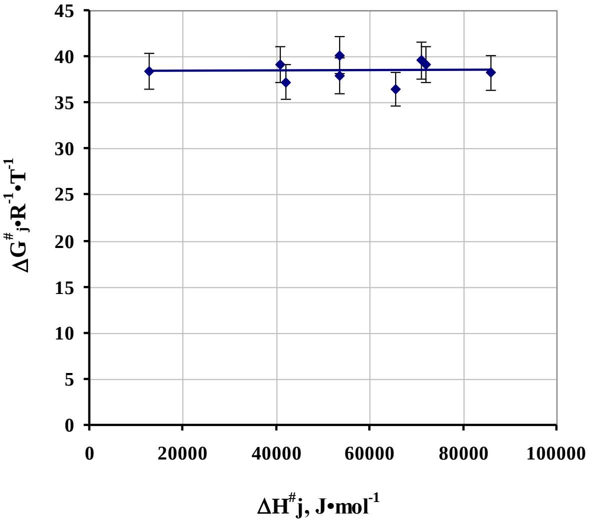


Fig. 6. Exner plot of the $\Delta G_j^{\neq}\cdot R^{-1}\cdot T^{-1}$ value vs. activation enthalpy. The error bars are 5 %

Extrapolation of the lines shown in fig. 4 to the lower and higher temperatures reveals a significant number of intersections of Arrhenius curves describing the investigated reactions. It is the reason for the established linear dependence of $\ln k_0–f(E_A)$ for all reactions involving ethanolamine, pentyl acetate, and their interaction products. The linearity of the dependence $\ln k_0–f(E_A)$ can be explained by the local isokinetic effects of several groups of aminolysis, O-N-acyl migration, and transesterification reactions. These reactions involve structurally similar substances differed by one or another substituent. However, this statement needs more detailed research.

Based on the obtained results, we can assume that transesterification and aminolysis reactions are the basis of transformations involving ethanolamine, pentyl acetate, and their interaction products catalyzed by cation exchange. The separate groups of reactions obviously have a similar mechanism, and the proposed kinetic model adequately describes the process of obtaining alkanolamides, ester amines, and ester amides. Such a model can be used for modeling the *N*-(2-hydroxyetyl)acetamide manufacture from ethanolamine and pentyl acetate.

Conclusions

A scheme was developed for the interaction of ethanolamine, pentyl acetate, and the products of their interaction with the formation of N-(2-hydroxyethyl)acetamide as the final product in the reactions of aminolysis, O-N-acyl migration, and transesterification catalyzed by H-cation exchanger.

The determined values of the rate constants for the quasi-homogeneous reaction model confirmed the assumption about the actuality of the esters aminolysis by ethanolamine or pentyl alcohol catalyzed by H$^+$ ions.

It was established that the reaction of N-(2-hydroxyethyl)acetamide formation by pentyl acetate with ethanolamine aminolysis has the lowest activation energy (15.8 kJ·mol^{-1}), and the reaction of 2-(acetylamino)ethyl acetate formation by N-(2-hydroxyethyl)acetamide with pentyl acetate transesterification has the highest activation energy (89.1 kJ·mol^{-1}).

We assume the compensatory effect and the absence of an isokinetic relationship for the entire set of reactions.

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