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RESEARCH ARTICLE

Kinetic regularities of neopentyl glycol esterification with acetic and 2-ethylhexanoic acids

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Abstract

Objectives. Development of a domestic technology for producing environmentally friendly non-phthalate plasticizers, lubricants and transformer fluids based on neopentyl glycol (NPG), an oxo-synthesis product.

Methods. The methodology of the work was to study the kinetic laws of NPG esterification with acetic and 2-ethylhexanoic acids under self-catalysis conditions with an 8-fold molar excess of monocarboxylic acids. The production of NPG esters was carried out by azeotropic esterification in the presence of solvents—benzene and *m*-xylene. The resulting diesters were isolated from the reaction mass by vacuum rectification. The purity of the obtained NPG diesters was no less than 99.7 wt %. Analysis of the qualitative and quantitative composition of reaction samples was carried out using infrared spectroscopy, gas chromatography–mass spectrometry and gas–liquid chromatography.

Results. The paper presents the results of kinetic studies on NPG esterification of with acetic and 2-ethylhexanoic acids. It compares the reaction rates and reactivity of the acids used. Under the given conditions, NPG diesters were produced, and some of their physicochemical properties were determined. This enabled the data obtained to be used for the development of industrial technology in the production of NPG diesters.

Conclusions. It was established that with an eightfold molar excess of acid under self-catalysis conditions, a yield of NPG diacetate equal to 95% is achieved within 20–22 h at an optimal process temperature of 100–110°C; NPG di(2-ethylhexanoate)—within 26–28 h at 160–170°C. The activation energies and pre-exponential factors for the formation of NPG mono- and diesters with acetic and 2-ethylhexanoic acids were established. The paper presents the kinetic models of esterification.

Keywords

neopentyl glycol, neopolyols, esterification, self-catalysis, esters, acetic acid, 2-ethylhexanoic acid, plasticizer

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НАУЧНАЯ СТАТЬЯ

Кинетические закономерности этерификации неопентилгликоля уксусной и 2-этилгексановой кислотами

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Аннотация

Цели. Разработка отечественной технологии получения экологически чистых нефталатных пластификаторов, смазывающих и трансформаторных жидкостей на основе продукта оксосинтеза — неопентилгликоля (НПГ).

Методы. Методология работы заключалась в исследовании кинетических закономерностей реакции этерификации НПГ уксусной и 2-этилгексановой кислотами в условиях самокатализа при восьмикратном мольном избытке монокарбоновых кислот. Наработку сложных эфиров НПГ вели методом азеотропной этерификации в присутствии растворителей — бензола и *м*-ксилола. Полученные диэфиры выделяли из реакционной массы вакуумной ректификацией. Чистота полученных диэфиров НПГ составляла не менее 99.7 мас. %. Качественный и количественный состав реакционных проб проводили методами инфракрасной спектроскопии, газовой хромато-масс-спектрометрией и газожидкостной хроматографией.

Результаты. В работе представлены результаты кинетических исследований реакций этерификации НПГ уксусной и 2-этилгексановой кислотами. Проведено сравнение скоростей реакции и реакционной способности используемых кислот. В заданных условиях наработаны диэфиры НПГ и определены их некоторые физико-химические свойства, позволяющие рекомендовать полученные данные для разработки промышленной технологии получения сложных диэфиров НПГ.

Выводы. Установлено, что при восьмикратном мольном избытке кислоты в условиях самокатализа выход диацетата НПГ, равный 95%, достигается в течение 20–22 ч при оптимальной температуре процесса 100–110°С; ди(2-этилгексаноата) НПГ — в течение 26–28 ч при 160–170°С. Определены энергии активации и предэкспоненциальные множители реакций образования моно- и диэфиров НПГ с уксусной и 2-этилгексановой кислотами. Представлены кинетические модели этерификации.

Ключевые слова

неопентилгликоль, неополиолы, этерификация, самокатализ, сложные эфиры, уксусная кислота, 2-этилгексановая кислота, пластификатор

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INTRODUCTION

In the current environmental situation, the production of phthalate plasticizers is strictly regulated by environmentalists. This requires modern manufacturers of plasticizers to actively develop and create alternative raw materials and options for their production. Thus, the synthesis gas required for the synthesis of olefins by oxo-synthesis can be obtained by steam reforming or partial oxidation of methane. As a result, natural gas is an accessible raw material for the production of alcohols and carboxylic acids which are the starting components in esterification reactions. Carboxylic acids are obtained by low-temperature oxidation of the products of lower olefins hydroformylation (aldehydes) in oxygen or air, while alcohols are obtained by catalytic hydrogenation.

Oxosynthesis processes are primarily aimed at producing oxygen-containing products of linear structure. However, 30–35% of the products are aldehydes of iso structure [1]. Regioisomeric isobutyraldehyde is among them. Its aldol condensation with formaldehyde followed by catalytic hydrogenation produces one of the most important neo alcohols: neopentyl glycol (NPG, 2,2-dimethyl-1,3-propanediol).

Due to the structural features of NPG (i.e., the presence of a quaternary carbon atom in the molecule), NPG esters can be characterized by their good ability to biodegrade under aerobic and anaerobic conditions [2]. They are thermostable and have low melting points [3]. They have a reduced potential for oxidation and hydrolysis when compared to natural esters [4]. For this

reason, they are considered as potential environmentally friendly insulating liquids [5].

A significant part of industrially produced NPG is used to produce esters of various structures, used in the cosmetic and polymer industries, as well as plasticizers and synthetic oils [6]. Plasticizers based on NPG belong to hazard class IV [7] and are environmentally safer compared to phthalate plasticizers, which belong to hazard class II [7].

The global NPG market was worth USD 1346 mln in 2020, and its average annual growth rate over the forecast period of 2021–2027 will be 4.1%[1]. NPG production is not currently carried out in Russia, although Russia possesses all the prerequisites for mastering modern oxo-synthesis processes and their improvement. This will allow domestic production of environmentally friendly plasticizing materials to be established and the amount of natural gas burned to be reduced.

The main industrial method for producing esters is esterification reaction using acidic homogeneous and heterogeneous catalysts: sulfuric and orthophosphoric acids; and sulfonic cation exchangers. The use of mineral acids as catalysts leads to tarring and a decrease in the color stability of the reaction mass, thus increasing the cost of isolating and purifying the target product. There is a tendency to use heterogeneous catalysts (ion exchange resins) in esterification reactions due to the ease of separation of the reaction mass from the catalyst and the absence of wastewater [8].

The carboxylic acids used for esterification are weak acylating reagents capable of autoprotolysis [9]. This enables the process to be carried out without the use of a catalyst: under conditions of self-catalysis. The pK values of carboxylic acids do not differ greatly from the pK of the catalyst [the pK values of acetic acid (AA) and the H_3PO_4 catalyst (in the first group) are 4.76 and 2.12, respectively]. Despite the longer reaction time under self-catalysis conditions, the problem of side reactions occurring in the system is resolved. This makes it possible to obtain esters which require minimal additional purification, if necessary.

The literature devoted to studies on NPG esterification contains practically no information about conducting kinetic studies of the esterification reaction under self-catalysis conditions. Therefore, we conducted studies of the kinetics of NPG esterification with acetic and 2-ethylhexanoic (2EH) acids under conditions of self-catalysis, in order to create a theoretical basis for the development of domestic technology for the production of environmentally friendly non-phthalate plasticizers.

EXPERIMENTAL

Materials

Two monocarboxylic acids—AA and 2EH—with a purity of at least 97 wt % and NPG with a purity of at least 99.8 wt % were used as reagents in the study of NPG etherification.

Synthesis of NPG esters

NPG is a diatomic alcohol. The esterification reaction with its participation is equilibrium, and proceeds sequentially through the formation of a monoester, ending with the formation of a diester (Fig. 1). In addition, a disproportionation reaction of monoesters is also possible. However, this reaction occurs to a very small extent, and its contribution to the process kinetics is insignificant [10].

The production of NPG diesters was carried out by means of azeotropic esterification at an acid/alcohol molar ratio of 8 : 1, under conditions of self-catalysis using a Dean–Stark trap to separate reaction water. Benzene (*Reaktiv*, Russia) was used as an azeotrope-forming agent in the synthesis of NPG diacetate, and *m*-xylene (*EKOS-1*, Russia) in the synthesis of NPG di(2-ethylhexanoate). The choice of acylating reagents is determined by the difference in the lengths of their alkyl chains. This allows for evaluation of the influence of the length of the acid carbon chain on the reaction rate, on the time of ester synthesis, on some physicochemical properties, and, as a consequence, on the scope of application of the resulting NPG diesters. The completion of the reaction was determined by the cessation of water formation. Next, the excess carboxylic acid was distilled off under vacuum. The resulting diesters were washed with a 5% $NaHCO_3$ solution to remove traces of the acid. In the case of NPG diacetate, purification from by-products was carried out by means of vacuum rectification. In the case of NPG di(2-ethylhexanoate), purification was carried out by treatment with bleached clay, in order to remove resins. Then the product was washed with an aqueous solution of sodium hypochlorite for clarification [11]. The purity of the obtained esters was no less than 99 wt % (determined by gas–liquid chromatography, GLC).

Identification and analysis

Identification of the components of the reaction mixtures was carried out by means of gas chromatography–mass spectrometry using an Agilent 6850 gas chromatograph (*Agilent Technologies*, USA) equipped with an Agilent 19091S-433E capillary column (30 m × 250 μm × 0.25 μm) on an HP-5MS

[1] Global neopentyl glycol market 2021 – industry statistics. Gen Consulting. 2020.

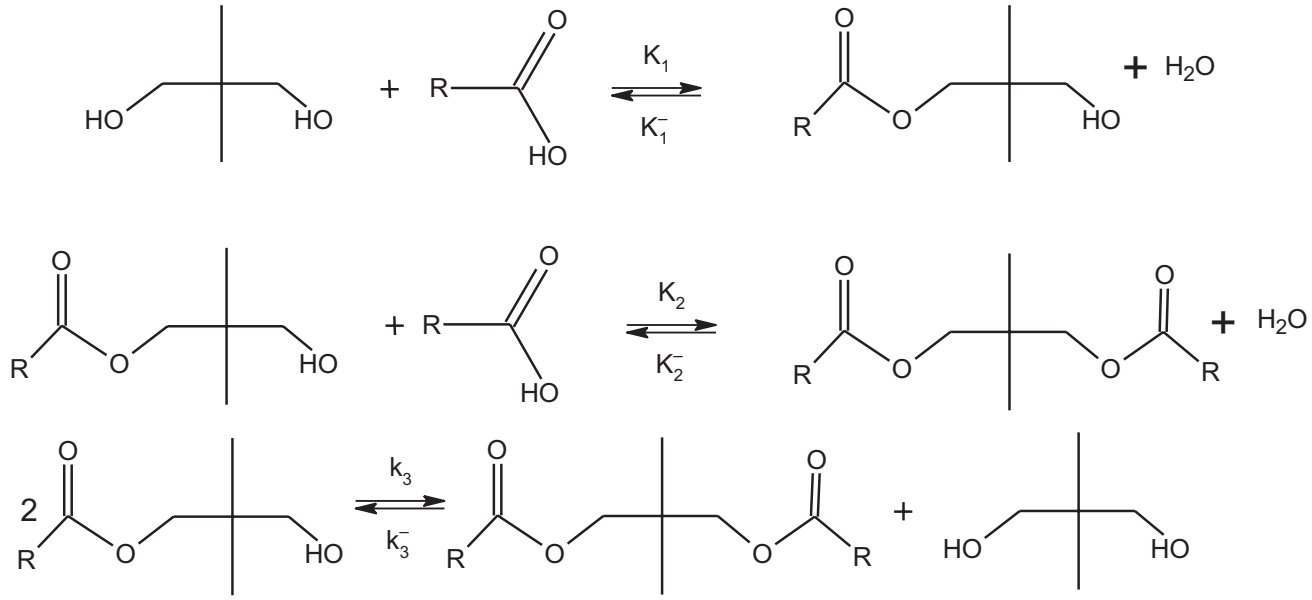

Fig. 1. Scheme of NPG esterification with monocarboxylic acids

chromatographic column (stationary phase: 5% diphenylpolysiloxane + 95% dimethylpolysiloxane) and an Agilent 5975C VL MSD mass selective detector at an ionizing voltage of 70 eV.

Furthermore, the structure of the NPG diesters obtained was confirmed by infrared (IR) spectrometry using an FSM 2201 IR Fourier spectrometer (*Infraspek*, Russia) equipped with a multiple attenuated total internal reflection horizontal type MNPVO36 attachment with a zinc selenide-based prism.

The reaction samples were analyzed by GLC using a Kristall-2000M chromatograph (*Chromatec*, Russia) equipped with a flame ionization detector and a capillary column measuring 100 m × 0.2 mm × 0.5 μm with a grafted stationary liquid phase DB-1 (dimethylpolysiloxane). The masses of the components were determined by GLC using an internal standard. Analysis modes are presented in Table 1.

Table 1. Modes of reaction mass analysis using GLC

Parameter	NPG + AA	NPG + 2EH
Column temperature, °C	100–170*	250
Evaporator temperature, °C	350	330
Detector temperature, °C	300	300
Carrier gas	Helium	
Flow rate, mL/min	0.7	
Split ratio	1/100	

* The temperature was maintained at 100°C for 10 min, then the column temperature was raised to 170°C at a heating rate of 20°C/min.

Kinetic studies

Kinetic studies were carried out under conditions of self-catalysis in the absence of an azeotrope-forming agent at an acid/alcohol molar ratio of 8 : 1 under nonequilibrium conditions (with distillation of reaction water) with intense stirring. The choice of the acid/alcohol molar ratio was determined by achieving the optimal equilibrium conversion of NPG based on the thermodynamic analysis of the system. The reactions were carried out under thermostatting in an open ideal mixing reactor system: a three-neck round-bottom flask equipped with a stirrer and a Liebig refrigerator. NPG is a crystalline substance, so the start time of the kinetic experiment was counted from the moment of its dissolution in the acid at the reaction temperature.

Under the conditions of kinetic studies, reverse hydrolysis reactions did not occur, since water was removed from the system [4]. This allowed the account the water concentration not to be taken into account in the kinetic equations, also allowing the rate constant values to be calculated only for direct reactions.

As a result, the system of kinetic equations looks as follows:

$$\frac{\partial C_{\text{ME}}}{\partial \tau} = k[\text{NPG}][\text{A}] - k_2[\text{DE}][\text{A}], \quad (1)$$

$$\frac{\partial C_{DE}}{\partial \tau} = k_2 [ME][A], \quad (2)$$

where A is monocarboxylic acid; ME is NPG monoester; DE is NPG diester; C_{ME} and C_{DE} are concentrations of monoester and diester, respectively; τ is time.

Based on the available literature data, the reaction order for each component was taken to be equal to 1 [10–13]. The rate constants k_1 and k_2 were determined by jointly solving kinetic Eqs. (1) and (2) for each temperature under the assumption that $\frac{\partial C_i}{\partial \tau} \approx \frac{\Delta C_i}{\Delta \tau}$ at $\Delta\tau$ = 10 min. Optimization of values was carried out using the Euler method.

RESULTS AND DISCUSSION

Table 2 presents the characteristics of the mass spectra of the samples of the NPG diacetate and di(2-ethylhexanoate) obtained. The data shows that the mass spectrum of NPG diacetate can be characterized by 100% relative intensity of the $C_2H_3O^+$ ion, and in the case of di-2-ethylhexanoate, of the *tert*-$C_4H_9^+$ ion. The maximum intensity of the latter is due to energetically favorable pathways of decomposition of the *n*-butyl fragment of the ester molecule acidic part followed by its isomerization into the *tert*-butyl cation [14]. One notable feature of the NPG esters fragmentation is the elimination of the $CH_3^\bullet$ radical from the quaternary carbon atom of the ester molecule alcohol part.

Besides, IR spectra of the synthesized esters were obtained. They are presented in Figs. 2 and 3.

All the spectra contain characteristic intense absorption bands in the region of 2860–2975 cm^{-1} indicating the presence of stretching vibrations of C–H bonds related to the alkyl moiety of the acidic part of the molecule. Absorption bands in the region of 1750–1735 cm^{-1} are characteristic of the C=O bond of the ester group. The band in the range of 1000–1260 cm^{-1} represents bending vibrations of the C–O bond. A small band in the region of 3550–3450 cm^{-1} characterizes the presence of an OH group, confirming the presence of NPG monoesters (up to 0.1 wt %) in the resulting diesters.

Determination of kinetic characteristics

The study of the kinetics of NPG diacetate formation was carried out in the temperature range of 70–110°C with steps of 10°C and a time interval of 0–300 min. The initial concentrations of the reagents in all the experiments were: NPG — 1.8 mol/L; and AA — 14.2 mol/L. Experiments involving 2EH acid were carried out at temperatures of 140–170°C with steps of 10°C and a time interval of 0–160 min. The initial concentrations of the reagents in all the experiments were: NPG — 0.8 mol/L; and 2EH — 6.1 mol/L. In order to control the experiment, material balance was calculated at each time point to assess the relative deviation of the analytically determined masses of the components from the mass of the loaded components. The average deviation did not exceed 10%.

Typical chromatograms of reaction masses are presented in Figs. 4 and 5.

Figure 6 shows the results obtained for one of the study temperatures. They indicate the concentration dependencies of the reaction mixture components on time, illustrating the sequence of NPG transformation into monoesters and of monoesters into diesters.

The dynamics of the reactions over time show that the rate of the reaction with the participation of AA is higher than in the case of 2EH. This may be due to the strength of the acids used (the dissociation constant of AA is greater than that of 2EH) and due to spatial factors.

The values of the rate constants k_1 and k_2 obtained during the experiments are presented in Table 3.

The pre-exponential factors and activation energies were determined graphically on the basis of the obtained approximation equations for the dependence of the natural logarithm of the rate constants on the inverse temperature. The resulting Arrhenius equations for a system with CM have the form:

$$k_1 = 5.74 \cdot 10^4 \cdot e^{\frac{(-57.6 \pm 2.2)}{RT}}, \quad (3)$$

$$k_2 = 1.94 \cdot 10^3 \cdot e^{\frac{(-49.9 \pm 12.1)}{RT}}, \quad (4)$$

Table 2. Characterization of the main series of ions in mass spectra of synthesized NPG diesters

NPG ester	Main mass spectrum ion series 70 eV, *m/z*, (structure, % rel.)
Diacetate	**188** ($M^{+\bullet}$, 0); **145** ($[M^{+\bullet}–C_2H_3O^\bullet]^+$, 1); **115** ($[M^{+\bullet}–C_3H_5O_2^\bullet]^+$, 20); **86** ($[M^{+\bullet}–C_2H_3O_2^\bullet$; $–C_2H_3O^\bullet]^+$, 15); **56** ($[M^{+\bullet}–2C_2H_3O_2^\bullet$; $–CH_3^\bullet]^+$, 25); **43** ($C_2H_3O^+$, 100)
Di(2-ethylhexanoate)	**356** ($M^{+\bullet}$, 0); **341** ($[M^{+\bullet}–CH_3^\bullet]^+$, 1); **328** ($[M^{+\bullet}–C_2H_4]^{+\bullet}$, 3); **300** ($[M^{+\bullet}–C_4H_8]^{+\bullet}$, 8); **213** ($[M^{+\bullet}–C_8H_{15}O_2^\bullet]^+$, 45); **156** ($[M^{+\bullet}– C_8H_{15}O_2^\bullet$;$–C_4H_9^\bullet$, 35$]^{+\bullet}$); **127** ($[M^{+\bullet}–C_4H_9^\bullet$; $–C_8H_{15}O_2^\bullet$; $–2CH_3^\bullet]^+$, 85); **99** (*sec*-$C_7H_{15}O^+$, 43); **57** (*tert*-$C_4H_9^+$, 100)

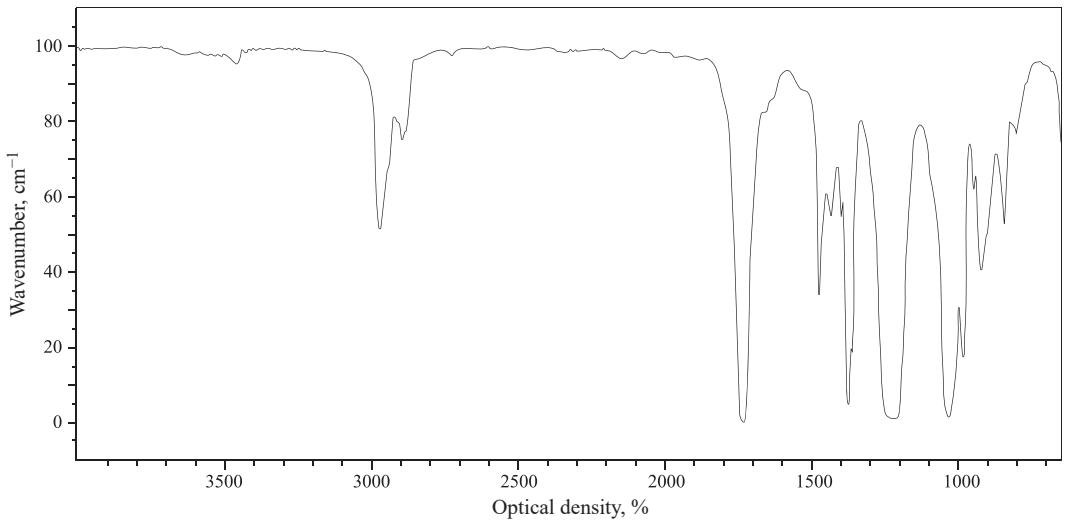

Fig. 2. IR spectrum of NPG diacetate

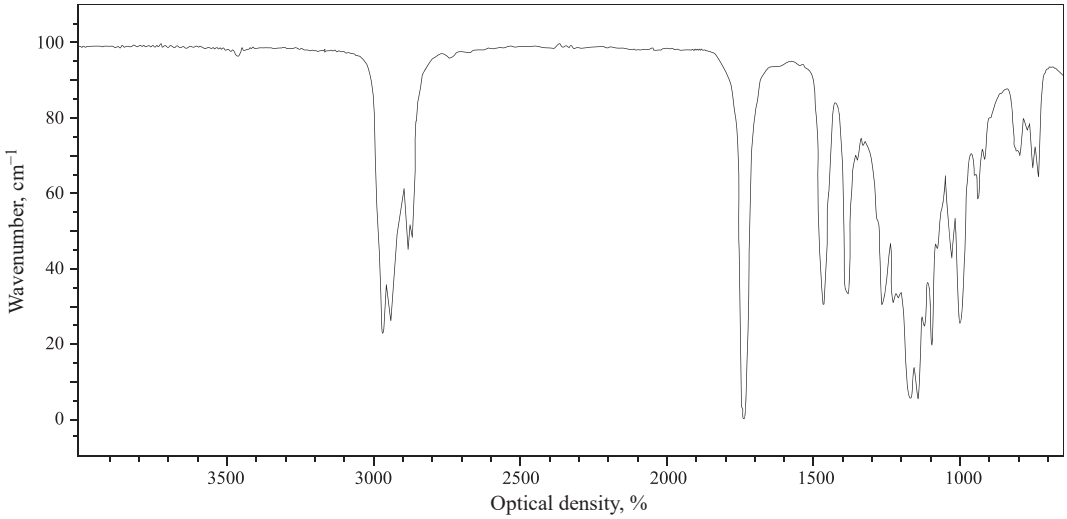

Fig. 3. IR spectrum of NPG di(2-ethylhexanoate)

where R is the gas constant, T is the absolute temperature. In case of esterification with 2EH acid:

$$k_1 = 5.94 \cdot 10^3 \cdot e^{\frac{(-57.5 \pm 6.2)}{RT}}, \quad (5)$$

$$k_2 = 4.16 \cdot 10^2 \cdot e^{\frac{(-50.9 \pm 5.2)}{RT}}. \quad (6)$$

It can be seen from Eqs. (3)–(6) that the activation energies for each stage are almost the same. However, at the same time there is a strong difference in the values of the pre-exponential factors. This can be explained by a change in the reactivity of carboxylic acids with increasing length and branching of the main carbon chain. This creates spatial obstacles to interaction due to the shielding of the active centers by the alcohol molecules. Thus, the ethyl radical at the α-carbon atom of 2EH acid reduces the acid strength and complicates the nucleophilic attack of the nearby carbon atom of the carboxyl group [15]. This significantly affects the rate of esterification in the case of isomeric acids with similar dissociation constants [13].

The viability of the proposed kinetic model (Eqs. (3)–(6)) is confirmed by comparison of experimental and calculated data, as presented in Fig. 7. The average deviation of the calculated values from the experimental values does not exceed 6%.

The time to reach 95% yield of NPG di(2-ethylhexanoate) is 26–28 h; in the case of NPG diacetate, 20–22 h (Fig. 8).

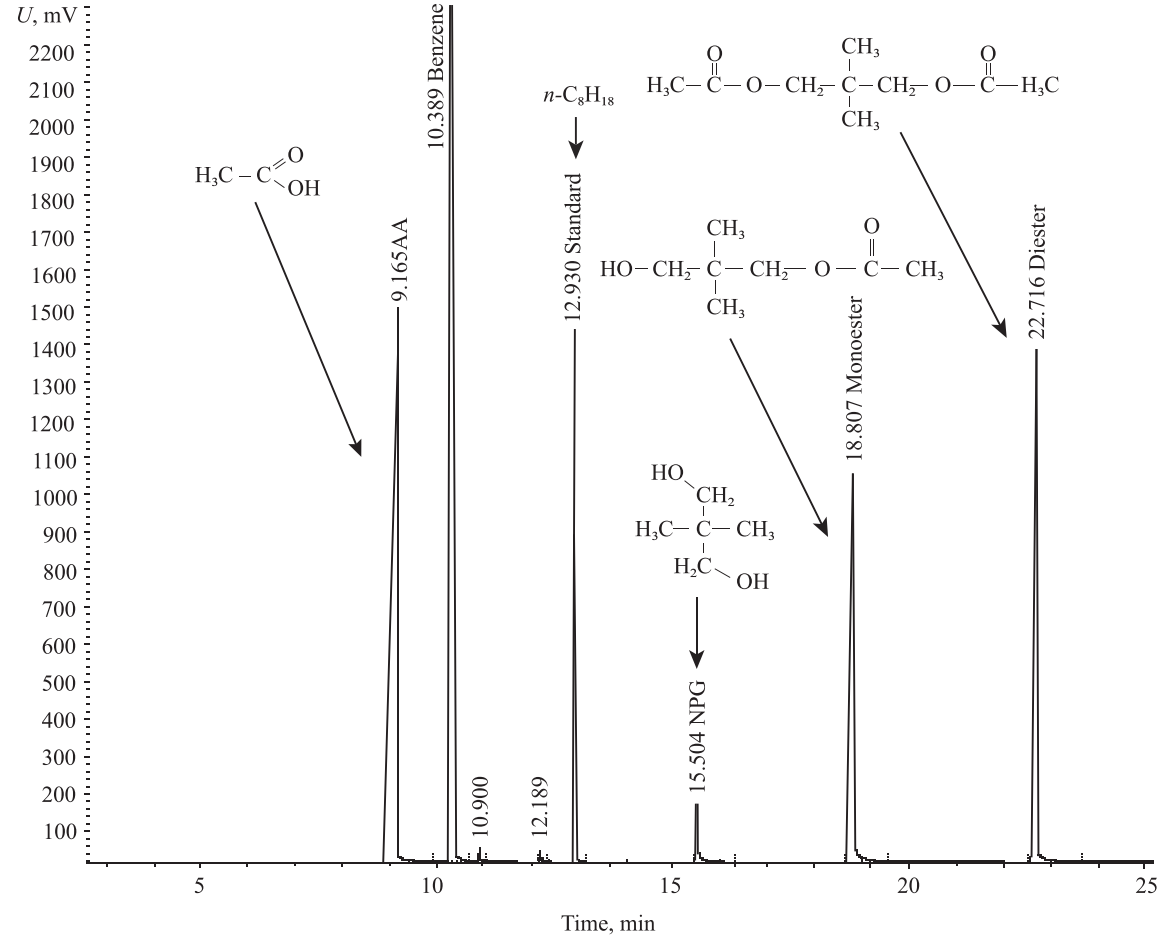

Fig. 4. Chromatogram of the reaction mass of NPG diacetate synthesis

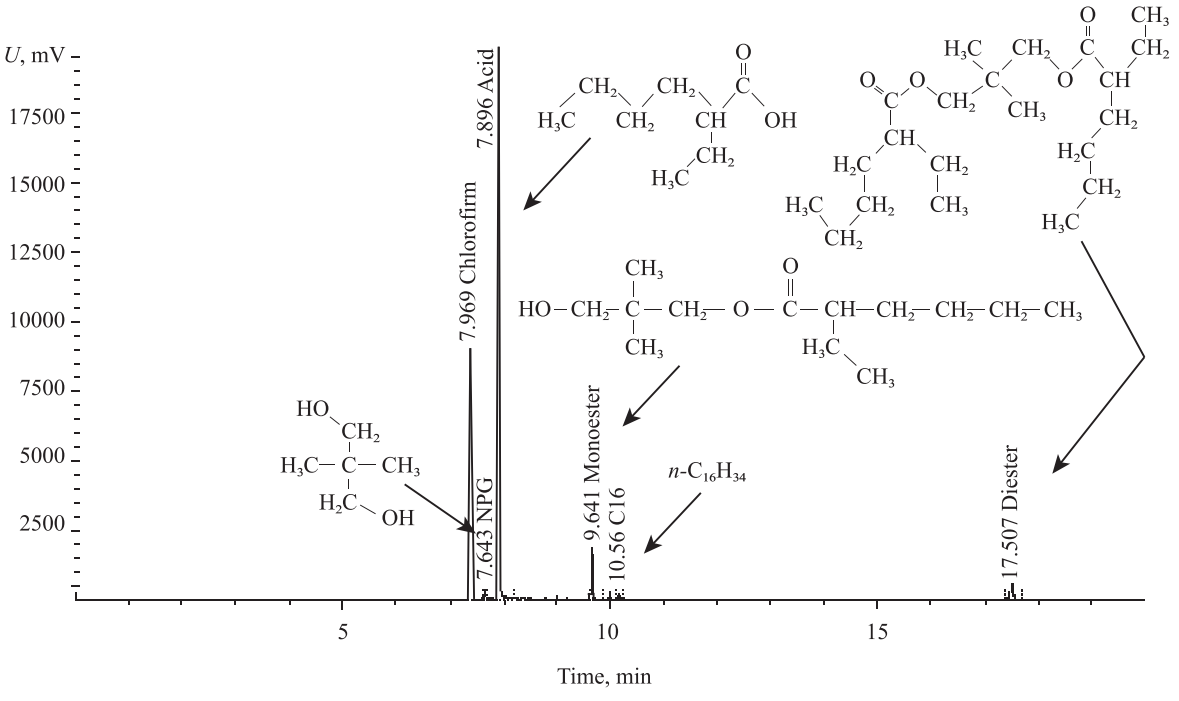

Fig. 5. Chromatogram of the reaction mass of NPG di(2-ethylhexanoate) synthesis

Table 3. Values of rate constants of NPG esterification by AA and 2EH acid

AA			2EH		
t, °C	$k_1 \cdot 10^4$, L/(mol·min)	$k_2 \cdot 10^4$, L/(mol·min)	t, °C	$k_1 \cdot 10^4$, L/(mol·min)	$k_2 \cdot 10^4$, L/(mol·min)
70	0.9	0.3	–	–	–
80	1.9	1.2	140	3.0	1.4
90	2.9	1.7	150	5.2	2.3
100	5.0	1.9	160	6.3	2.8
110	8.1	2.6	170	9.9	4.2

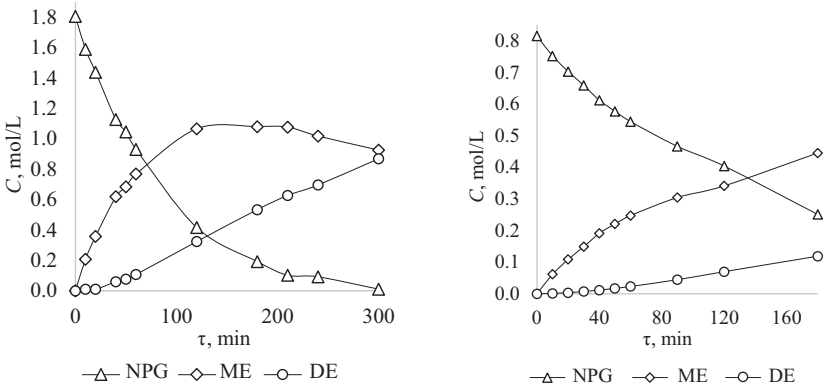

Fig. 6. Kinetic dependencies of NPG consumption, accumulation of mono- and diesters.
(a) AA + NPG at 110°C;
(b) 2EH acid + NPG at 170°C

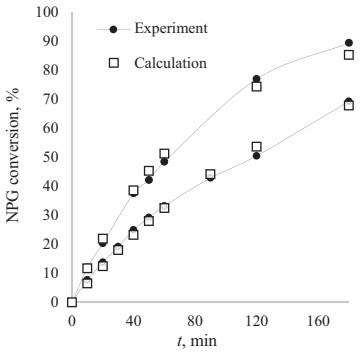

Fig. 7. Comparison of experimental and calculated values of the NPG conversion change in time. (a) AA + NPG at 110°C; (b) 2EH acid + NPG at 170°C

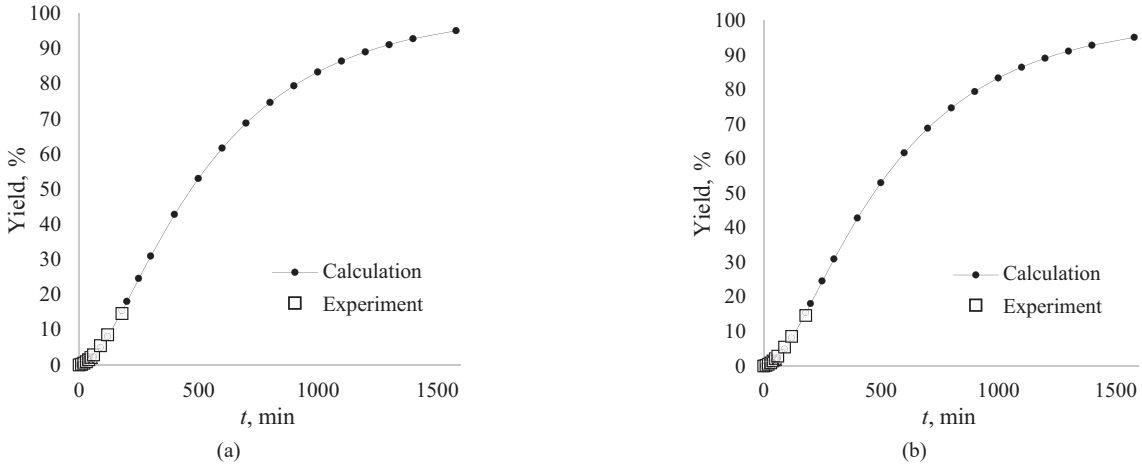

Fig. 8. Dependence of the yield of diesters on the reaction time.
(a) AA + NPG at 110°C;
(b) 2EH acid + NPG at 170°C.

Table 4. Comparison of a number of physicochemical properties of the obtained NPG esters and industrial phthalate plasticizer

Substance	Flash point in open crucible, °C	Mass fraction of volatiles, %	Density at 20°C, g/cm^3	Hazard class
NPG diacetate	100 ± 5	44.9	1.018	IV
NPG di(2-ethylhexanoate)	173 ± 2	0.4	0.918	IV
DOP (dioctyl phthalate) (GOST 8728-88)	205	up to 0.1	0.982–0.986	II

NPG esters with a content of the main substance of at least 99.7 wt % were produced under the given conditions. Their physicochemical parameters were determined in accordance with the methods of GOST 8728-88[2] (Table 4).

The data presented in Table 4 indicate that NPG diacetate is a more volatile compound due to the low molecular weight of AA used. When using NPG diacetate as a plasticizer, it will diffuse and evaporate from the polymer material, which, under high-temperature processing conditions, can lead to the ether boiling. Therefore, NPG diacetate can be recommended for use as a viscosity regulator for plastisols and provide improved resistance to staining of vinyl floor coverings. This is due to its volatility [12]. NPG di(2-ethylhexanoate) has a high boiling point and a low volatility, which makes it possible to use it as a plasticizer.

CONCLUSIONS

The study established that the optimal conditions for NPG esterification with monocarboxylic acids include a temperature range of 100–170°C with an 8-fold molar excess of the acid without the use of a catalyst. This helps prevent tarring and darkening of the reaction mass. The observed activation energies for the formation of NPG diacetate and di(2-ethylhexanoate) are similar and amount to 53.7 ± 7.2 kJ/mol and 54.2 ± 5.7 kJ/mol, respectively. This is consistent with the literature data on the esterification of propionic acid with NPG: 55.3 kJ/mol. Any differences in the values of pre-exponential factors, in the ester synthesis time and in the physicochemical parameters are due to the influence of the reactivity of the acids used and spatial hindrance. The research results obtained can be used to create domestic technology for the production of NPG esters applied as plasticizers, bases or components of lubricants.

Authors' contribution

All authors equally contributed to the research work.

The authors declare no conflicts of interest.

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