Journal of Siberian Federal University. Chemistry 2020 13(3): 330-339
~ ~ ~

DOI: 10.17516/1998-2836-0186

УДК 544-431+544-021

Mercarbide Catalyst for Alcohol Ethoxylation

Ella O. Butenko*[a] and Alexey E. Kapustin[b]
[a]Priazovskiy State Technical Universty
Mariupol, Ukraine
[b]Havighurst Center, Miami University
Oxford, Ohio, USA

Received 23.12.2019, received in revised form 20.04.2020, accepted 16.08.2020

Abstract. Mercarbide catalyst was studied for the ethoxylation of methanol and 1-heptanol. Mercarbide catalyst is very active for the narrow-range ethoxylation of 1-heptanol. The narrow distribution of ethoxylation units in the ethoxylates is elucidated by the constrained reaction on the mercarbide catalyst. In the proposed surface reaction scheme, the following points are presented. The relatively basic reactants, ethylene oxide and alcohols or ethoxylates, are adsorbed on the relatively acidic sites of the surface. There is a decrease of ethoxylation rate in each additional ethylene oxide insertion step, due to a smaller number of the ethylene oxide molecules adsorbed near the growing point of alcohol ethoxylates. The difference in ethylene oxide insertion rates with the numbers of oxyethylene units in the ethoxylate products causes peaking of the distribution.

Keywords: mercarbide, catalysis, ethylene oxide.

Citation: Butenko E.O., Kapustin A.E. Mercarbide catalyst for alcohol ethoxylation, J. Sib. Fed. Univ. Chem., 2020, 13(3), 330-339. DOI: 10.17516/1998-2836-0186

* Corresponding author E-mail address: butenkoeo@rambler.ru

Меркарбид как катализатор оксиалкилирования спиртов

Э.О. Бутенко[а], А.Е. Капустин[б]
[а]Приазовский государственный технический университет
Украина, Мариуполь
[б]Хавихурст центр, Университет Майами,
США, Огайо, Оксфорд

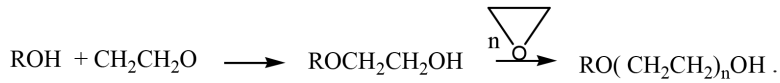
Аннотация. Меркарбид исследовали в качестве катализатора реакции этоксилирования метанола и 1-гептанола. Меркарбид как катализатор очень активен для узкого диапазона этоксилирования 1-гептанола. Узкое распределение продуктов этоксилирования в этоксилатах объясняется локальной реакцией на меркарбидном катализаторе. Предложена схема протекания процессов на поверхности. Обладающие основными свойствами реагенты, оксид этилена и спирты, а также и этоксилаты, адсорбируются на относительно кислотных участках поверхности. Происходит уменьшение скорости этоксилирования на каждой дополнительной стадии введения этиленоксида из-за меньшего числа молекул этиленоксида, адсорбированных вблизи точки роста этоксилатов спирта. Различие в скоростях этиленоксидов с различным количеством оксиэтиленовых звеньев в продуктах этоксилирования является причиной пикового распределения.

Ключевые слова: меркарбид, катализ, оксид этилена.

Цитирование: Бутенко, Э.О. Меркарбид как катализатор оксиалкилирования спиртов / Э.О. Бутенко, А.Е. Капустин // Журн. Сиб. федер. ун-та. Химия, 2020. 13(3). С. 330-339. DOI: 10.17516/1998-2836-0186

1. Introduction

The ethoxylation of aliphatic alcohol has been utilized for the commercial production of non-ionic surfactants [1]. Similar types of ethoxylation for other organic compounds having active hydrogens have been also applied in the production of various wetting and emulsifying agents [2]. Ethoxylation of aliphatic alcohol, long-chain alkyl group, *n*: mole ratio of EO/ROH:



In the ethoxylation of aliphatic alcohols, homogeneous basic catalysts, such as NaOH, KOH or $NaOCH_3$, are generally used to facilitate ethylene oxide (hereafter abbreviated as EO) insertion to the alcohols at relatively low temperature and pressure [3-4]. In this homogeneous type of alcohol ethoxylation, distributions of oxyethylene units ($–CH_2–CH_2–O–$) in the ethoxylated product mixture are much broader than the statistical Poisson-type distribution [4-5] which can be calculated by Eq. (1). The main cause of the broad distributions in the homogeneous ethoxylation has been explained as the formation of intramolecular complexes between alkali metal ions and the terminal oxygens of

alcohol ethoxylate during the ethoxylation reactions. This phenomenon effect contributes in stabilizing ethoxylated oligomers and enhancing the ethoxylation rate of the oligomers to broaden the product distribution:

$$[RO\text{-}(CH_2CH_2O\text{-})_nH] = [ROH]_0 \cdot e^{-u} \cdot \frac{u^n}{n!}.$$

where R is the alkyl group, *n* is the number of oxyethylene groups, *u* is the average mole ratio of EO/ROH and $[ROH]_0$ is the initial ROH concentration.

Regarding the oxyethylene unit distributions in the aliphatic alcohol ethoxylation, the statistical Poisson-type distribution is still far from satisfactory since the Poisson-type distribution always accompanies a considerable amount of free alcohol and less valuable alcohol ethoxylates which are either too short or too long [6-8]. Recently, much attention has been focused on this field to reach the narrower oxyethylene distribution than the Poisson-type distribution using various solid ethoxylation catalysts. The narrow-range alcohol ethoxylates are supposed to be environmentally benign and suitable for production of high quality final products [9-12].

This problem can be solved by using the mercarbide as an ethoxylation catalyst. Mercarbide, $[CHg_4O_2](OH)_2$, is a mercury derivative of ethane in which all of the ethane hydrogen atoms are substituted by mercury atoms [13]. Mercarbide exhibits basic and anion exchange properties. The scientific interest in mercarbide arises from its unique properties and amazing stability. Thus mercarbide does not undergo changes in the presence of acids and bases and is stable towards oxidizing and reducing agents. Even long heating in HNO_3/HCl does not result in visible changes in its structure.

In this paper, we report about the catalytic properties of mercarbide in methanol and heptanol ethoxylation and we propose a surface ethoxylation scheme that is plausible for the explanations of the narrow oxyethylene unit distribution of the products and the dependence of catalytic activity on the mercarbide interlayered compositions.

For these purposes, we use well-defined mercarbide materials and ideal surface models for the interpretation of catalytic properties.

2. Experimental

Methanol and heptanol were of reagent grade and were purchased from Fluka. Ethylene oxide of 99,5% were supplied from Aldrich and used as received.

The synthesis of mercarbide was carried out by the precipitation method using mercury oxide and alcohol [13]. A typical synthesis was the following. 300 ml of ethanol, 150 g of yellow mercury oxide and 30 g of potassium hydroxide were put into 500 ml glass reactor. A reactor was painted in black for the removal of influence of sun light on the reaction undergoing (in the unscreened part the formation of metallic mercury was observed). The reaction mixture was heated at 363 K for 36 h vigorously stirring, filtred, and then washed with distillated water, alkali solution and nitric acid. The obtained materials was washed with distillated water and then was drying in vacuo at 298 K.

The strength and concentration of basic sites were determined by indicator method [14]. Acid-base indicators change their colors according to the strength of the surface sites and pK_{BH} values of the indicators. The strength of the surface sites are expressed by an acidity function H_0. The H_0 function is defined by the following equation:

$$H_0 = pK_{BH} + \lg [B^-]/[BH],$$

where [BH] and [B^-] are, respectively, the concentration of the indicator BH and its conjugated base, and pK_{BH} is the logarithm of the dissociation constant of BH.

The reaction of the indicator BH with the basic site B is the following:

$$BH + B \rightleftharpoons B^- + BH^+.$$

The amount of basic sites of different strength can be measured by titration with benzoic acid. A sample is suspended in a nonpolar solvent and an indicator is adsorbed on the sumple in its conjugated base form. The benzoic acid titer is a measure of the amount of basic sites haning a basic strength corresponding to the pK_{BH} value of the indicator used.

The indicator method can express the strength of basic sites in a definite scale of H_0, but this has disadvantages too. Although the color change is assumed to be the result of an acid-base reaction, an indicator may change its color by reaction different from an acid-base reaction. In addition, it requires a long time for benzoic acid to reach an adsorption equilibrium when titration is carried out in a solution. In some case the surface of solid may dissolved into a titration solution. If this happens, the number of basic sites should be overestimated. There for, special care should be taken with the indicator method.

Mercarbide at the OH-form has the yellow color, so it is very difficult to determine the basicity by the direct method, therefor the method of titration in the presence of white comparison standard was used [15]. Benzene was used as a solvent, calcined barium oxide was used as a comparison standard. The followed indicators were used – bromothymol blue (*pKa* = 7,2), dinitroaniline (*pKa* = 15,0), 4-chloro-2-nitroailine (*pKa* = 17,2), 4-chloroaniline (*pKa = 26,5*). Mercarbide (1 g) was placed at the glass filled with benzene and 0,01 M benzoic acid solution was used for titration; the concentration of indicators was 0,1 g/l.

Ethoxylation was performed in a 20 cm^3 batchtype glass cover stainless steel stirred pressure reactor. The reactor was equipped with a magnetic stirrer and electric heating system. A typical reaction procedure is illustrated as follows. Powdered mercarbide catalyst, alcohol and ethylene oxide were charged to the reactor. The reactor was heated to set temperature within required time. After then the reactor was immerged in cold water to cool the liquid product below 20 °C. The reactor was disassembled and remaining alcohol and products were collected for analysis.

Liquid product was separated by filtration of crude product and was analyzed using a gas chromatography method. Chrom-5 chromatograph with a flame ionization detector on capillary column have been used. The mixed ethoxylated standard sample with definite concentration of ethoxylates was used for quantitative analysis of oxyethylene unit distribution.

3. Results and discussion

The composition of mercarbide is given in Table 1. Finding data show the good accordance of composition to the mercarbide formula $[CHg_4O_2](OH)_2$.

Mercarbide in hydroxide form is a solid base which represents polymeric matrix, carring positive charge, localized on Hg atoms, and negative hydroxyl ions.

While titration of solid bases it is necessary to consider, if the basic sites located in inside cavities of solid body can be reached by molecules of acid. The titration by Hammett showed, that in presence of bromthymol blue (pK_a = 7,2), the concentration of basic sites is E = 1,5 meq/g, as well as in

Table 1. Element composition of mercarbide

	Hg	C	H
Calculated, %	93,22	1,85	0,30
Analysis, %	93,05-93,10	1,80-1,83	0,33-0,34

Table 2. The concentration of mercarbide basic sites according to ionic exchange with alcoholates

Alcoholate	CH_3O^-	$C_2H_5O^-$	$C_3H_7O^-$	$C_7H_{15}O^-$	$C_{12}H_{25}O^-$
E, meq/g	1,35	1,38	1,22	0,95	0,11

2,4-dinitroanilin presence (pK_a = 15,0). The results, received by the titration in presence of 4-clorine-2-nitroaniline (pK_a = 17,2) gave following values of basic sites concentration: E = 0,8 meq/g). The sites with H_0 = 26,5 intensity is not exists; indicator – 4-clorineanilin).

During the titration of hydroximercarbide by the solutions of sulphuric and hydrochloric acids, the similar value of exchange capacity was calculated (E = 1,35 – 1,37 meq/g). The same result was reached during the study of ionic exchange with chlorides. It is necessary to notice, that in case of complete replacement of the hydroxide ions to the iodine anions, the theoretical value of capacity for tetramercurmethane is E = 2,2 meq/g. The results of basic sites determination through the alcoholates of different achohols is shown in Table 2.

The results, shown in Table 2, describe the prohibition of basic sites in mercarbide by hydrocarbon radicals. So, one can calculated that for the prohibition of each site the increase of hydrocarbon radical in 3 -CH_2- groups required. Fig. 1 represents ethylene oxide consumption rates for mercarbide catalyst.

The results of experiments at different initial concentration of catalyst are shown at Fig. 2.

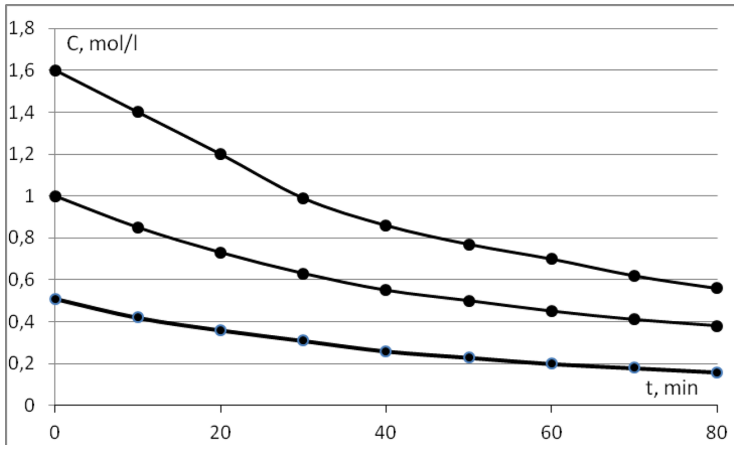


Fig. 1. Ethylene oxide consumption rates of mercarbide catalyst (t = 100 °C; C_{cat} = 0,1 mol/l; $C_{eo,0}$: 1 – 1,6 mol/l, 2 – 0,98 mol/l, 3 – 0,52 mol/l)

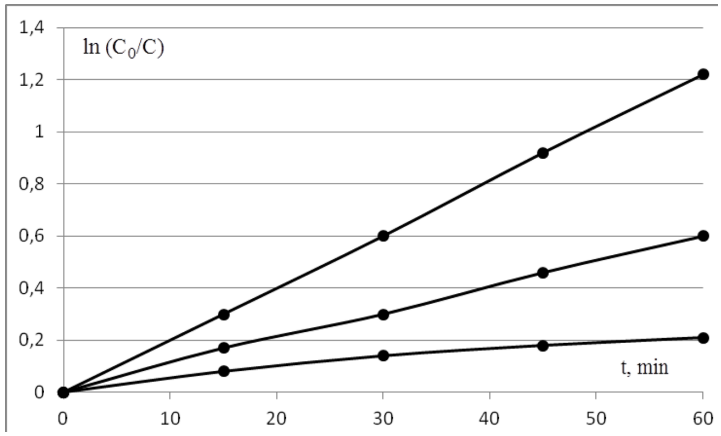


Fig. 2. Heptanol ethoxylation in the presence of mercarbide (t = 110 °C, $C_{eo,0}$ = 1,0 mol/l, C_{cat}: 1 – 0,5 mol/l, 2 – 1,0 mol/l, 3 – 2 mol/l)

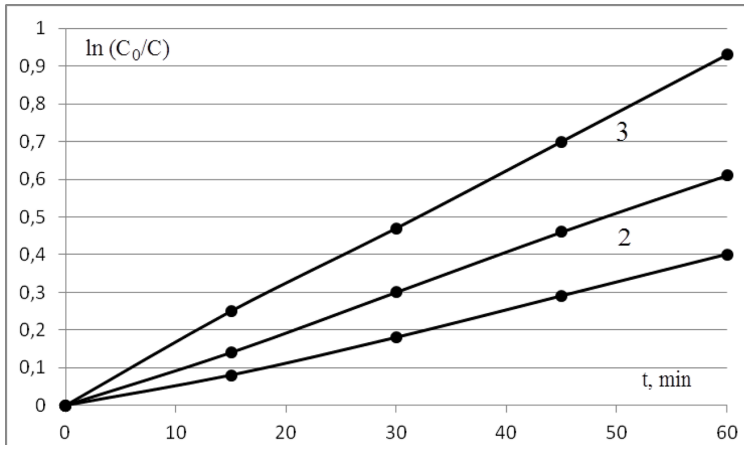


Fig. 3. Heptanol ethoxylation in the presence of mercarbide at different temperatures (C_{cat} = 3 mol/l; $C_{eo,0}$ = 1,0 mol/l, t: 1 – 100 °C, 2 – 110 °C, 3 – 115 °C)

The "concentration of catalysts" is the concentration of active sites in the reaction solution. It can be calculated as

$$C_{cat} = E \cdot m/V,$$

where E is the mercarbide capacity, meq/g; m – the mass of mercarbide, g; V – the volume of reaction mixture.

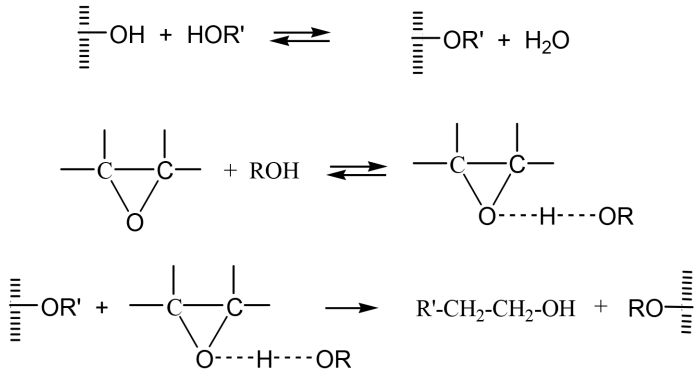
The kinetic experiments show that the reaction is first order with respect to ethylene oxide, mercarbide and alcohol (Fig. 3).

(Reaction was studied in excess of the alcohol, but it is known [2-5] that the ethoxylation reaction is first order to alcohol). The kinetic equation is the followed:

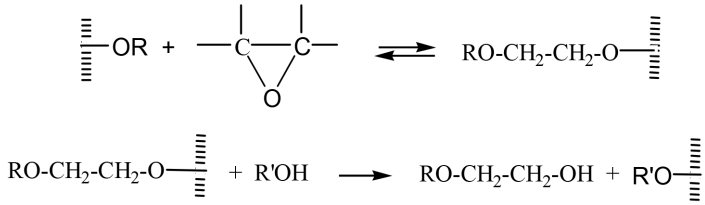
$$- \frac{dC}{d\tau} = k\, C_{eo}\, C_{alc}\, C_{cat},$$

where C_{eo} is the concentration of ethylene oxide, mol/l; C_{alc} – the concentration of alcohol, mol/l.

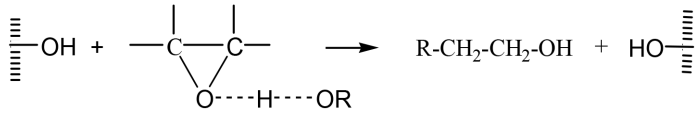
This equation is corresponded with the followed mechanism of interaction of ethylene oxide with alcohol in the presence of solid base. This equilibrium is defined by the concentration of the alcohol and its acidity. Alcohol ethoxylation reaction mechanism:



The interaction of the alcohol reactant with ethylene oxide proceeds through a threemolecular transition state. In the first stage the ethylene oxide ring is activated by formation of hydrogen bonding. The activated C---O bond is opened by nucleofilic attack of the surface alkoxide OR'. Similarly a two-step mechanism can be envisaged. Alternative two-step mechanism of ethoxylation:



Because of the equilibrium is defined by the concentration of alcohol and its acidity, and all alcohols, except methanol, are less acidic than water, so reaction according to the followed scheme can occur. Threemolecular mechanism of ethoxylation:



From experiments at various temperatures it was established, that the reaction proceeds in the kinetic area and the activation parameters of reaction (Table 3) were determined.

The high reaction rate of methanol ethoxylation is explained by the high acidity of this alcohol.

Table 3. Kinetic parameters of alcohol ethoxylation reaction in the presence of mercarbide as catalyst

Alcohol	$k \cdot 10^4$ $l^2/mol^2 \cdot s$ (100 ^{0}C)	E, kJ/mol
Heptanol	1,71	77 ± 3
Methanol	7,7	64 + 4

The process of alcohol ethoxylation in the presence of mercarbide at high concentration of ethylene oxide can be represented by the followed scheme of consecutive-parallel reactions:

$$ROH \xrightarrow[k_0]{C_2H_4O} RO(C_2H_4O)H \xrightarrow[k_1]{C_2H_4O} RO(C_2H_4O)_2H \xrightarrow[k_2]{C_2H_4O} \ldots \xrightarrow[k_{n-1}]{C_2H_4O} RO(C_2H_4O)_nH.$$

In general, the polyethoxylation reaction rate duscribed by the followed equation:

$$-\frac{dC_{eo}}{d\tau} = k\, C_{eo}\, C_{alc}\, C_{cat}\, Z\, \rho^2,$$

where ρ is the density of reaction mixture increasing with the increase of ethoxylation degree.

The coefficient Z takes into account the mole part of each ethoxylated product in the reaction mixture.

$$Z = n_0 + b_1 n_1 + b_2(\Sigma n_1 - n_0 - n_1),$$

where b_1 and b_2 are the distribution coefficients, $b_1 = k_1/k_0$; $b_2 = k_2/k_0$.

Studies of the composition of products obtained in ethoxylation show that the rate constants of these reactions starting from the third step are similar.

Thus the composition of products of ethoxylation process relies on two parameters – the correlations of the concentrations of alcohols (including ethoxylated products) to the concentration of ethylene oxide and on the correlation of rate constant on every stage of polyaddition. For example for basic homogeneous catalyst the distribution coefficients of alcohol ethoxylation are b_1 = 2-3; b_2 = 3-4.

The use of basic heterogeneous catalysts allows to diminish the distributing coefficients due to the porous structure of catalyst. A diffusion for the molecules of greater molecular weight is decline of in the pores. The reaction rate goes down for products and is increased for the initial sudstences. Distribution of reaction products on the molecular weight becomes narrow. Chromatographic analysis of reaction products allowed to define the distribution coefficients (Table 4).

From the data (Table 4) it is visible, that for metanol the distribution coefficients are similar to the same for homogeneous basic catalysis. Distribution coefficients for heptanol considerably smaller, their values approach the coefficients for the acid catalysis (b_1=b_2=1). A cause of this is space difficulties, arising up in case of penetration of alcohol molecules into the pores of catalyst.

Mercarbide has a layered structure. The polymeric trimercurated oxonic ion $[OHg_3CCHO]^+$, forms two structures, one has a pillared structure, the other has polymeric planes [13]. The reliable structure is the polymer, in which present both trimercurated and monomercurated oxonic ions, with a formula $[CHg_4O(OH_2)]\,(OH)_2$. The basic sites of Bronsted type are in the interlayered space.

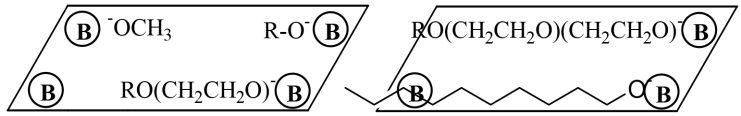
Indirect confirmation of our supposition is very low rate of ethoxylation of alcohols with bulky hydrocarbon radicals. For example, for 2-butylheptanol the rate of reaction is about the non-catalytic

Table 4. Distribution coefficients for different alcohol

	b_1	b_2
Methanol	2,3±0,2	4,3±0,5
1-Heptanol	1,3±0,7	2,1±0,3

reaction, because of impossibility of penetration of alcohol molecules to the active sites in the inner space of catalyst.

In addition, the blocking of neighbouring active sites is by the growing polyethoxylated links in the heterogeneous catalyst take place. Blocking of active sites by polyethoxylated radicals ("B" – basic active site):



Blocking of active sites by the long radicals also explains that fact, that reaction rate of methanol ethoxylation is higher then for heptanol. In this case the blocking of active sites is absent.

We assume, that length of one group $-CH_2CH_2O-$ is approximately equal to the length of three CH_2- groups. The results of change of ion-exchange capacities depends on the lengths of alcohol radical are reported in Table 2. Thus, it is possible to estimate the distance between the active sites in mercarbide. It averages equal about three $-CH_2-$ groups. The closed results were obtained and for other heterogeneous catalysts [12, 16].

4. Conclusions

Mercarbide catalyst was studied for the ethoxylation of methanol and heptanol. Mercarbide catalyst is very active for the narrow-range ethoxylation of heptanol, but nof for methanol. The narrow distribution of oxyethylene units in the heptyloxylates is elucidated by the constrained reaction in the inner space of mercarbide catalysts. The large activity difference of mercarbide for methanol ethoxylation may be correlated with the numbers of active sites at the closed distanse. The small activity difference of mercarbide for heptanol ethoxylation may be correlated with the blocking of active sites by the long ethoxylated radicals.

Mercarbide is an excellent basic heterogeneous catalyst for the processes of organic and petrochemical synthesis. However, the word «mercury» scares the engineers and production workers. They consider, that because of a mercury is a toxic element, and is avoided as usage in chemical processes from the point of view of green sustainable chemistry. Actually, the absence of protons in mercarbide does impossible the formation of methylmercury. This does the mercarbid quite inoffensive catalyst for the green chemistry processes.

References

1. Alam M.S., Siddiq A.M., Natarajan D. Physicochemical properties and bioactivity studies of synthesized counterion coupled (COCO) gemini surfactant, 1,6-bis (N,N-hexadecyldimethylammonium) adipate. *J. Mol. Liq. 2019,* Vol. 273, P. 16-26. https://doi.org/10.1016/j.molliq.2018.09.082

2. Abd El-Ghaffar M.A., Sherif M.H., Taher El-Habab A. Synthesis, Characterization, and Evaluation of Ethoxylated Lauryl-Myrisityl Alcohol Nonionic Surfactants as Wetting Agents, Anti-Foamers, and Minimum Film Forming Temperature Reducers in Emulsion Polymer Lattices. *Journal of Surfactants and Detergents 2017.* Vol. 20, P. 117-128. https://doi.org/10.1007/s11743-016-1898-4

3. Hermann P.D., Cents T., Klemm E. Determination of the Kinetics of the Ethoxylation of Octanol in Homogeneous Phase. *Ind. Eng. Chem. Res.* 2017, Vol. 56, P. 6176-6185. https://doi.org/10.1021/acs.iecr.7b00948

4. Zhang J., Li T. Facile Synthesis of a Highly Effective Layered Double Hydroxide Catalyst and Its Application in the One-Step Ethoxylation of Butyl Acetate to Oligo-Ethylene Glycol Butyl Ether Acetates. *Industrial & Engineering Chemistry Research 2019*, Vol. 58, P. 16320-16325. https://doi.org/10.1021/acs.iecr.9b01892

5. Verkoyen P., Frey H. Long-Chain Alkyl Epoxides and Glycidyl Ethers: An Underrated Class of Monomers. *Macromolecular Rapid Communications 2020*. Vol. 41, P. 200-225. https://doi.org/10.1002/marc.202000225

6. Hussain S.M.S., Shahzad M.K., Soling T. Surface and thermal properties of synthesized cationic poly(ethylene oxide) gemini surfactants: the role of the spacer. *RSC Adv. 2019*, Vol. 9, P. 30154-30163. https://doi.org/10.1039/C9RA06577F

7. Lara-Martin P.A., Gonzalez-Mazo E., Brownawell D.J. Environmental analysis of alcohol ethoxylates and nonylphenol ethoxylate metabolites by ultra-performance liquid chromatography-tandem mass spectrometry. *Anal. Bioanal. Chem. 2012*. Vol. 402, P. 2359-2368. https://doi:10.1007/s00216-011-5449-6

8. Samoilov N.A., Mnushkin I.A. (2012). Mathematical Modeling Fractionation Stage of Reactive Distillation Process for Production of Ethylene Glycol. *Electronic Scientific Journal "Oil and Gas Business" 2012*, Vol. 4, P. 158-164. dx.doi.org/10.1016/s0009-2509(00)00119-6

9. Onuorah P., Gunorbon J. Simulation and Control of the Reactor for the Non-Catalytic Hydrolysis of Ethylene Oxide to Ethylene Glycol. *Mathematical Theory and Modeling 2018*, Vol. 8, P. 23-45. https://doi:10.13140/RG.2.2.14841.72801

10. Kao S.-C., Lin Y.-C, Ryu I. Revisiting Hydroxyalkylation of Phenols with Cyclic Carbonates. Advance *Synthesis and catalysis 2019*. Vol. 361, P. 3639-3644 https://doi.org/10.1002/adsc.201900287

11. Zhu L., Xiao-Qin L., Jiang H.-L. Metal-Organic Frameworks for Heterogeneous Basic Catalysis. *Chemical Reviews 2017*, Vol. 117, P. 8129-8176. https://doi.org/10.1021/acs.chemrev.7b00091

12. Di Serio M., Tesser R., Russo V. Catalysts for the Ethoxylation of Esters. *Journal of Surfactants and Detergents 2015*. Vol. 18, P. 913-918. DOI:10.1007/s11743-015-1719-1

13. Kapustin A. Mercarbide: An unusual organomercury polymer. *Coordination Chem. Rev. 2010*. Vol. 254, P. 1290-1294. https://doi.org/10.1016/j.ccr.2009.12.014

14. Purwaningsih A., Kristanti A. N., Mardho D.Z. Determination of Brønsted Acid Sites In Porous Aluminosilicate Solid Catalysts Using Volumetric And Potentiometric Titration Method. *Earth and Environ. Science 2019*, Vol. 217, P. 1-5. DOI: 10.1088/1755-1315/217/1/012002

15. Kapustina E.V., Kozlovskiy R.A., Kapustin A.E. Determination of Acid-Base Surface Properties of Mercarbide. *Proceedings of Universities. Applied Chemistry and Biotechnologies 2013,* Vol. 2, P. 6-9.

16. Zhang A., Wang J., Ye J. Oxyalkylation modification as a promising method for preparing low-melting-point agarose. *Inter. Journal of Biological Macromolecules 2018*, Vol. 117, P. 696-703. https://doi.org/10.1016/j.ijbiomac.2018.05.171