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RESEACH METHOD ON OBTAINING DERIVATIVES OF EPIHCHLORHYDRIN

DIPLOMA WORK

Speciality: 5320400 – Chemical technology (production of organic substances)

Scientific advisor: d.ch.sc., prof. Maksumova O.S.

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Tashkent Chemical- Technological Institute

Faculty:Chemical technology of fuels and organic compounds

Department: ORGANIC CHEMISTRY AND TECHNOLOGY OF THE MAIN ORGANIC SYNTHESIS

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_____ Qodirov.Kh.E

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TASK

On completing course Diploma paper

RESEACH METHOD ON OBTAINING DERIVATIVES OF EPIHCHLORHYDRINE

Speciality: 5320400 – Chemical technology (production of

organic substances)

Student of the 4-course group 18-12 Abdumalikova H.B.

Scientific advisor: d.ch.sc., prof. Maksumova O.S

CONTENT

Programs of targeted projects on modernization and technical renovation of basic sectors of our economy provide the opportunity to introduce modern innovative technologies designed to give a powerful impetus on exitting Uzbekistan to a new level, to ensure the competitiveness of our country on the world market.

Islam Karimov

INTRODUCTION

Relevance of the work. One of the actual problems of modern synthetic organic chemistry is providing a convenient ways of obtaining new classes of organic compounds and multifaceted study of their useful properties. In this aspect, epichlorohydrin is an important product of basic organic synthesis. Having high reactivity due to the presence in the molecule of movable chlorine atom and epoxide group, epichlorohydrin is used widely . It is easily reacted with compounds of different classes, which allows to obtain on its base a number of products which are used in many branches of industry. Among many compounds epichlorohydrin is one of the most important outcoming product precursors for synthesis of organic compounds of different classes, expressing biological activity. Special interest represent reactions of epichlorohydrin with amines, organic acids and other functional derivatives of aliphatic and aromatic hydrocarbons. Epichlorohydrin, due to its essential structure has endles obtainings possibilities for obtaining new polifunctional organic compounds, possessing the complex of useful properties.

Compounds, which are obtained with the usaga of epichlorohydrin are more widely used as a means of improving the dyeability of textile and synthetic fiber, emulsifiers and coagulants as a starting material in obtaining the pharmaceutical, preparatus, detergents, lubricants, adhesives, emulsifiers. As defoaming agents and blowing agents in the production of epoxy resins and epichlorohydrin rubbers epoxypoliamide rubbers, ionites, synthetic glycerol, polyols and various glycidyl

ethers. The Power of epichlorohydrin production in the world at present is about 2.0 million tons.

According to that, great interest represents the study of epichlorohydrin reaction with amino compounds. It is known, that nomerous works devoted to the synthesis and study of epichlorohydrin derivatives with amines, aminocarboxylic acids, fatty acids and other classes of organic compounds.

However, there is little data on the synthesis and study of derivatives of epichlorohydrin with primary and secondary amines. From primary amines - urea are producedin Ltd. Maxam-Chirchik, which are technical products. In this connection, interest of studying the interaction of epichlorohydrin with urea is presented by us. As a secondary amine was selected piperidine.

The Object of the work. Synthesis and investigation of polifunctional derivatives of epichlorohydrin with nitrogen-containing compounds.

The work includes the following main objectives:

- investigation the reaction of epichlorohydrin with urea;
- study the reaction of epichlorohydrin with piperidine.

The object and subject of the study:the object of research are epichlorohydrin, urea, piperidine. The subject of the research is to develop methods for obtaining new polifunctional derivatives of epichlorohydrin.

Methods of investigation:FT-IR spectroscopy (SISTEM-200), differentially thermal analysis, thin layer chromatography on the plate of SilifolUV-254.

The scientific novelty of the work:

- Methods of synthesis of epichlorohydrin with urea, piperidine are developed and their composition and structure are established.
- Conditions of reactions for disclosure of epichlorohydrin epoxide ring under the influence of secondary amino piperidine;

The practical value of the work:

- Synthesized new derivatives of epichlorohydrin conbining ured fragments and piperidine can be used as a mean of biologically active compounds; - physico-chemical constants of obtained substances are reference materials and can be useful for specialists,involved in the synthesis of biologically active compounds, as well as in the education al process in reading lectures on organic chemistry.

Aprobation of the work. The main provisions of the scientific work were presented at the Scientific - Technical Conference for master students "Umidli kimyogarlar" 2015 (Tashkent, TCTI 2015).

CHAPTER 1 MODERN STATE OF SYNTHESIS AND RESEARCH THE DERIVATIVES OF EPICHLOROHYDRIN

Due to the high reactivity and wide usage in various spheres of national economy epichlorohydrin attracts the attention of many researchers all over the world. Due to the having of epichlorohydrin highly reactive properties ,which are associated with the presence of molecules in the substance from epoxide group and chlorine atoms. Particularly ,this substance is widely extended in chemical industry. It is used as one of the components for the synthesis of glycerol derivatives , various dyes and besides,with the help of this using the substance various materials for treatment of various surfaces are produced.

Epichlorohydrin has a very high chemical reactivity, so it is used for a variety of reactions that are associated with the formation of organic molecule structures in substances, which contain epoxide group. The substance is practically indispensable as a synthesis of substances with glycerine also. Among the extended reactions in for the industry various condensations are applied which are used production of epoxy resins, amination reactions, esterification, hydration and hydrolysis and in other reactions, which are mentioned below.

The method of obtaining glycidyl ether of poly (oxyalkylene) glycol is worked out , by the ways of adding epichlorohydrin in the presence of trifluoride boron to the poly (oxyalkylene) glycols dehydrochlorination which are resulted chlorohydrins aqueous NaOH alkali solution or KON and subsequent isolation of glycidyl ethers, and where the selection of glycidyl ethers is carried by delamination of organic and aqueous saline phase, where the water-salt phase represents by itself the is this or that saturated at the temperature of delamination solution of metal chlorides (NaCl or KCl) [1]. Epichlorohydrin is attached to a particular poly (oxyalkylene) glycol which contains trifluoride boron as the catalyst, by keeping gradually the temperature 55-65 °C. Dehydrochlorination of formed chlorohydrins formed is carried out with the help of stoichiometric

amounts of sodium hydroxide or potassium hydroxide at the temperature of 40-50C, where in 20-22% water or 40-55% solutions of alkalin are used and solid alkali also, but in all cases after the dehydrochlorination process this amount of water is added so that to the reaction mass after delamination of reaction mass into organic and aqueous-salt phase, the last was presented by itself at the of temperatures delamination (typically room temperature) solution of metal chlorides.

Besides, The set task is solved that the dehydrochlorination is carried out by solid alkali KOH orNaOH with the addition of water prior to formation of saturated at the temperature of delamination solution of metal chlorides NaCl or KCl.

It is known that the method of obtaining amidoepichlorhydrynresin polyethylenepolyamine in the interaction with by reacting a dicarboxylic acid at 160 - 200 ° C in the presence of 1,3-dimetilolimidazolidin-2-one, which is used as aqueous solution, followed by treating the obtained reaction product by epichlorohydrin at 45-70o, carried out at the molar ratio of polyethylenepolyamine 1,3-dimetilolimidazolidin-2-он: dicarboxylic acid: epichlorohydrin ratio is equal to 1: 0.1-1: 1-3: 1-2, respectively [2]. The method was illustrated by the following example. The reactor (four-neck flask) equipped with the mechanical stirrer, by thermometer and a dropping funnel was charged with 60 g (1 mole) of ethylenediamine (EDA) in 40 ml of H2O (60% aqueous EDA), is heated to 80- 100 ° C and at this temperature was added dropwise 49.9 g (0.5 m) of EDC, is maintained at 100 ° C 2 hours was cooled to 40 60 ° C, then it was charged with 73 g (0.5 m) and AK mixture temperature were raised to 180 ° C and 170 was produced distilled off low-boiling components and water . After removing the calculated amount of water (4 hours), the reactor contents were cooled to 100 -120 ° C, were dissolved in 500 ml of demineralized water and 46.25 g (0.5 m) pihlorgidrin was added at 40-48 the and stirred for 2 hours. 194 g (92 %) resin (dry resin weight) was obtained.

It is known the method of obtaining aminoepichlorhydrine resin, which can be used for water purification from mechanical and organic impurities, as well as

waste water of various technological processes [3]. The method concludes that the heated to 40-49 ° C 25-40% aqueous solution of dimethylamine was dosed epichlorohydrin either to the heated till 40-49 ° C epichlorohydrin was dosed 25-40% aqueous solution of dimethylamine at the molar ratio of 1, 0-1,1: 1.0 accordingly. Then ethylenediamine or polyethylene amine in an amount of 0.1-2.0 wt.% is administered from the total quantity of epichlorohydrin and dimethylamine and the reaction al mixture was kept at 71-85 ° C for 1.5-2.0 hours. The method allows to improve the quality of the end product and significantly reduce in the content of harmful compounds - epichlorhydrine and 1,3- and 2,3-dichlorohydrins. The method is explained by the following examples. In 4-necked flask equipped with mechanical stirrer, thermometer, reflux condenser and addition funnel is charged with 45 g (1 mol) of 25% aqueous solution (187.5 g) of dimethylamine and heated to 40 ° C and at this temperature 92,5g 1 mole is dosed of epichlorohydrin (molar ratio of dimethylamine: epichlorohydrin = 1: 1) for 3 hours after the reaction temperature is raised to 71 ° C and kept at this temperature for 1.5 hours. 135.3 obtained (98.4%) of product (dry weight) is obtained.

The method of obtaining amidoepichlorhydrin resin in the interaction with the selected from the group: interaction product of di-, tri-, tetra- or polyamine with dichloroethane or dichloropropane at 60-125oC with a molar ratio (1-2): 1, with a dicarboxylic acid, at 160-180oC followed by reaction with epichlorohydrin at 40-48 C in a molar ratio of amine selected from the above mentioned group: dicarboxylic acid: epichlorohydrin is (1-2): 1: (1-2), respectively [4]. The method is explained by the following example. In the reactor, equipped with a mechanical stirrer, thermometer and dropping funnel is charged with 60 g (1 mole) of ethylenediamine (EDA) in 40 ml of H2O (60% aqueous solution of EDA) is heated to 80-100oC and is added dropwise 49.5 g (0.5 mol) of ethylene dichloride (EDC) at this temperature is kept heated at 100oC for 2 hours, is cooled to 40-60oC and then is charged with 73 g (0.5 mole) adiline acid (AA), the reaction al mixture is raised to 170-180oC, is produced distilled off low-boiling components and water. After removing the calculated amount of water / 4h / reactor contents are cooled to

100-120oC, are dissolved in 500 ml of H2O and are added 46.25 g (0.5 mol) of epichlorohydrin (ECH) and are stirred at 40-48oC for 2 hours. 194 g (92%) of the resin (on a dry weight of resin), the dynamic viscosity of 0.0095 · P s ability flocculation 84% is obtained.

It is known the method of obtaining of water-soluble copolymer comprising the interaction of epichlorohydrin excess with the primary or secondary amine or with the mixture of primary or secondary amine with ammonia and subsequent administration as the inhibitor of gelation of tertiary aliphatic amine [5]. Epichlorohydrin was dosed into an aqueous solution of a primary or secondary amine or a mixture of primary or secondary amine with ammonia at the temperature of 25-400S. Then reaction al mixture was heated to 90 0 C, after which the additional amount of epichlorohydrin was dosed where, the total mole ratio of epichlorohydrin to the primary or secondary amine or a mixture of primary or secondary amine with ammonia was (1,03-1,10): 1. Gelation inhibitor was administered in the amount of 0.2-0.5 moles per 1 mole the excess of epichlorohydrin. The invention allows to obtain the copolymer structure in which a long period gelation didn’t occur.

Within the framework of the proposed method can be used for obtaining various copolymers of different primary or secondary aliphatic amines, such as, methylamine, dimethylamine, methylethylamine, or mixtures thereof, or mixtures thereof with ammonia. The use of ammonia in this process in place of part of the amine reduces the cost to the obtaining copolymer. Tertiary amines used as gelation inhibitors preferably were lower aliphatic amines, such , trimethylamine, tri-ethylamine, methyldiethylamine, dimethylethylamine etc. Introduction of gelation inhibitor in the amount of 0.2-0.5 moles per 1 mole of epichlorohydrin excess was sufficient for inactivate of the rest epoxied groups contained in copolymer.

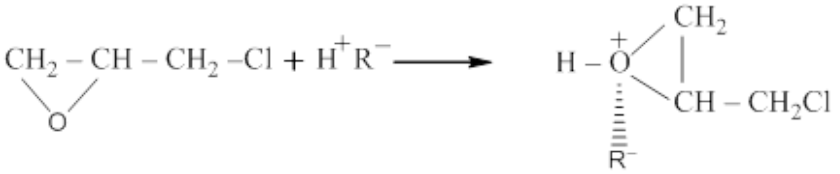
By authors was developed the method of obtaining flame retardant coatings on the base of polymeric binder, and can be used in various branches of industry to protect the fiberglass [6]. The invention provides a high fire protection coating for

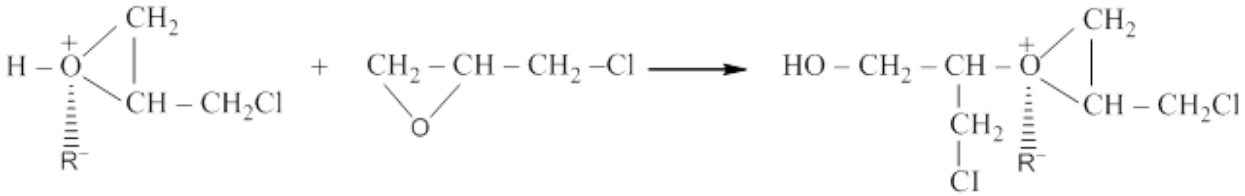
fiberglass. Fire-retardant composition comprises a polyvinyl resin, organic solvent, an intumescent additive. As the organic solvent, the composition comprises the mixture of butyl acetate and acetone in a ratio of 1: 1. As the intumescent additive composition contained phophorchloreontaining oligomer. Oligomer was beforehand obtained as a result of interaction epichlorohydrin with methylyphosphate borate in a weight ratio of 3.5: 3.0.

One-step method of synthesis epoxied-based oligomers on the base of diphenylpropane (TPA) and epichlorohydrin, was developed containing 15-45 wt. epoxyphosfasenes [7].The interaction of chlorcyclophasfazenes GHF and reacting the mixture with the excess TPA in the melt of the last or in inert solvents were obtained and characterized by oligohydroxidrilaxylphosfazes by reaction of which with epichlorohydrin were synthesized oligomer epoxiphosfazene with a molecular mass of 1800 - 2500 and the by the content containing of epoxy groups 18-20%. It was revealed that, underestimated in comparison with the calculated (21.3%) due to the number of epoxide side reactions of hydrolysis of epoxide groups and their interaction with chlorobenzoic acid. Significant increase of adhesion to metal adhesive compositions of epoxy-modified by obtained oligomers.

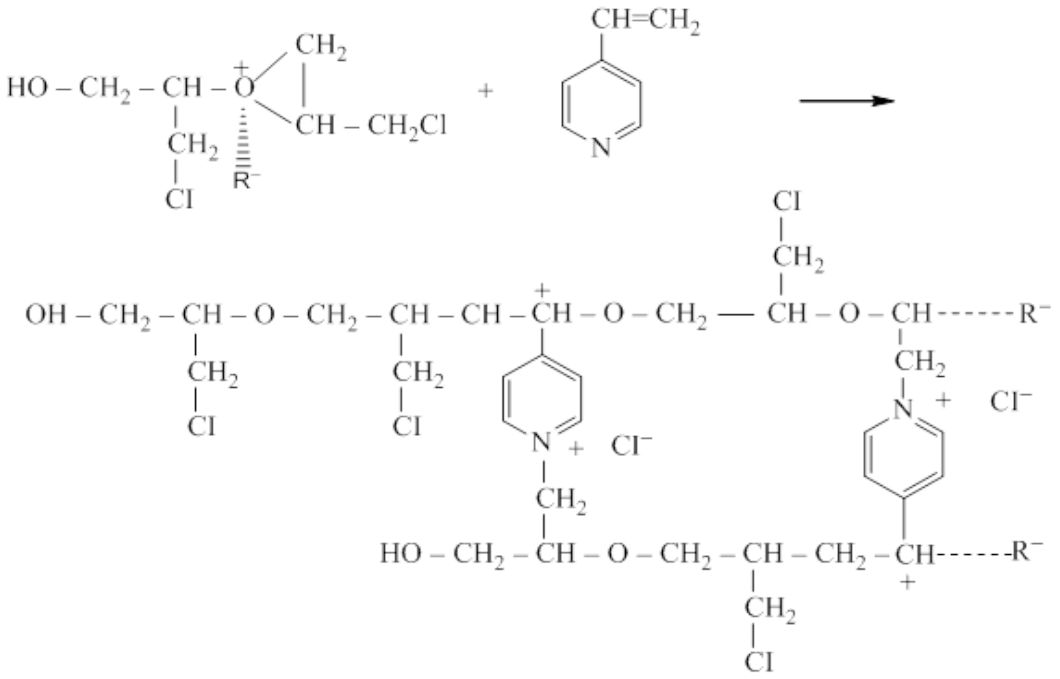
The Sorption of heavy metal ions (Cu2 +, Ni2 +, and CO 2 +) new anionites on the based of oligomer epichlorohydrin and 4-vinylpyridine [8] were investigated.

The first step concluded in obtaining epichlorohydrin of oligomer under the effect of the H + - catalyst according to the scheme:





In the second step oligomer ECHG was reacted with 4-din vinilpiri in the presence of benzol peroxide (BP) with the formation of anionite by network structure:

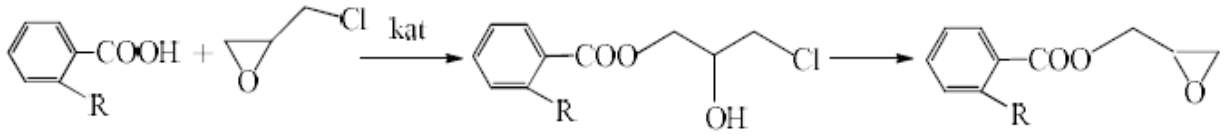


It was shown that the new macroporous anionites had the selective properties and can be used for separating cations Cu2 + and Ni2 + from ions CO2. More perspective anionite for purifying the wastewater in hydrometallurgy from copper and nickel ions is OECH9-VP-I, having more higher sorptional capacity.

Epoxide resin was obtained by reacting of epichlorohydrin with reactivity compounds, containing active hydrogen [9]. The compounds were used as reactive resin with coal pyrolysis hydroxyl content to 4.50 meq / g, and the carbonyl groups to 1.90 meq / g and optionally the oil slurry having pouring temperature not higher than -40 ° C, the a density was not more than 20 ° c 0.88 g / cm3 and conventional viscosity at 50 ° c and was not more than 1.5 s, whichwas the eutectic mixture of liquid products processing of fossil fuels, containing monohydric and polyhydric phenols and and alkylphenols in a weight ratio of resin to pyrolysis oil sludge 7-10: 0-3. Epichlorohydrin was introduced into the eutectic mixture with constant stirring and reflux temperature of the reaction mixture at a weight ratio of

epichlorohydrin to eutectic mixture 5: 1-0,5: 1, the reaction mixture was again brought to boiling point, followed by isothermal exposure at the temperature from 80 to 150 ° C till termination of gassing. The invention allowed to extend technological and explatational properties of epoxide resins with reducing their cost.

The kinetics of the reaction of epichlorohydrin benzoic acids acidolysis catalyzed by organic bases in the temperature range of 303 ÷ 363 K [10]:



For determining the order of reactions an substituted benzoic acids were studied reaction rate acid I-VI (a = 0.300 mol / l) with ECG (s = 12,23 ÷ 12,32 mole / l) in the presence of bases (b = 0,005 mol / l) in the investigated temperature range. Kinetic curved in coordinates the degree of conversion of carboxylic acids I-VI (ax, mol / l) from time (t, c) in the reaction with the ECG (see. Fig.) carried out rectilinear character with the correlation coefficient r> 0.98, which indicated to the zero order of reaction with respect to the carboxylic acid. Zero order of reaction on acid reagent was determined. It was shown that the reaction had low sensitivity to acidic properties of reactant and catalyst nature. Activation al parameters of reaction were calculated and to assess their compensational effect by varying the reagent structure and nature catalyst were assessed.

The mechanism of catalytic fenoliza and acidolysis of epichlorohydrin (ECH) [11] was investigated. For explaining the catalytic activity of trialkylamines and tetraalkylammonium salts in reactions of nucleophilic reagents with a-oxides as a catalyst was used (3-chloro-2-hydroxypropyl) trimethylammonium chloride, obtained in the reaction of trimethylammonium chloride with ECG. The kinetics of the reaction of ECH with carboxylic acids and phenols were studied.

Kinethetical dependence of reactions of benzoic, 3-nitrobenzoic acid 4-nitro-2,4-dinitrophenol and epichlorohydrin (s = 12.6 mol / l) in the presence of (3-chloro-2 , benzoic, 3-nitrobenzoic -hydroxypropyl) trimethylammonium chloride (b =

0.00300 mol / l) in the coordinates of the nucleophile concentration (C) from time (t) had the form of straight

(R = 0.993-0.999), that in conditions of excess epichlorohydrin indicates to the prseudozero reaction order and zero order reaction on acid reagent.

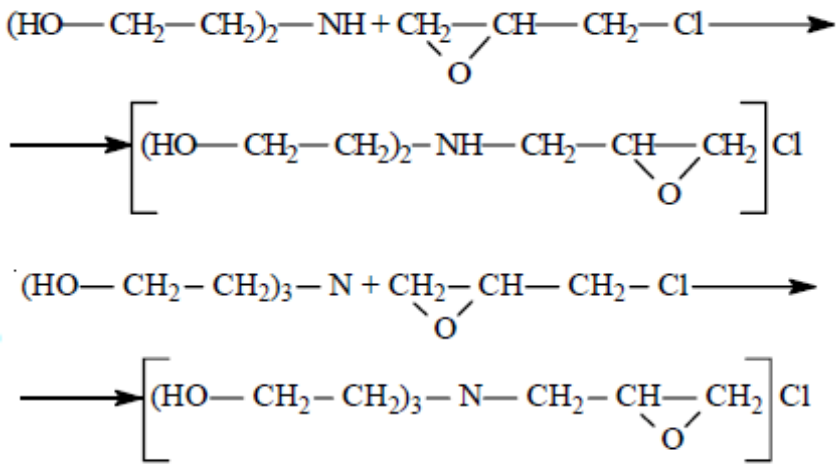
The reaction kinetics of epichlorohydrin with benzoic acid and 4-nitrophenol in the presence of catalysts chloride, tetraethylammonium bromide and iodide at the temperature of 333 K [12] was investigated in the work. The behavior of tetraethylammonium halides as catalysts for the oxirane ring open was studied, of investigations of halides behavior in the reaction of tetraethyl aci doliza fenoliza epichlorohydrin and it showed that the halide anion catalyzes the formation of chlorohydrin ether on the mechanism of transfering the anion of the nucleophilic reagent ion pair, and then was regenerated due to the formation of the glycidyl ether. The observed kinetic essentials of the reaction corresponded to the rapid formation of ion pair in the reaction of halide anion with oxirane compound and spending a nucleophilic anion in the composition of ion pair.

It was found out by authors found that the interaction with benzoxazolinone and a - amino acids in aqueous and organic media at relatively low temperatures (343-293K) flew the process spontaneous polymerization [13]. In this study the spontaneous polymerization with benzoxazolinone and α - amino acids with different molar ratios of the starting components in a wide range of temperatures (20-50 ° C) showed that the highest yield of polymer is achieved at the equimolar ratio of starting monomers. In the reaction of epichlorohydrin with benzoxazolinone and a - amino acids due to the high reactivity of epichlorohydrin and nucleophilicity benzoxazolinone and α-amino acid and chlorine atom occurs salt formation of amino compounds in the interval product which enhances the activity of functional groups, which in its turn leads to the leakage of spontaneous polymerization. This suggests that to the reaction of spontaneous polymerization , mainly enter taking part in salt formation reaction of amine compound molecule epichlorohydrin. It should be noted that the content of chlorine ion in polymers, varies slightly with the obtaining various molar ratios of the starting components.

For studing the effect on nature solvents of the polymerization, the process was carried out in solvent media with different dielectric constants (dioxane, acetone, benzene, DMSO and ethanol). It is shown that the spontaneous polymerization rate depends on the polarity of the environment (E) and occurs rather easily in aqueous and organic media. Increasing the polarity from 2,00 to 46,6 e accelerates the rapidity of spontaneous polymerization process, the highest rate is observed in DMSO environment.

It was carried out by authors that systematic study of reaction opening of the epoxide of epichlorohydrin to the residues on N-protected amino acids and also dipeptides, and nucleophilic substitution of chlorine atom in α-glycerol monohlorgidrine, α, γ-glycerol dichlorohydrin under the action of the lasts. [14] It was shown that the starting reaction of the epoxy ring and nucleophilic substitution depend on the structure of N-protected amino acids and dipeptides. Among the obtained substances were identified the compounds with selective regulatory effect on germination and raising energy of wheat seeds.

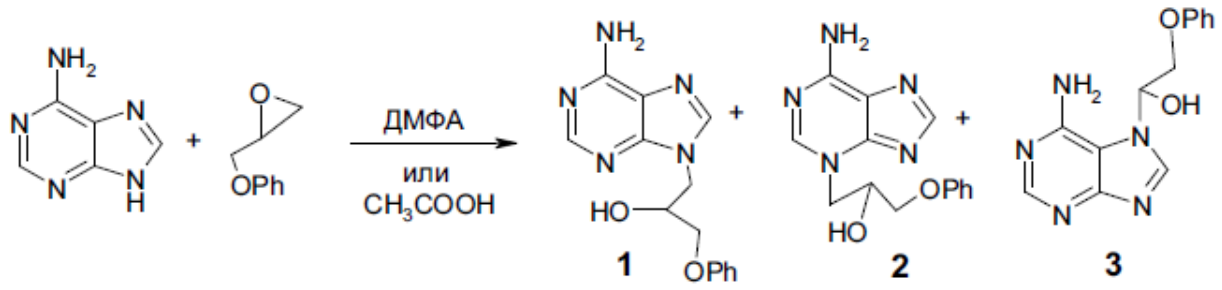
Quaternary ammonium salts on the base of di- and triethanolamine and epichlorohydrin [15] were synthesized and characterized. The reactions can be represented as follows:



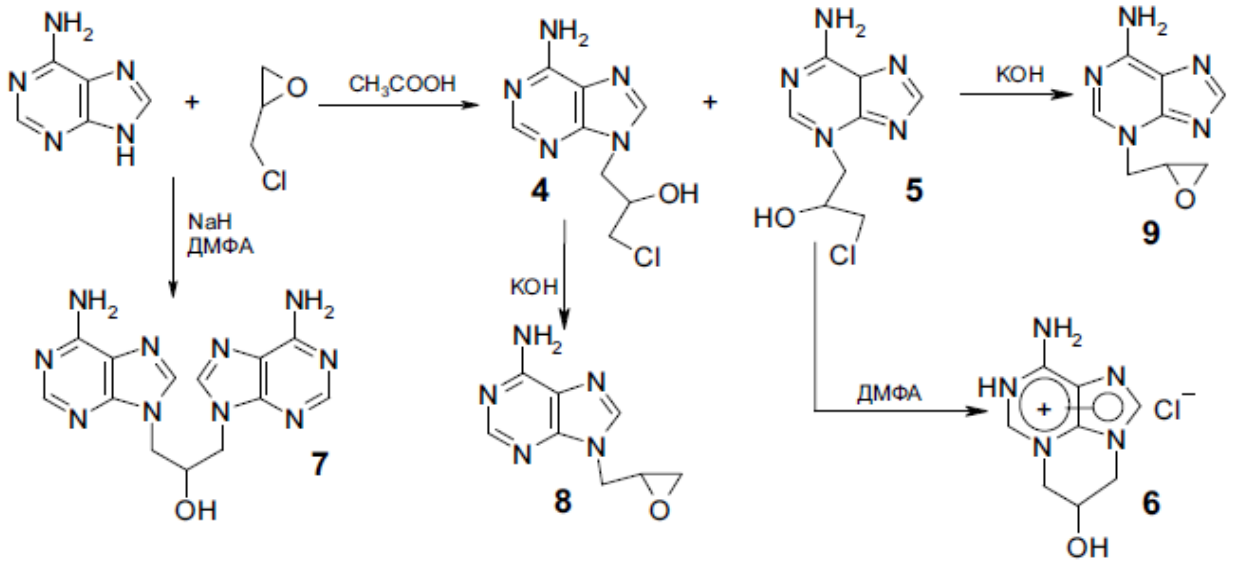
HOUR Syntheses were carried out at atmospheric pressure, by constant stirring in the solution of demineralized water and without solvent. The molar ratio of reactants EA: ECG ranged from 1.0: 1.0 to 1.0: 1.3, temperature - from 20 to 90 °

obtaining were chosen, Optimal conditions of obtaining on the base of EA reagents in aqueous solution were: temperature - 60 ° C, reaction helding time - 6 hours, molar ratio of reacting substances were 1.0: 1.1. The inhibitory properties of obtained compounds were investigated.

The reaction of adenine with epichlorohydrine(1-chloro-2,3-epoxypropane) carried more complicated character taking into account that in the substrate are some nucleophilic centers in the exo and endo-nitrogen atoms, and in alkilating agent had a reactive epoxy ring and a movable chlorine atom. At playing the experimental conditions of synthesis N- (3'-chloro-2'-hydroxypropyl) -adenine in in preparative version (downloading tens of grams of reagents) by authors chromatography and spectrally found that as a result of the given reaction was formed the mixture of two isomeric derivatives of adenine as a result of (4, 5) and its recrystallization of it from 50% of acetic acid was managed to isolate a compound in pure form (4) with a yield of only 11% [16, 17]. After evaporation of the filtrate and fractional reprecipitation of the solid residue from alcohol diethyl ether was obtained in a yield of 45% pure compound (5)



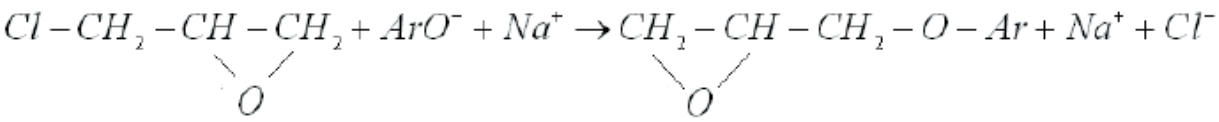
Interestingly, the isomer (5), in contrast to (4), by heating in DMF was undergoing intramolecular cyclization to form a soluble salt-tricyclic derivative: chloride 10-amino-5,6-dihydro-5-hydroxy-pyrimidin-4H [1 , 2,3-cd] purine-3 (6) with a yield of 65%, and by reacting (4) or (5) with aqueous sodium hydroxide was formed respectively N- or N- (2 ', 3'-epoxypropyl) - adenine or a yield of 75-80%.



Interaction with epichlorohydrin adenine allowed to obtain compounds having alkyl chains simultaneously in two different functional groups, which allowed to synthesize products intra- and intermolecular alkylation. The reaction of 2 equiv. adenine sodium salt with 1 eq. epichlorohydrin in the presence of sodium hydride in absolute DMF occured simultaneous opening epoxy ring and replacement of chlorine atoms with epichlorohydrin in the substrate ,which was alkylated preferably on the position 9 with the formation the bis-adenilproizvodnogo: 1.3 dyad-9-yl-propan-2-ol (7) with a yield of about 30%.

This work was devoted to the study of the kinetics of reactions arylates (4-methoxy-phenol, 2,4-dibromophenol and pentabromphenolate) sodium with ECG in various solvents and their mixtures with water. [18] Monitoring on the going process was carried out with the help of spectrophotometric method, based on measurement ,depending the law of Lambert-Beer, light absorption in the field of λ = 290-320 nm corresponding arylate- ion,reducing in the course of the reaction. The measurements were carried out a spectrophotometer SF-4A in temperature-controlled quartz cuvettes square (cross section of 1 cm2). The outgoing concentration of sodium arylate, prepared by addition excess of sodium hydroxide to the solution corresponding phenol showed b = (0,6 ÷ 1,7) · 10-4 mol / l, and ECG - and ÷ 1.120 = 0.085 mol / l. Special experiments showed that these reactions in aprotic solvents such as dimethyl sulfoxide and dimethyl formamide at 293 ÷ 323 K were not held practically. It was not observed that their flow and in

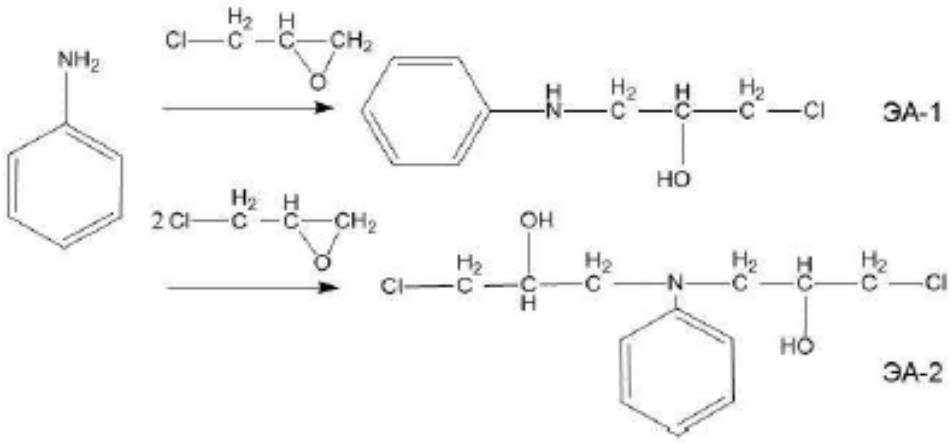
pure monoalkylsellozolves. At the same time, in such aprotic solvent, as acetonitrile (ACN), protic solvents - alcohols, their binary mixtures - arylglicide ester formation proceeds at an appreciable rate, which was described by an equation of the second order (for each of the first reagent) according to the scheme:



The basic method of synthesis of novel 3-O-aryl ester (R, S) -9- (2,3-dihydroxypropyl) adenine was the alkylation of adenine- base arylglicide ethers in the media of anhydrous dimethylformamide at a temperature of 105-110 ° C in the presence of potassium carbonate [19] . Outgoing arylglicide starting ethers were obtained by reacting the corresponding phenols with epichlorohydrin in an alkaline medium:

According to to the given on PMR spectroscopy and thin layer chromatography, the alkylation reaction of potassium salt adenine, used epoxides occured under these conditions with high regioselectivity and did not cause the side-7-substituted derivative adenine. Synthesized 3-O-aryl ethers of (R, S) -9- (2,3-dihydroxypropyl) -adenina were well soluble in acids, ethanol, dimethyl sulfoxide and presented the interest as potential antiviral agents. It was shown that several compounds of the originator - (R, S) -9- (3-phenoxy-2-hydroxypropyl) adenine exhibited the activity against Coxsackie virus B4 (EC50 = 240 pg / ml) at a value cytotoxicity than 400 mkg / ml.

By authors were studied the interaction reaction of epichlorohydrin with an aniline [20]. It was shown that the outgoing reagents ratio 1: 1 EA- it was formed the product 1, and with a ratio of 2: 1 - EA-2. Possible schemes of their interactions were shown below:



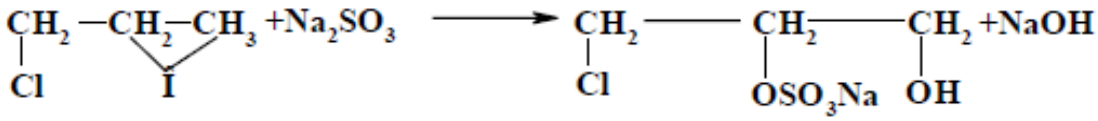
It was determined the optimum reaction conditions (t = 25˚C, reaction time 24 hours). The structure of the compounds was confirmed by PMR and IR spectral investigations.

It was synthesized oligomeric surface-active substances (surfactants) in the interaction of epichlorohydrin (ECH) with nitrogen and silicon containing furan compounds [21,22]. It was determined by IR spectroscopic and kinetic investigations the mechanism of interaction, the reaction order on components, dependence of chemical structure of oligomer from the staff of outgoing mixture. It was established , that the process was carried out as a result of donor-acceptor interaction of nitrogen and halogen ion and due to the opening of epoxy ECG. According to the depending on the ratio of reactants and temperature can be formed both linear and reticulated oligomeric substances.By the mathematical modeling method were defined the optimal conditions of synthesis furan-epoxide resins.

Synthesized oligomeric quaternary ammonium salt ECG with DAEDFS had the properties of effective surfactant [23]. The surface tension of water at 293 K was reduced to 53.72 mN / m by introducing into it 3.10-2 mol / l of salt synthesized. Increasing the salt concentration of the oligomer caused the shift of the maximum electrocapillary curves toward more positive values, which were characteristic to cationic surfactant type. The critical concentration micelle formation in aqueous solution for ECG with DAEDFS showed 0.015%, the

saturation adsorption layers oligomer was developed in a very narrow concentration range.

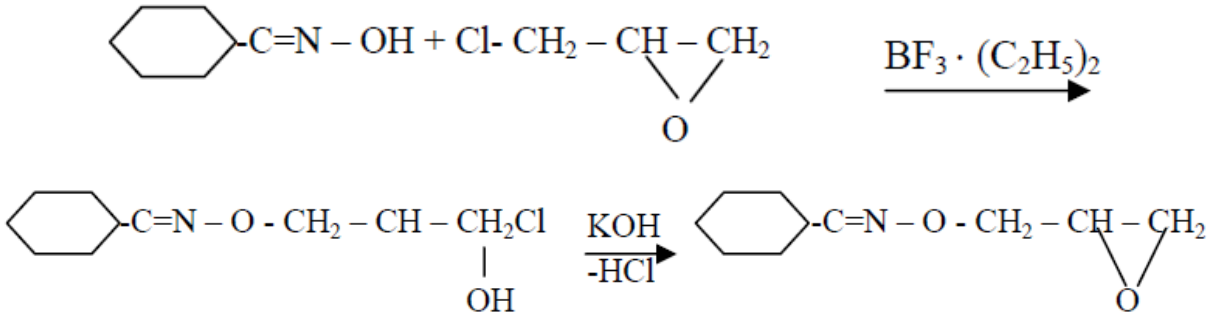
The given work was devoted to the study interaction of epichlorohydrin and sodium sulfite. [24] In three-necked flask with cubic content of 250 ml ,equipped stirrer, thermometer and reflux condenser were charged with 0.13 moles of epichlorohydrin and an equal molar amount of sodium sulfite ,it was downloadedd epichlorohydrin and the same molar amount sodium sulfite beforehand soluted in 65 ml of water. On the basis of the following reaction equation:



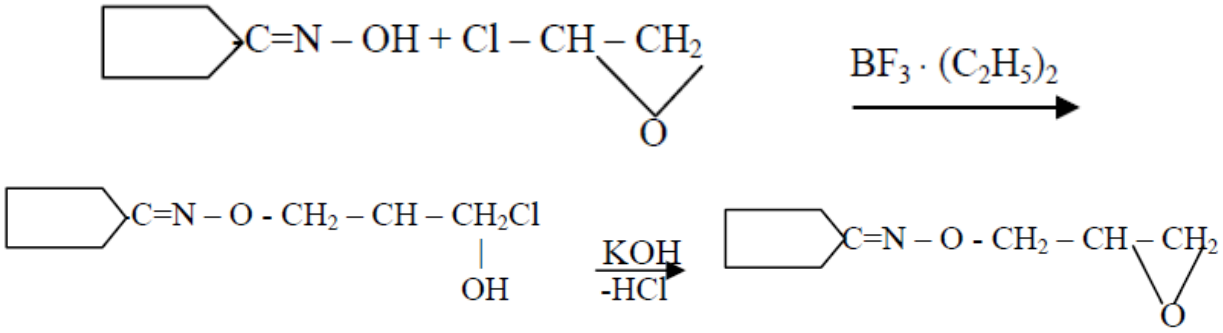
During the reaction time was separated caustic soda, and the reaction was accompanied by separation of heating and significantly heating up of reaction mass. For avoiding the strong heating and kickback of reaction mass the speed of adding of sodium sulfite solution was regulated so that, the temperature in the flask did not exceed 30 ° C. Besides that , the reaction flask during synthesis was placed in the ice bath.

The interaction process of epichlorohydrin with sodium sulfite was controlled by the number of separated alkali, due to the content of which was judged the degree conversion of epichlorohydrin.

It was studied the interaction reaction of cyclopentanone and cyclohexanone oxime with epichlorohydrin in the presence of BF3 · O (C2H5) with the obtaining the chlorohydrin ethers corresponding of cyclic oximes [25]. The condensation reactions of epichlorohydrin with cyclic oximes were carried out in the medium of ether under catalysis of boron trifluoride etherate in an amount of 0.01% relative to the epichlorohydrin. The reaction time was 2.1 hours. The reactor was charged oxime ,soluted in ethyl ether and catalyst were BF3 · O (C2H5) 2 on dropwise for 1 hour was added epichlorohydrin. The reaction proceeded in the as following :



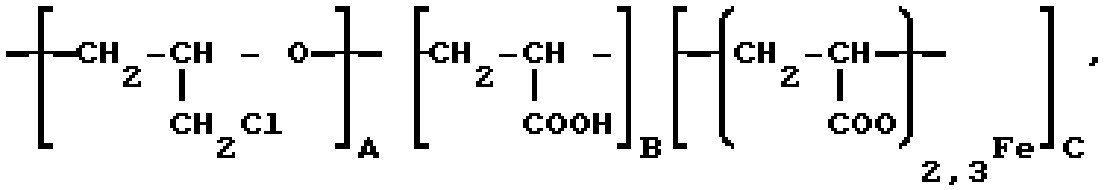
In the second reaction step,obtained chlorohydrin oximes under the action by alkali of potassium hydroxide were transferred to dehydrochlorination in epoxy ethers:



Synthesized chlorohydrins of epoxy ethers were subjected to physical - chemical analysis.

In the article it was investigated the synthesis of oligomeric derivatives of gossypol with epichlorohydrin and allyl halogens [26]. The structure of oligomeric derivatives of gossypol was confirmed by IR spectroscopy and elemental analysis. It was studied the antioxidizing capacity of oligomeric derivatives of gossypol by the inhibition of polyethylene with low density (LDPE). The study of the antioxidant properties of the synthesized oligomeric antioxidants by mass chromatography showed that the comparison of the LDPE degradation products allowed us to conclude about the influence of antioxidants on the rupture process of the C-C bonds. The main criterion of the stability the stabilized samples can be served as the amount R-In connections by the destruction of LDPE.

It was synthesized by authors that water-soluble copolymers of acrylic acid with epichlorohydrin of the following structure [27]:



Copolymers were received by copolymerizing of acrylic acid with epichlorohydrin in the presence of oxidative-renovating system of ammonium persulfate Mohr's salt. 8% aqueous solutions of copolymers -WIDE were 2-6 times faster glued paper and glass, 2-2.5 times faster wooden surface and unlike SC-1 bonded steel surface. Glue seam 8% aqueous solutions of the copolymers can withstand up to 190 cycles of temperature changes from -196 to 120 ° C. SC-1 120 cycles. The composition and structure of the copolymers were studied by elemental analysis and IR spectroscopy.

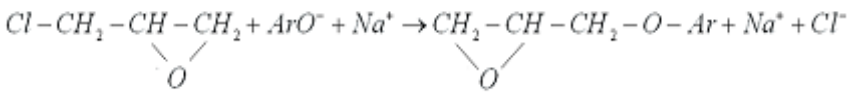
It waws studied synthesis conditions and were investigated the properties of polyelectrolyte from epichlorohydrin (ECH) and dimethylamine (DMA) at different sequence of input starting components [28]. It was established the effect of temperature synthesis to the indicator of dynamic viscosity of polyelectrolyte, conditioning the efficiency of its usage in the wastewater treatment process of organochlorine production. It was found that the sequence of input raw materials did not significantly affect to the structure of the resulting polyelectrolyte EHGDMA, but affected to the dynamic viscosity indicator, extending the boundaries of its applicability;

It was shown that increasing the polymerization temperature from 60 to 80 0C leaded to decrease the viscosity with 142.5 to 110 cps, which was associated with the increase formation of supplementary products in the increasing temperature. It was established the absence of negative impact to the synthesized polyelectrolyte EHGDMA on the activity of microorganisms and the biochemical activity of the sludge in the biological treatment of wastewater.

The authors found that the interaction with α-amino acids and benzoxazolinone in aqueous and organic media at relatively low temperatures (20-50 0 C), the process proceeds spontaneous polymerization [29]. In this study the

spontaneous polymerization benzoxazolinone and α-amino acids with different molar ratios of the starting components in the specified temperature range showed that the highest yield of the polymer was achieved at an equimolar ratio of starting monomers. In the reaction of epichlorohydrin with α-amino acids and benzoxazolinone due to the high reactivity of chlorine and nucleophilicity benzoxazolinone epichlorohydrin and α-amino acids occured atom salification compounds in the intermediate product which enhanced the activity of the functional groups, which in turn leaded to leakage spontaneous polymerization. This suggests that spontaneous polymerization reaction generally took part in salt formation reaction of epichlorohydrin amine compound molecule.

Arylates reaction kinetics (4-methoxy phenolate, 2,4-dibromo phenolate tetrabromo phenolate) with epichlorohydrin in sodium protic and aprotic solvents and mixtures thereof with water [30]. It was established that these reactions in dimethylformamide, dimethylsulfoxide at 20-50 ° C were practically. At the same time, in an aprotic solvent such as acetonitrile, protic solvents - alcohols / their binary mixtures - education aryl glycidyl ethers proceeded at an appreciable rate under the scheme:



Considering the possibility of aimed product (4-methoxy, 2,4-dibromo, pentabrominated phenyl glycidyl ether) in the presence of water, and toxicity of methanol,its mixtures with isopropyl alcohol, the authors proposed the process of interaction with epichlorohydrin sodium arilata carried out in isopropanol.

Thus, the learned literature review showed that epichlorohydrin having high reactivity ,conditioning by the presence in the molecule of movable chlorine atom and epoxy group was widely used. It easily reacted with compounds of different classes, which allowed to obtain on its base a number of products used in many industries. In this connection, the synthesis and study of derivatives of epichlorohydrin represents undoubt great interest for science and industry.

CHAPTER 2 .OBJECTS AND METHODS OF EXPERIMENTAL INVESTIGATIONS

2.1. Objects of research

The initial reagents and solvents were purified according to the previously known methods [31].

EPICHLORHYDRIN (1-chloro-2,3-epoxypropane; chlormetiloksiran, chlorpropilen 2-oxide) - organic substance, chloro derivative of propylene oxide with the formula CH2-O-CH-CH2Cl. It was widely used in organic synthesis, it was also used in the production of epoxy resins and glycerol. It was a colorless transparent liquid with the movable irritating odor of chloroform, poorly soluble in water, well in most organic solvents.

CAS NR	106-89-8
Synonyms	1-Chloro-2,3-epoxypropane; 2-chloropropane oxide
Gross	C_3H_5ClO
Qualification	99,8%
Addit. information	Production of Russia, Poland, Czech Republic

Appearance - clear liquid with a sharp, unpleasant smell.

Density: 1.181 g / ml (20 ° C).

Boiling temperature: 116 ° C

content of main substance: at least 99.8%

It was well soluble in organic solvents; solution in water was limited.

Piperidine (hexahydropiridin, pentamethylenimine), it was said that 85.15 m.; colorless liquid with a pungent odor amine; mp-90 degrees C .; bp. 106,17 0C, 36,7 ° C / 70 mm Hg .; 0.8606; 1.4530; pK 11,25 (250C). Miscible in all proportions with water and most organic solvents; It formed an azeotrope with

water (t.kip.92,8 0C, 35% water by weight). It possessed properties of secondary aliphatic amines. According to their chemical properties piperidine was a typical secondary aliphatic amines.

Piperidine as a high-boiling secondary amine was used for the conversion of ketones to enamines which can be alkylated or acylated in the α-position (Stork reaction).

UREA (carbonic acid diamide, urea) $(NH_2)_2CO$, mol. wt. 60,06; colorless crystals, odorless; melting temperature 132,7 °C; density 1330 kg/m^3 (25 °C); n_D^{20} 1,484; C° 93,198 J/mol·K); thermal conductivity(135°C) 0,42 W/(m·K); p 2,3 Om·m. Solubility (g per 100 g solvent): in water -51,8 (20°C), 71,7 (60°C), 95,0 (120°C); liquid NH_3-49,2 (20°C, 709 кПа), 90 (100 °C, 1267 кПа); methanol -22 (20 °C); ethanol-5,4 (20 °C); isopropanol -2,6 (20 °C); in isobutane-6,2 (20 °C); ethyl acetate -0,08 (25 °C); not sol. chloroform.Urea molecule had a planar structure.

By heating to 150 ° C and above urea successively changed to NH_4NCO, NH_3, CO_2,biuret, cyanuric acid.

Ethyl alcohol (ethanol)- CH_2CH_3OH. Colorless liquid, T_{boil}=78,39 ^oC; $d=0,80645^0_4$; $n=1,3611^{20}$; well soluble in water; soluble in chloroform, benzol, methanol.

Acetone (dimethyl ketone, 2-propanone) - an organic substance, having the formula $CH_3—C(O)—CH_3$, the simplest representative of saturated ketones.

Acetone its name wastook from the Latin word «*acetum*»—vinegar. It was connected with the fact that the earlier acetone was received from acetates, and from acetone itself was taken the synthetic glacial icy acetic acid.Acetone - a colorless mobile liquid (at standard conditions) with characteristic pungent odor. In all proportions it was miscible with water, diethyl ether, benzole, methanol, ethanol, many compound ethers and so on.

Dimethylformamide(*DMFA*)— an organic compound with the formula (CH3) 2NC (O) H. Colorless fairly viscous liquid with weak specific "fishy" odor , because of the decomposition of the product - dimethylamine. In pure form it was

practically odorless. Due to the presence of two resonance forms the order communications of dimethylformamidewere reduced C = O and C-N is increased.

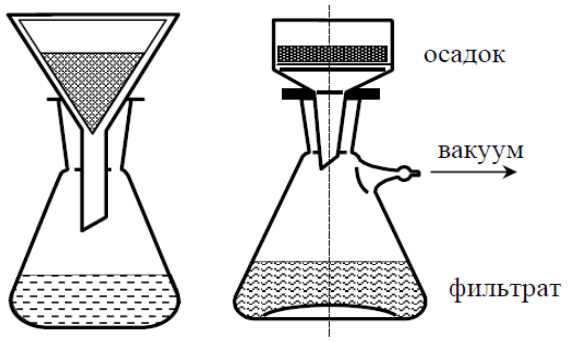
BENZOLE(C_6H_6, PhH)—an organic chemical compound, colorless liquid with a specific sweet smell. The simplest aromatic hydrocarbon. Benzol was a part of gasoline which was widely used in industry,it was the feedstock for the production of drugs, a variety of plastics, synthetic rubber, dyes. Although benzol was a part of crude oil on an industrial scale ,it was synthesized from other components. Toxic, carcinogenic. Colorless liquid with a pungent odor. Melting point = 5,5 ° C, boiling point = 80,1 ° C, density = 0.879 g / cm^3, molar mass = 78.11 g / mol. Like the unsaturated hydrocarbons, benzol burnt strongly smoky flame. C forms explosive mixtures with air, mixes well with ether, and gasoline and other organic solvents with water forms an azeotrope with a boiling temperature of 69,25 ° C (91% benzol). Solubility in water 1.79 g / l (at 25 ° C).

2.2. Methods of investigation of initial reagents and synthesized substances

Filtration

For the separation of synthesized crystalline reaction products from soluble contaminants were used the filtration method [31,32]. In the simplest case, filtration was carried out through a funnel in which was embedded a pleated paper filter (Figure 1, A). The flowability of liquid was carried out only under its own weight filtered mixture so the filtration rate was low, besides the precipitate was almost impossible to completely separate the solvent residues.

Devision of crystalline products reaction and also were carried out the process of suction through paper filter. For carrying out this operation it was used the device, consisting of Buchner funnel and flask Bunsen (Fig. 1b). Filtering in this case was performed in the following way. Good suitable size filter paper laid on the perforated surface of the Buchner funnel, soaked with solvent and sucked his connecting Bunsen flask to the vacuum system.



а б

Fig.1. Devision of crystalline product by filtration through the funnel with paper folded filter (a) and through a Buchner funnel and flask Bunsen (b).

Thereafter, to the filter was poured filterable mixture, collecting filtrate to the flask. For removing the excess of solvent precipitate squeezed flat glass stopper and optionally washed crystals solvent in which the substance was poorly soluble. Dimensions Buchner funnel selected depending on the amount of sediment.Thereafter, the filter was poured filterable mixture, collecting the filtrate in a flask. For removing the excess of precipitate solvent squeezed it was glass stopper and optionally it was washed by solvent crystals , in which the substance was poorly soluble. Dimensions of Buchner funnel were selected depending on the amount of precipitate.

Distillation

Distillation was used for cleaning initial reagents and for separating individual substances from liquid mixtures, in which the reaction product was highly soluble and can not allocate extraction [31,32].

At atmospheric (simple) distillation liquid was transferred to a vapor and then it was condensed to another part of the device.

The standard device for simple distillation consists of distilling flasks, refrigerator with a tap (alongem) and the receiver (Fig. 2). As distillation flask was

used Wurtz flask , equipped with side pipe for returning vapor. To the neck of the flask was inserted thermometer with cork to determine the temperature of the vapor. For the distillation flask it was used with deflegmatorm.

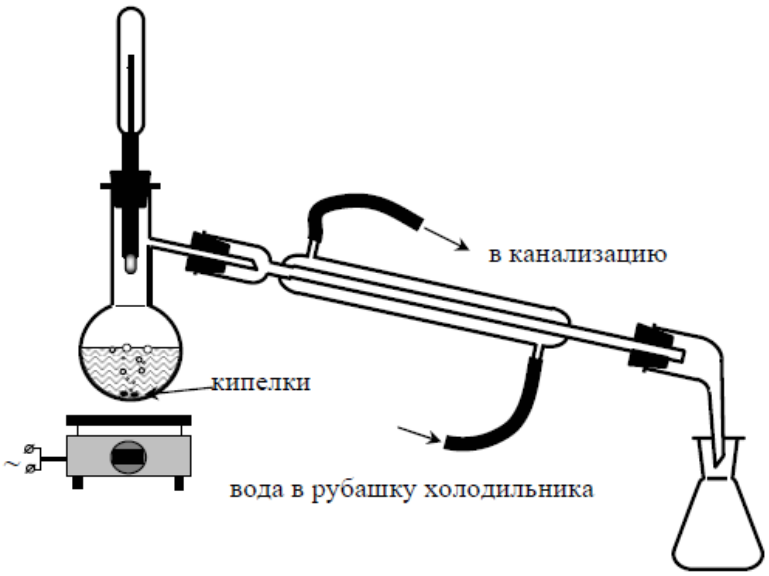


Fig.2. Distillation unit at atmospheric pressure.

Determination of refractive index

Refraction index was refered to the major characteristics of substances and it can be used to identify and verify its purity. The importance of refractive index depended on the temperature, and wherein the temperature increased the value of its fell. Depending on the wavelength of light concentration of solvent value index was changed. As a rule, measurements were carried out for spectral lines of sodium yellow flame at 20 °C (D). In designating the refractive index it was indicated the wavelength and temperature, for example ,e.g.$n^{20}{}_{D}$.

The refractive index was determined by laboratory refractometer. Before starting the work on the refractometer IRF-22 (3), it was opened the hemisphere measuring head (1), it was rubbed flat prisms cotton, wool knob soaked with ether, and it led them to the horizontal position with handwheel (4). Then, in the measuring prism surface was coated with a glass rod of few drops of test liquid, and head was closed. The illumination mirror (5) was adjusted so that light from the source through the window went into the lighting prism and equally illuminated field of view. In this position, the mirror was fixed with

screw. Turning the knob (4) and observing through the eyepiece (8) of the telescope (7), it was found the boundary between light and shadow. If that boundary was blurred and painted, the handwheel (3) eliminated coloration. Then with handwheel (4) was exactly combined light and shadow interface with crosshair grid and it was removed the scale reading of the refractive index. The refractive index was measured with an accuracy of four decimal places.

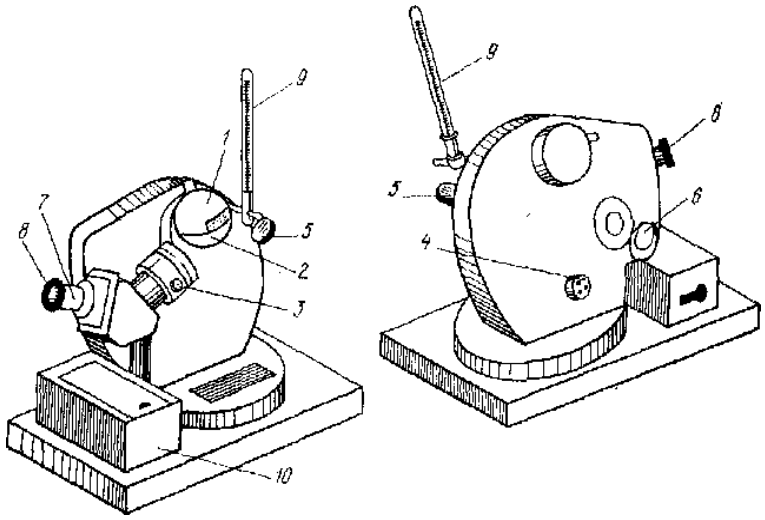


Figure 3. Laboratory refractometer

Recrystallization

For cleaning the solids recrystallization method was used [31]. The method was based on the different solubilities of compounds in a solvent at different temperatures. For each case solvent was selected ,in which the substance at ambient temperature partially was dissolved. By crystallization the synthesized substance was soluted, the solution prepared for the crystallization (separation of insoluble impurities), the resulting crystals were filtered and washed by clean solvent.

Determination of melting point

For determination of melting temperature was applied Thiele device. Thermometer was placed in heat transfer medium, which was used as dialkyl phthalate, silicone or paraffin, and sometimes sulfuric acid. The substance was placed in a capillary (capillary tube) having a diameter of 1 mm. The sample

preparation was carried as in the following. The capillary length of 6-8 cm sealed with one hand over the flame of a spirit lamp to form the glass droplet. Then small amount of material, powdered, was placed on a clean hard surface. Tapping unsealed capillary end on the layer of substance it was injected inside. Then, the capillary was turned open end up, and dropped several times on a hard surface capillary inside the glass tube. This substance was typed into the capillary, tamp the bottom of the capillary. The height of the column of substance in the capillary to be 4.6 mm. The sample was then prepared to determine the melting temperature. Prepared capillary material was introduced into the side arm Thiele device so that sample material was on the level of thermometer bulb. Device for a spirit lamp heated flame such a way that the rate of temperature increase not exceeding 4.6 deg. / Min, and fixed the temperature range , in which the solid phase transformation took place in the liquid.

Determination the viscosity of oligomers solutions

Measurement of solution viscosity of oligomeric was held using Ubbelohde capillary viscometer at 25 °C according to the method[33]. The distilled water was used as solvent.

Determination of thermal stability

One of the methods of physical and chemical analysis, widely used in the investigation of inorganic and organic substances, was thermal analysis. The essence of thermal analysis was to determine the temperatures ,at which the physical state of the substance or its chemical composition were changed . Thermal analysis was based on the determination of the change:

1) Energy - differential thermal analysis (DTA);

2) Weights (mass) - thermogravimetric analysis (TG);

3) Sample size - dilatometry (DM);

4) Conductivity and viscosity of testing substance.

The thermal stability of the synthesized substances were determined on the instrument Netzsch Simultaneous Analyzer STA 409 the PG, K-type with thermocouple (Low RG Silver) and aluminum crucibles. All measurements were

carried out under inert nitrogen atmosphere with a speed nitrogen flow rate of 50 ml / min. Temperature measurement range was 20-450 °C, heating rate - 5 K / min. Quantity of sample per measurement was 5-6 mg.

IR spectroscopy

IR spectra of initial and synthesized compounds were recorded to FTIR spektrofotormetre SISTEM-200, designed for re-registration spectra of absorption of various substances and measurement the transmittance in the range was from 4000 to 450 cm-1. The radiation source (detector) was made from alloy of $LiTaO_3$. Solvability – error of spectrophotometer on the scale of wavy numbers was ± 0,5 cm -1. Filtering of higher order spectrum in operating range was held by means of interference filters. Preparation of samples occurred as follows: solid material was ground in the agate mortar manually to a "powder". The sample was ground into a powder, mixed with the immersion medium - potassium bromide and was studied. Identification of IR spectra spectra of testing compounds was carried out using [34,35].

The purity of synthesized compounds was controlled by the method of thin layer chromatography on plates Silufol: eluent benzene-acetone, manifestation – pairs of iodine.

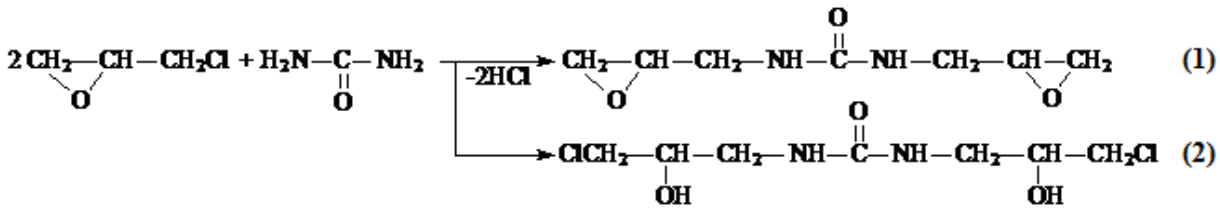
CHAPTER 3: SYNTHESIS AND STUDY OF NEW DERIVATIVES EPICHLOROHYDRIN (discussion of the results)

3.1 The study of reaction interaction epichlorohydrin with carbamide

Epichlorohydrin had highly reactive properties which were associated with the presence of molecules in the substance from epoxy group and chlorine atoms. The given substance hada very high chemical activity, so it was used for a variety of reactions that were associated with conversion of organic molecule structures in compounds which contained epoxy group. The substance was virtually indispensable as a synthesis of substances with glycerine. Among the extended reactions in industry it was used a variety of condensations, applied used for the production of epoxy resins, amination reactions eretification, hydration and hydrolysis. Besides that, epichlorohydrin widely used in other reactions.

The aim of this work in this section was synthesis of new compounds with epichlorohydrin carbamide

The reaction of epichlorohydrin with carbamide tooks place according to the following scheme:



The structure of the synthesized product based on carbamide on the base of

epichlorohydrin was studied by by IR spectra analysis. For comparison were taken and IR spectra of initial reactants of epichlorohydrin and carbamide (fig.1,2).

In IR spectra of carbamide appeared specific absorption bands ,which associated with the vibrations of bonds NH2, and C = O, which shown in the field 3500-3300 cm^{-1} and 1360-100 cm^{-1} (Figure 7). Absorption in the field 3500-3300

cm^{-1} conditioning the valency vibration bonds of NH2. The stretching vibrations of C = O groups were in the region 1720 cm^{-1}.

The IR spectra of the signals of epichlorohydrin stretching vibration of C - Cl bond (1270 cm^{-1}) attributable to the group CH2Cl epichlorohydrin epoxy characteristic signal in the field 1250, 930-850 cm^{-1}.

The comparison of IR spectra of initial epichlorohydrin, carbamide and its co-products (1) it was found that in the product range of the disappearance of the valency vibrations of H_2N - groups at 3210 cm -1 and the appearance of new bands at 3105 and 1127 cm^{-1}, which refers to the valency vibrations -NH groups it was observed characteristic absorption bands at 1250 cm^{-1} and 850 cm^{-1}, which can be attributed to the vibrations of the epoxy ring.

By experimental investigations was established that the yield of the product of the first reaction (1) was 57% and the second output (2) of the product 31%. The properties of both products (Table. 1).

Table 1

The properties of the synthesized products based on epichlorohydrin with carbamide

№ of substances	Yield, %	Solubility				
		benzol	ethanol	acetone	water	DMF
1	57	-	+	badly	+	+
2	31	-	+	badly	+	+

DMF - dimethylformamide.

Thermogravimetric investigations of synthesized compounds were carried out. (1) (Figure 1)

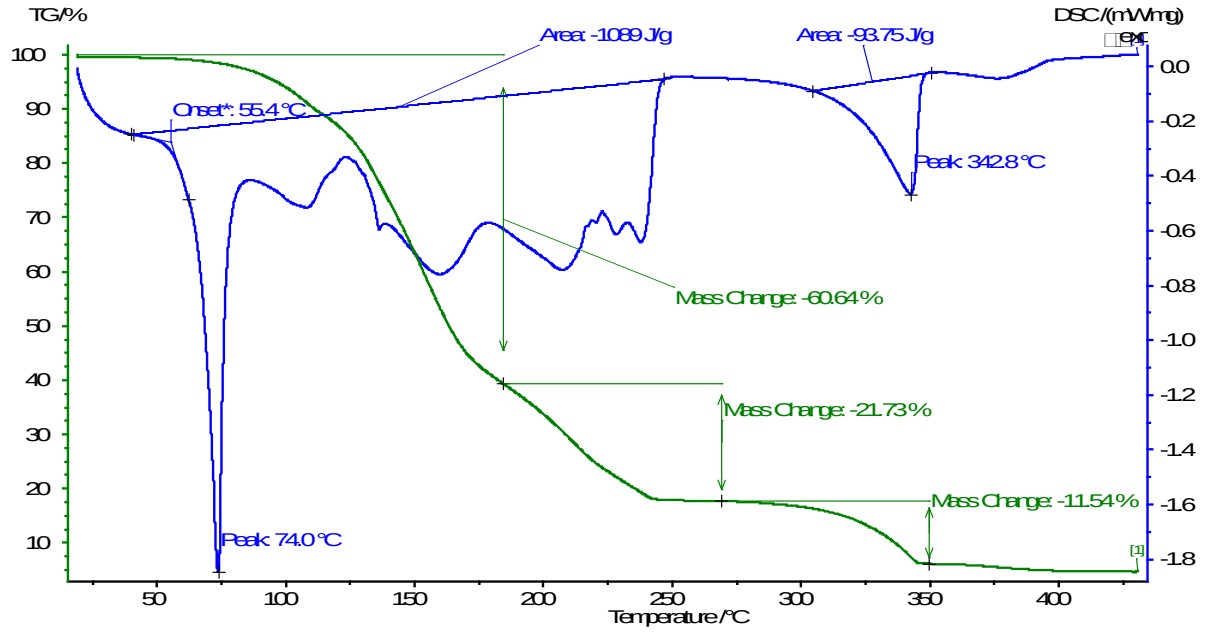


Fig. 1. Thermogravimetric analysis of the reaction product of epichlorohydrin with carbamide (1).

As seen from the thermograms synthesized compound (1) was stable up to 55 °C in temperature. At a temperature of 55.4 ° C melting material occured (with endothermic peak Tmax = 74 ° C followed by decomposition of sample. In the temperature range of 54-185 °C was observed the first stage of mass loss Δm = 60,64%. (Corresponding to the endothermic peak had a max at 159.9 °C,). That corresponded to a yield loss of mass of volatile CO2 component, 2NH3, H2O (theoretical calculation gives a value 60%). The second stage of mass loss Δm = 21.73%, associated with the release of hydrogen chloride was observed in the temperature range 183-268 ° C (had an endothermic peak max at 207 °C). The total absorbed energy to coke was 1089 J / g. The third stage of weight loss in the amount of 11.54% corresponded to the sublimation of the residual coke (theoretical value of 10%).

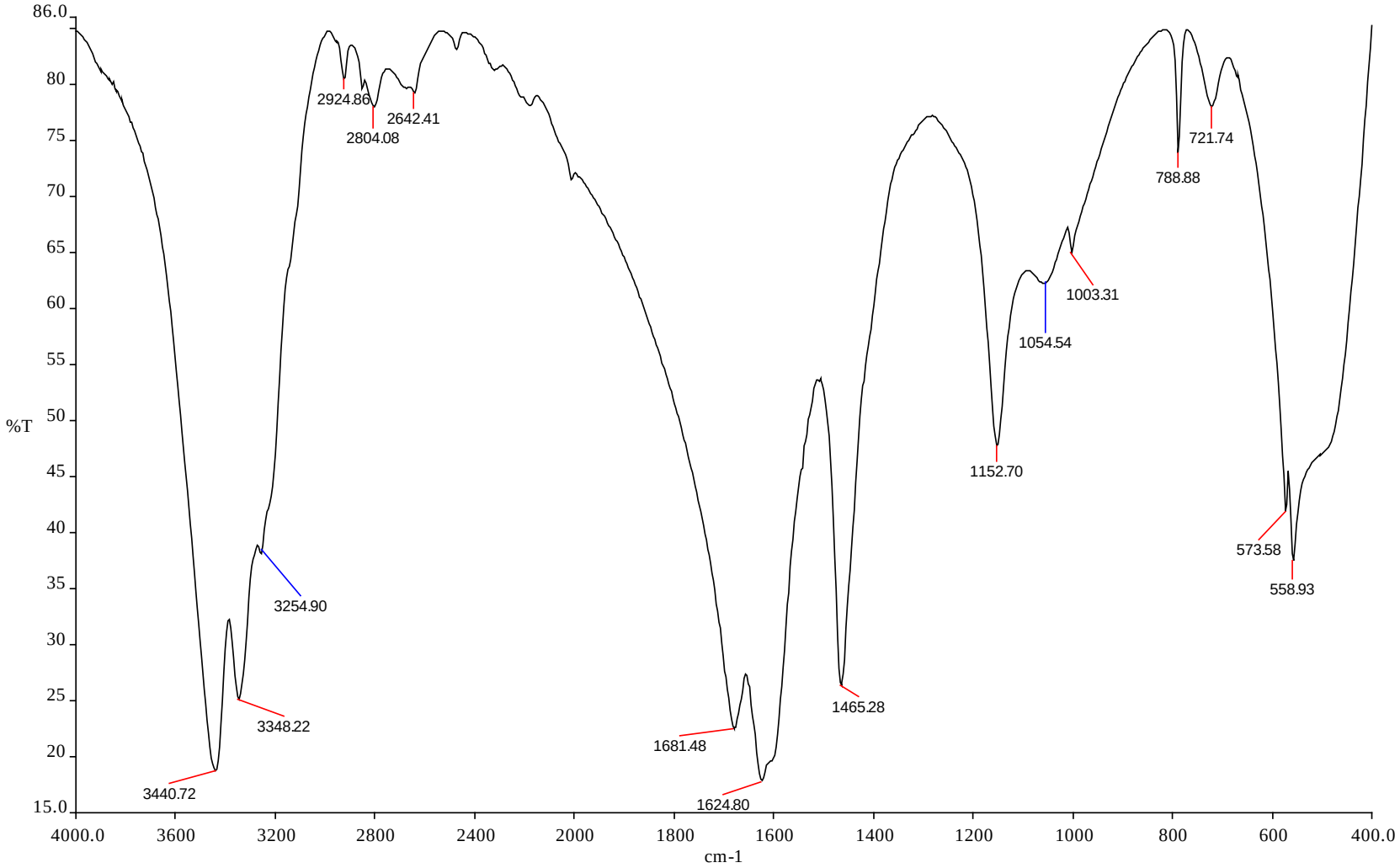
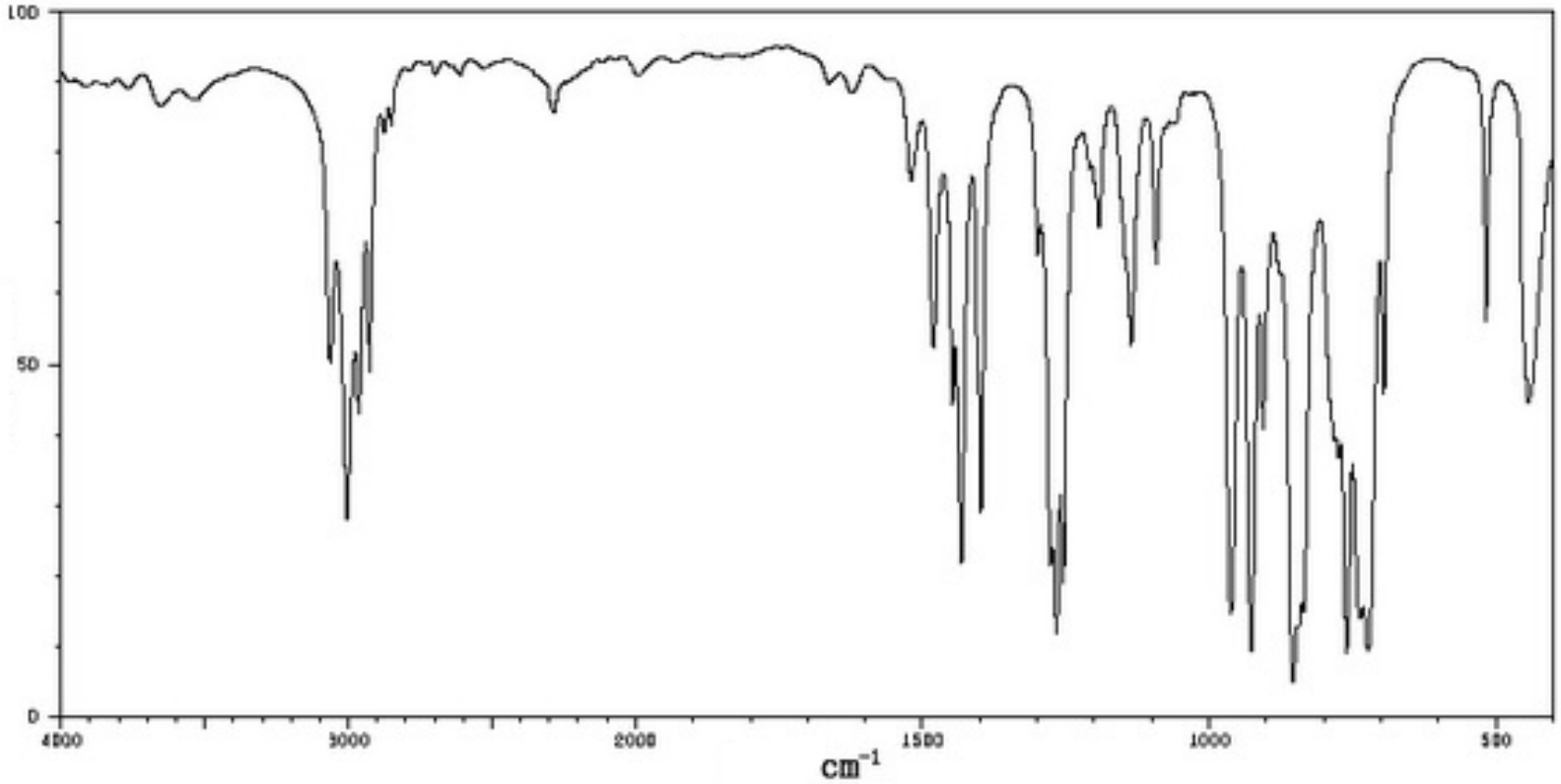


Fig. 1. IR carbamide



3637	84	2286	81	1300	64	1092	62	775	36
3063	49	1624	84	1277	20	962	14	761	8
3004	26	1519	72	1267	11	927	9	736	13
2963	41	1480	60	1255	18	906	38	723	8
2926	47	1448	42	1209	74	854	4	695	44
2874	79	1433	21	1193	86	844	12	516	53
2850	81	1398	27	1137	60	836	14	444	43

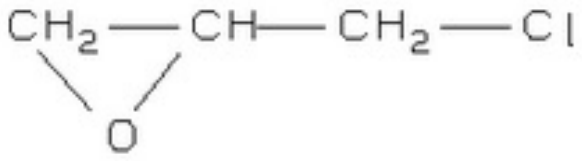


Fig.2. IR epichlorohydrin.

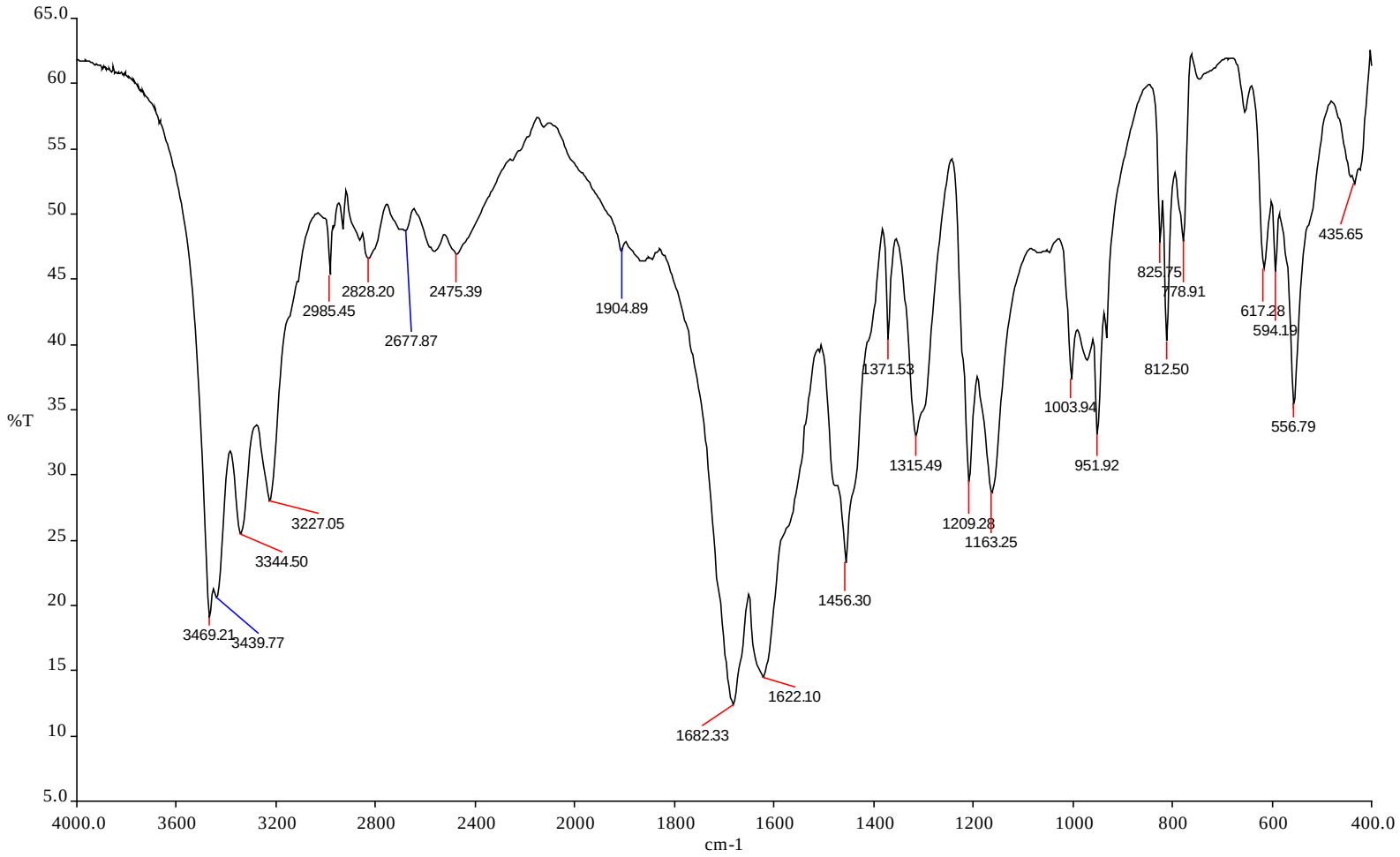


Fig. 3. IR spectrum of epichlorohydrin with carbamide (1).

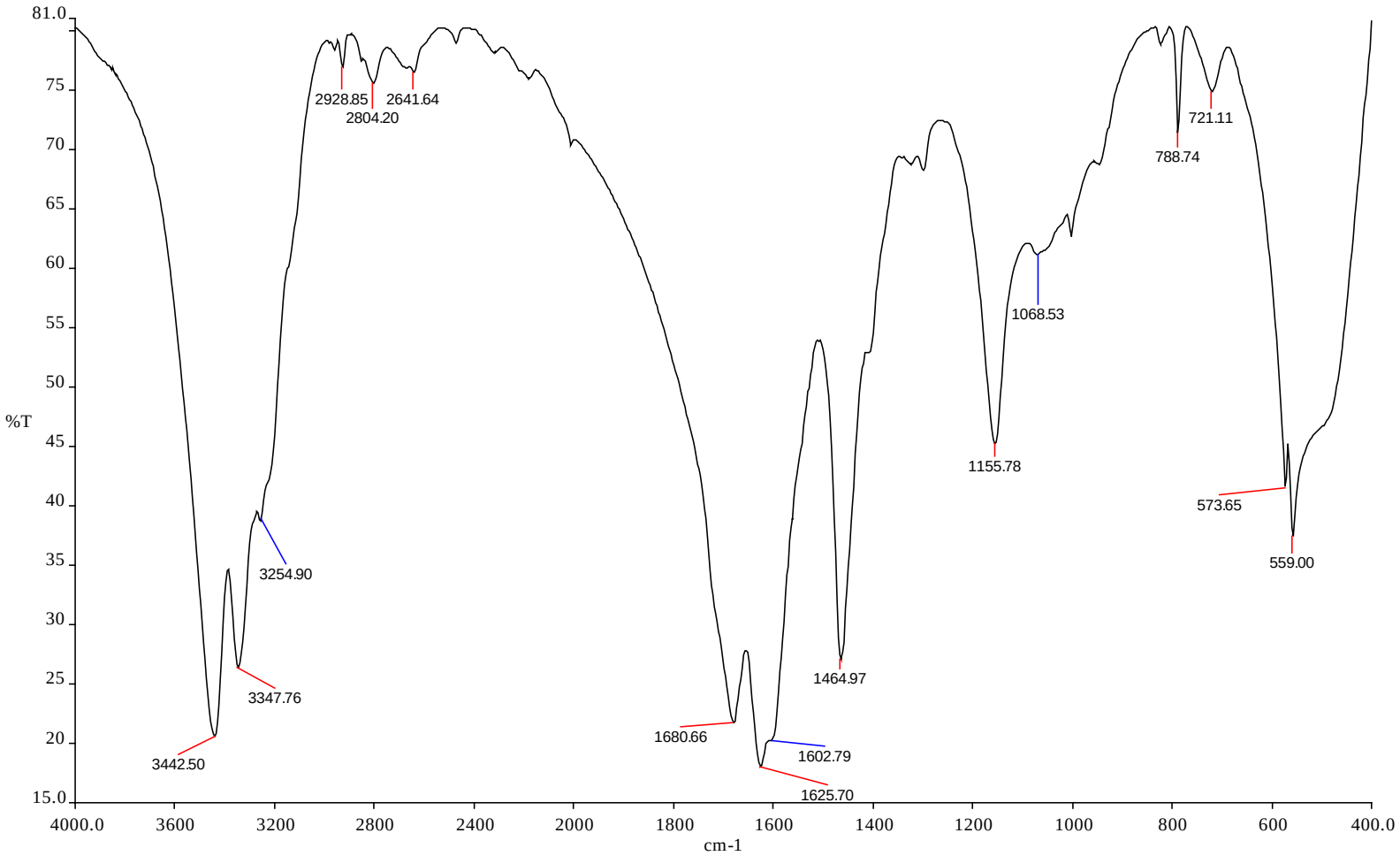


Fig. 4. IR epichlorohydrin with carbamide (2).

Besides that, the interaction reaction of carbamide with epichlorohydrin was carried out in the presence of acidic catalysts by means which was selected sulfuric acid. The influence of various factors on the reaction rate: the temperature and the ratio of the initial reagents.

For determining the dependence of reaction rate and the interaction between the ECG and carbamide temperature process was carried out in a temperature range of 60-80 ° C (Figure 5).

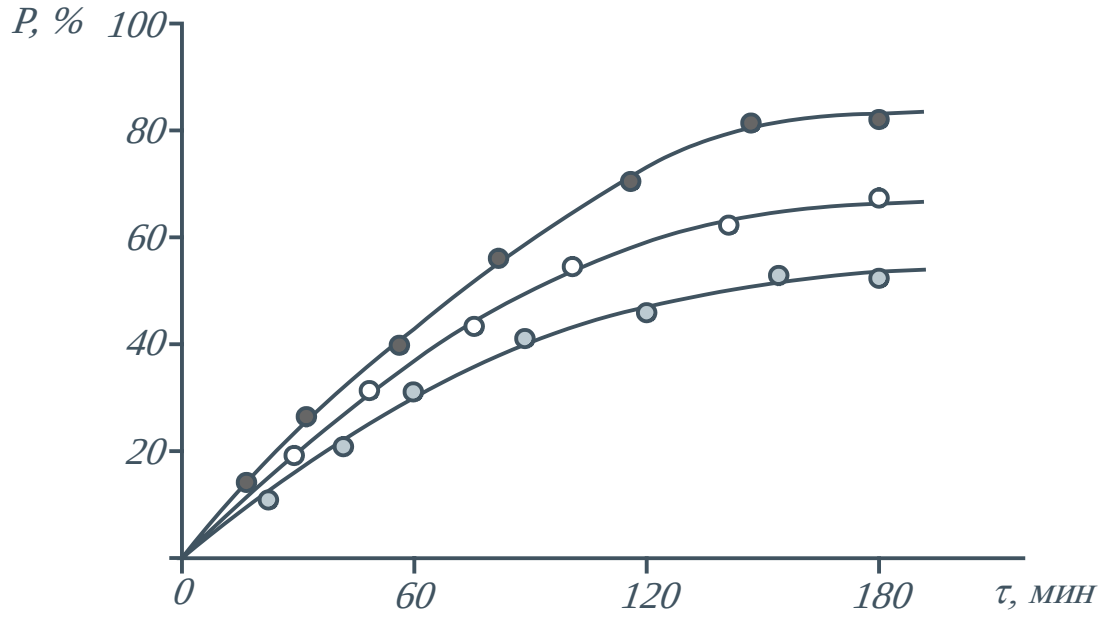


Fig. The dependence of yield of ECH interaction with carbamide temperature, ° C: 1-60; 2-70; 3-80. Catalyst [H2SO4] = 2%.

As seen from the figure with the increase of temperature, the reaction rate and yield increased.

Besides that , the influence concentration of sulfuric acid on reaction rate and final yield of the product (Figure 6) was also studied. As can be seen from Fig. at 2% concentration of sulfuric acid had the highest reaction rates and highest product yield.

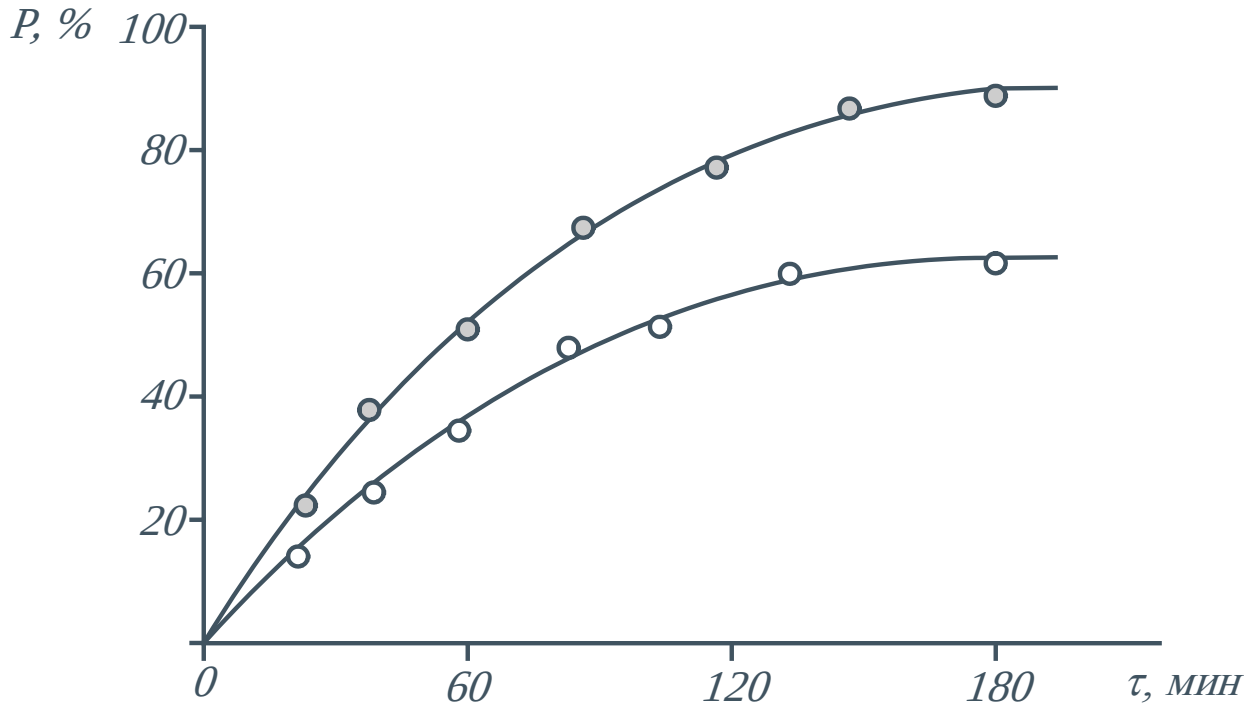


Fig. 6. The yield dependence ECG interaction with carbamide from concentration H2SO4,%: 1-1; 2-2. T = 80 °C.

The structure of obtained product on reaction interaction of epichlorohydrin with carbamide concentration was investigated IR spectral analysis (Figure 7). In IR spectra of the resulting product were observed valence vibrations -CH2- groups in 2978 cm-1; CH = group at 2877 cm-1; C = O groups at 1789 cm-1, appearance of a new band was observed at 3105 and 1127 cm-1was attributable to the valence vibrations -NH groups were not observed characteristic absorption bands at 1250 cm-1 and 850 sm^{-1}, which can be attributed to the fluctuations of the epoxide ring. This suggests that the reaction was carried out with opening of epoxy ring epichlorohydrin .

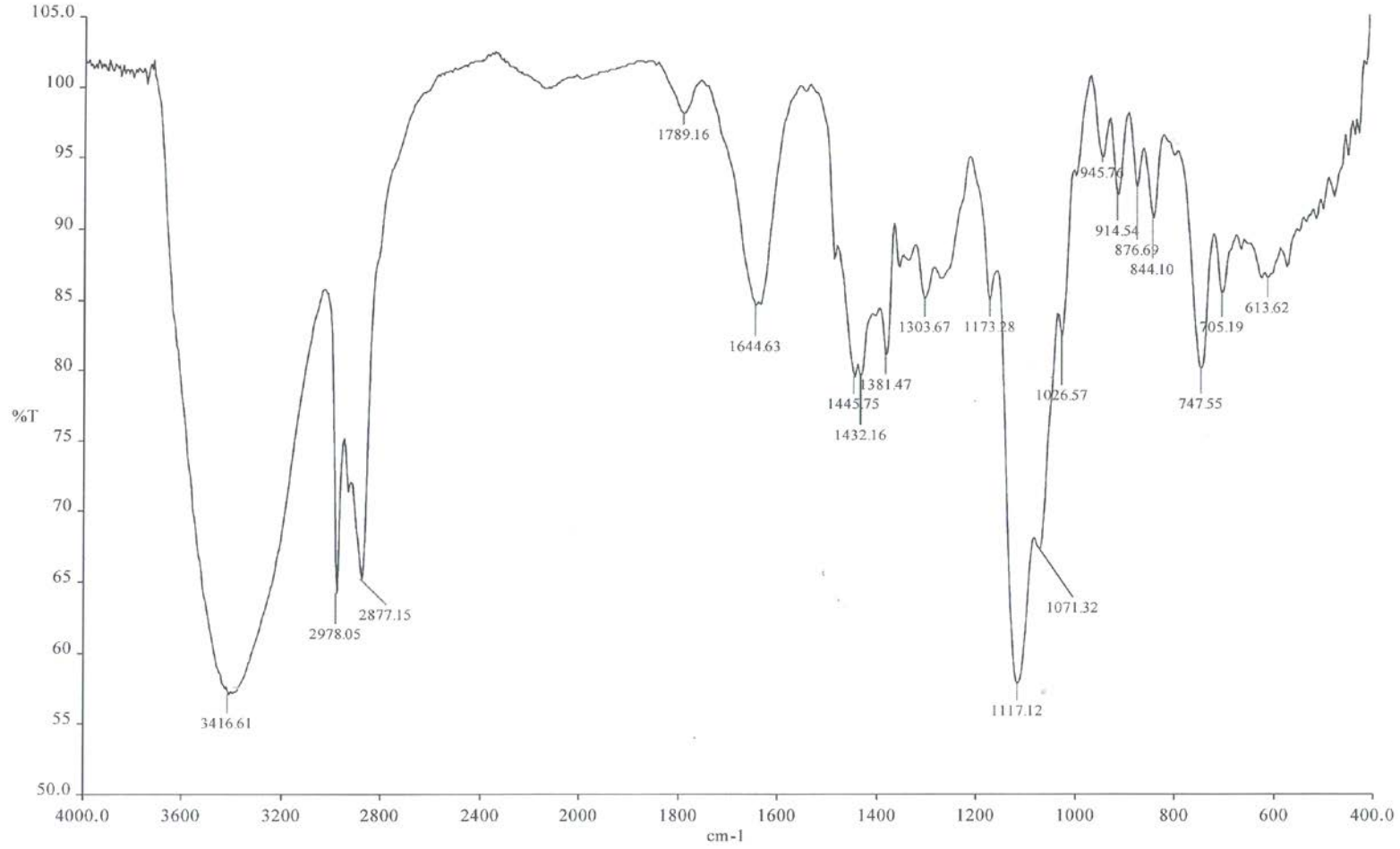


Fig. 7. IR spectrum of the reaction product of epichlorohydrin with carbamide in the presence of sulfuric acid catalyst.

Based on the experimental data compiled fundamental technology for producing epichlorohydrin the reaction of the product with carbamide in the presence of sulfuric acid (Figure 8).

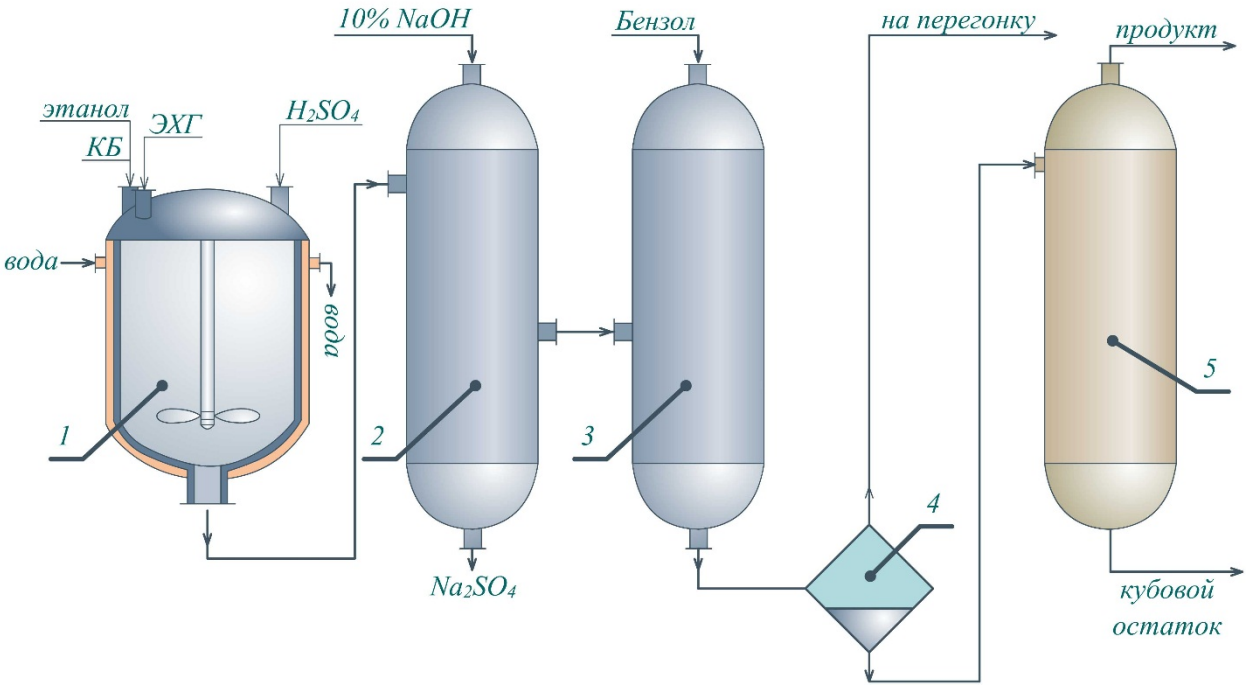


Figure 8. Process flow diagram of the preparation of epichlorohydrin.
1 - stirred tank reactor; 2 - converter; 3 - separator; 4 - separator; 5 - column distillation.

The initial mixture of reactants comprising epichlorohydrin, ethanol, urea, and sulfuric acid as the catalyst, was fed to the stirred reactor (1) through the meter. The residence time of the reaction mass in the reactor and the ratio of the starting reagents were chosen such that the reaction liquid contained only a small amount of unreacted starting reagents (all sulfuric acid remains in it). The reaction solution in the reactor was stirred for 3 hours at 80 ° C. After the reaction, the liquid was removed from the reactor and, after neutralization to the neutralizer (2) Na2SO4 withdrawn into the container. A reaction liquid from the catalyst (2) enters the separator (3), where benzol was fed for separation of mixtures. Then, that mixture was fed to the separator (4) for separation. After separation of the top part was sent to the distillation of water, ethanol, epichlorohydrin. Lower portion

entered the column (5), which was distilled from the top of the reaction end products, and on the bottom of bottoms residue.

3.2 Study of the reaction of epichlorohydrin with pyridine

Till recent times practically little studied in the oligomerization remained heterocyclic amines, including selected by us as objects of research piperidine. This compound, having properties of secondary amines were structural fragments of a large number of biologically active substances. The formulations based on them, including the sulfonamides were used as anesthetics, antibacterial agents, veterinary drugs, pesticides, etc.

At the time of our research in the literature, there were no data on the interaction of epichlorohydrin such heterocyclic secondary amines like piperidine. In the present study, using as secondary amine - epichlorohydrin piperidine and coreactant, we were able to investigate the spontaneous polymerization of indicated monomers.

The interaction with epichlorohydrin piperidine proceeded much more effectively and gave an oligomeric product with a yield of 90-95% respectively. Thus, under in the given conditions, apparently, there was an opening epichlorohydrin epoxide molecule under the action of indicated amine.

Before experiments there was carried out the cleaning of initial reagents by the atmospheric distillation method. The boiling point of piperidine and epichlorohydrin corresponded to the reference data. Bp. 106 ºC; epichlorohydrin, colorless liquid with a pleasant odor was conducted to. 116 ° C.

For finding the optimal technological parameters of the reaction was studied the effect of different factors such as the influence on the nature of solvent, concentration of initial reagents, temperature and reaction time on the process of spontaneous polymerization.

The investigation of this reaction with different molar concentrations of epichlorohydrin and piperidine showed that the highest yield was achieved with the oligomer equimolar ratio of initial reactants. To find the optimal process solvent was selected contact number of solvents: tetrahydrofuran, ethanol,

dimethylformamide. The experimental results showed that the rate of spontaneous polymerization depends on the polarity of the solvent. Increasing the polarity of the medium to accelerate the reaction, the highest rate was observed in dimethylformamide (Figure 9).

However, for helding the experimental studies as a solvent for spontaneous reaction of piperidine with epichlorohydrin it was selected by us ethyl alcohol, because it was available and cheaper. The reaction product was precipitated with ether and dried to constant weight. It was soluble in ethanol, acetone, dimethylformamide, water, but the reaction heterophase was observed in water.

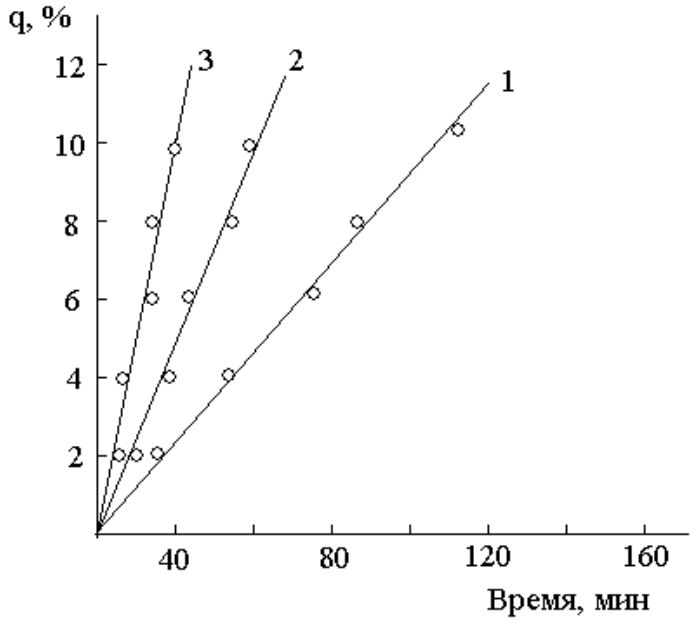
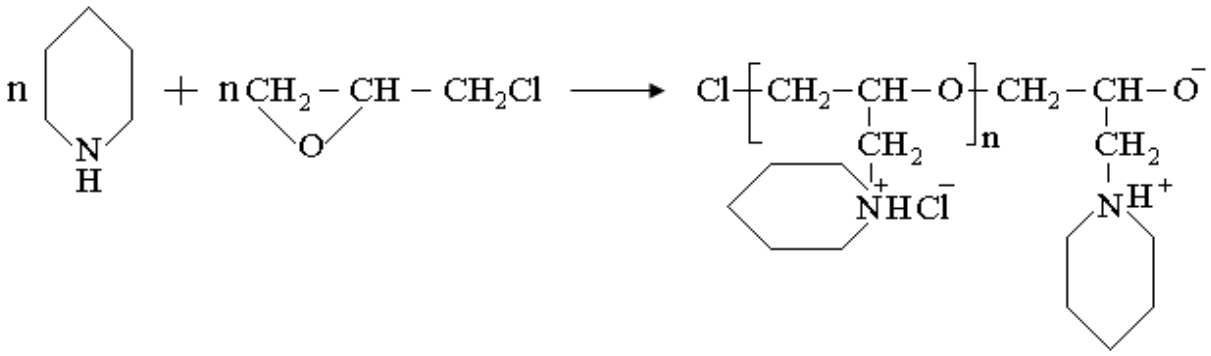


Fig. 9. Dependence degree of oligomer conversion based on piperidine with epichlorohydrin naturally solvent at an equimolar ratio of 1: 1 at 50 ° C. 1 tetrahydrofuran-2-ethanol, 3-dimethyl formamide.

For elucidating the structure of synthesized products interaction of piperidine with epichlorohydrin were taken their IR spectra. For comparison were taken and IR spectra of the initial reactants and reaction products of their interaction.

In IR spectrum of oligomer there was a broad band valence vibrations of the hydroxyl group in the 3232-3396 cm-1; 1634 cm-1 refered to the valence vibrations of N-C bond; bending vibrations of N-H groups of the piperidine ring at 1515 cm-1 completely disappeared due to the formation of new tertiary nitrogen groups in the 2943 cm-1. The valence vibrations typical of epoxy during 1265,

900-850 cm-1 in the IR spectra of the oligomer product was not observed. That indicated that the reaction was carried out by opening the epoxy groups. Based on the IR spectrum analysis of the oligomeric structure of the synthesized product based piperidine with epichlorohydrin was described as follows:



ENVIRONMENTAL ASPECTS IN THE SYNTHESIS

Epichlorohydrin applied to Class 2 hazard. The exposure zone industrial premises - 1 mg / m3; in water reservoirs sanitary and domestic articles - 0.01 mg / l.

ECH is an irritant and allergic effects. In animal experiments selectively affects the kidney. Absorbed through skin.

Epichlorohydrin is a highly toxic and flammable compound [3]. epichlorohydrin vapor inhalation of even small concentrations cause nausea, dizziness and watery eyes, and with long-term exposure to lead to more serious consequences (often causing severe pulmonary edema) [1]. Epichlorohydrin in contact with skin and prolonged contact causes dermatitis, until the surface necrosis. All work should be carried out with epichlorohydrin rubber gloves, rubber apron and with a strong gassed his pairs - in a gas mask grade A [5].

Epichlorohydrin - flammable. In case of fire extinguish with carbon dioxide, foam or water, evenly distributing it on the surface. MPC in the working area of industrial premises should not exceed 1 mg / m3 MAC in the atmospheric air of populated areas 0.2 mg/m^3 (recommended).

CONCLUSIONS

1. The reaction of epichlorohydrin interaction with carbamide was studied. The reaction of epichlorohydrin accession to the carbamide at different ratios of starting materials.

2. By the methods of IR spectral analysis was determined the structure of synthesized compound, thermal stability of the synthesized substances , which was established by thermogravimetric method. Total absorbed energy to the carbon residue showed 1 089 J / g.

3. The reaction of epichlorohydrin interaction with urea in the presence of sulfuric acid catalyst was studied. It was determined the optimal reaction conditions: temperature 80 ° C, the catalyst concentration of 2%. It was presented the principle technological scheme process .

4. The reaction of reaction of epichlorohydrin interaction with piperidine at low temperatures (20-50 ° C) was studied.The interaction of various factors on the reaction was studied: reagent concentrations, temperature and process duration. It was found that in the process of the oligomer formed, the structure of which was set by the IR spectral analysis.

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ATTACHMENT