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SYNTHESIS OF NITROGEN-, SULFUR-, OXYGEN- AND PHOSPHORUS-CONTAINING COMPLEXING ION EXCHANGERS

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Abstract. In this paper, it is observed that in the acidic and neutral medium, the absorption lines corresponding to the epoxide group are absent in the IR spectra of the product obtained by the reaction of urea and thiocarbamide with epixlorgidrin. The interaction of thiocarbamide with epixlorgidrin indicates that the chlorine atom in epixlorgidrin and the epoxide group are opened, and that the amine group in thiocarbamide interacts with the hydrogen. A polyfunctional anion exchanger based on diglycidylthiourea and phosphoric acid has been synthesized. The composition, structure, and thermal stability were studied by IR spectroscopy, elemental and thermogravimetric analyses.

Keywords: *Epoxide group, amine, thiocarbamide, epixlorgidrin, viscosity, IR spectrum.*

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1. Introduction

Usually, in the synthesis of ionic resins by polycondensation, dioxins, tri- and polyamines are used as monomers, along with various modified reagents that enhance the exploitation properties of halogen-containing epoxygids, epixlorgidrin, and ionites.

From ion condensation of epixlorgidrin and ammonia in the presence of water (or glycols), ion exchange materials with a capacity of 7 mg-eq/g were obtained (Wolf, 1969).

The heterocyclic compounds were exposed to condensation products with ammonia epixlorgidrin and obtained weak oxidation-resistant and well-kinetically based anionites with high exchange capacity. Polyelectrolytes have been synthesized by epixlorgidrin, which has the ionic properties of polyethylenpolylamine from polycondensation (Samborski *et al.*, 1964).

Pedinova and others obtained epixlorgidrin from aqueous solution of ammonia and condensed oligomers containing quaternary ammonium groups. Then, using polyethylenopolyamines, he stripped chlorethyl and epoxyguruh. The ratio of reagents is 0.5 mol (ammonia-trimethylamine) and 1 mole of epixlorgidrin, and the synthesized anionites have high retention properties of pyrolysis products of glucose, in addition to the usual properties of ionizing materials (Ismailov *et al.*, 1993).

Therefore, the leading scientific centers pay special attention to the study of the physicochemical aspects of the production and properties of ion-exchange materials,

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complexing ion-exchange materials and ion-exchange membranes. The obtained sorbents are used in ecology, hydrometallurgy, etc., for example, in the extraction of heavy metals from wastewater, noble metals from refining solutions (Turaev *et al*., 2012).

At present, scientific research is being carried out in priority areas on the problems of synthesis and study of the properties of complexing epoxy compounds, their use in the process of sorption of metal ions, and the development of a technology for their production (Eshkurbonov *et al*., 2020). It follows from the literature data that nitrogen- and phosphorus-containing compounds are of interest for their use as raw materials for the production of complexing ion exchangers (Eshkurbonov *et al.*, 2013).

Recently, one of the promising directions for obtaining sorption materials is the use of polyfunctional reactive oligomers. Their use as a starting product makes it possible to carry out reactions under mild conditions, makes it possible to study the kinetics and mechanism of intermediate processes, and to control the composition and properties of polyelectrolytes (Eshkurbonov *et al*., 2022).

Given the high cost of imported complexing ion exchangers, it was decided to synthesize the corresponding phosphorus-, sulfur- and nitrogen-containing compounds based on thiourea, epichlorohydrin with orthophosphoric acid (Eshkurbonov *et al.*, 2013). The resulting diglycidylthioureas, which contain the $–NH_2$ functional group, can be used to obtain the corresponding amide salts of various structures.

The proposed synthesis scheme makes it possible to construct functionally substituted phosphorus-nitrogen-containing compounds with a supposed complex of useful properties of complex-forming ion exchangers by fragmenting the molecule according to the main functional groups (nitrogen and phosphorus-containing) and a long-chain heterochain radical at donor atoms (Izzatillaev *et al*., 2013).

It is known that recently extensive research has been carried out in the direction of the synthesis of new functional materials, the study of their structure and physicochemical properties (Asadov *et al.*, 2015; Madatov *et al.*, 2019; Ibragimova *et al.*, 2022). Interesting physical properties can be observed in studies conducted by various analytical methods (Azimova *et al*, 2020; Madatov *et al*, 2015; Huseynov, 2021). In this study, new functional materials containing nitrogen, sulfur, oxygen and phosphorus were synthesized and their various properties were studied.

2. Materials and methods

The reaction of thiocarbamide with epixlorgidrin is characterized by a complex process involving the functional groups with different reaction capabilities.

The chemical reaction was carried out in a 1:1 mol ratio of the initial substance in an alcohol solution at a temperature range of 40-80 °C. The study of the kinetics of the process revealed a change in the concentration of chloride ions in the reaction mass.

The reaction of urea and thiocarbamide with epixlorgidrin is characterized by a complex process involving functional groups with different reaction capacity. The reaction was first carried out in various ratios of matter in an alcoholic solution at a temperature range of 40-80 °C. The study of the kinetics of the process revealed a change in the concentration of chloride ions in the reaction mass.

3. Results and discussion

Table 1 shows the effect of the ratio of initial monomers on the synthesis of diglitsidylcarbamide and diglitsidylthiocarbamide on the reaction yield and the molecular weight of the products obtained.

Table 1. Influence of the ratio of reagents on product content in the production of diglitsidyl (thio) urea (t = 40 °C, τ = 4.5 s)

Ratio of monomers:	Reaction potential, %	Average mol. mass. (cryoscopic)	Element analysis, %			
			Nitrogen		Oxygen	
			Estimated	Found	Computed	Found
Urea + epixlorgidrin						
3:1	52.7	121	23.4	15.6	27.0	21.8
2:1	57.2	117	24.1	14.9	27.2	23.7
1:1	54.8	118	23.1	16.0	27.1	22.0
1:2	94.1	172	18.1	15.6	27.2	26.1
1:3	84.2	229	12.2	11.8	28.07	27.5
Thiocarbamide + epixlorgidrin						
3:1	53.3	141	21.0	15.1	12.0	12.8
2:1	56.7	138	21.2	15.9	12.2	12.2
1:1	54.8	134	21.2	15.0	12.1	13.1
1:2	92.8	188	14.8	12.0	17.02	15.8
1:3	84.2	244	11.4	11.2	19.6	19.5

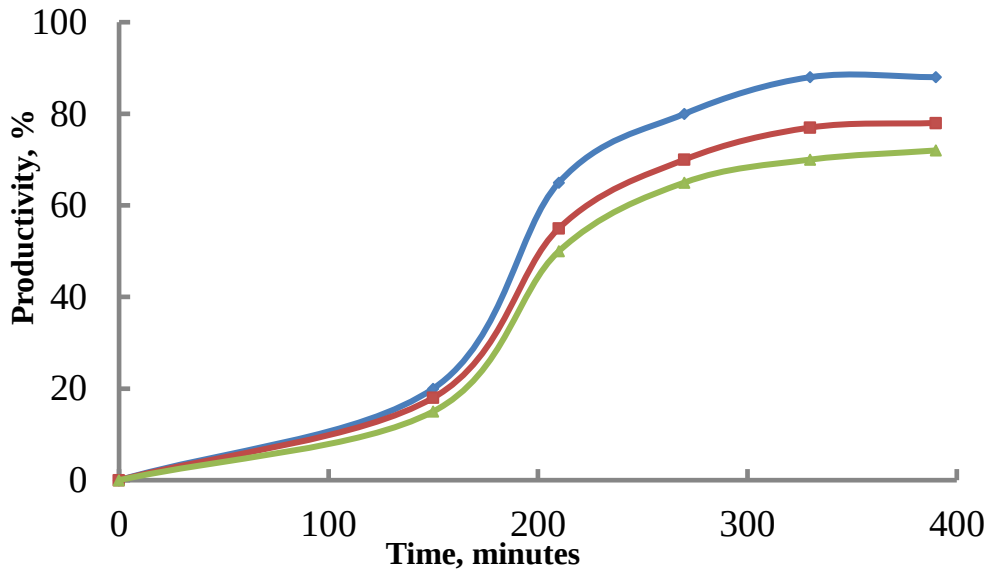


Fig. 1. Kinetic curve of interaction of urea with epixlorgidrin at a ratio of 1: 2 mol and at different temperatures (1. 40 °C ( ), 2. 60 °C ( ), 3. 80 °C ( )).

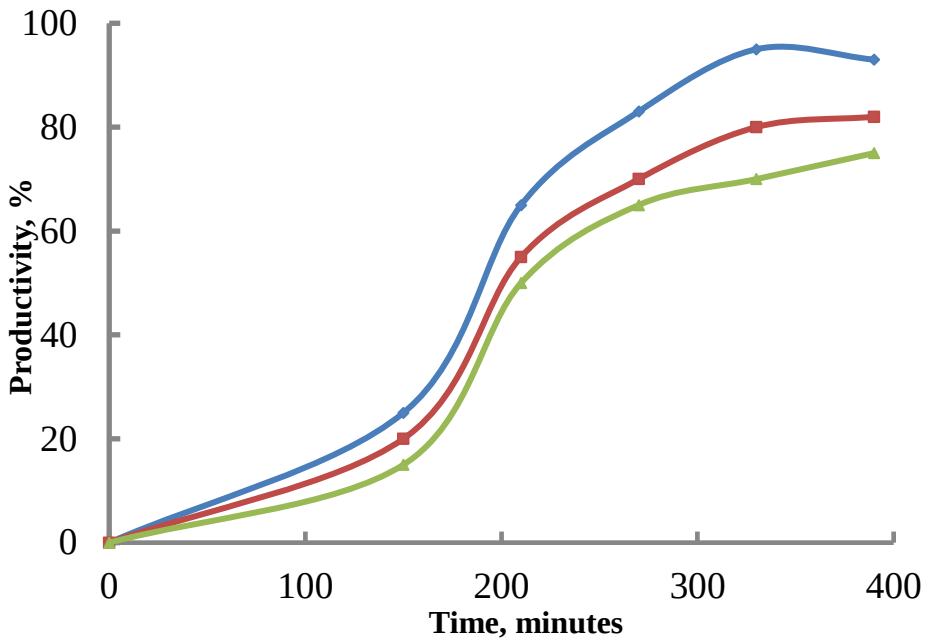


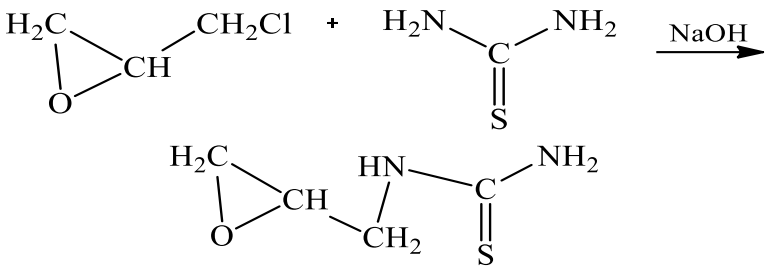
Fig. 2. Kinetic curve of thiocarbamide interaction with epixlorgidrin at a ratio of 1: 2 mol and at different temperatures (1. 40 °C ( ), 2. 60 °C ( ), 3. 80 °C ( )).

The data in the table show that when the initial monomers are obtained at a ratio of 1: 2 mol, a high yield is obtained. As the temperature increases to 80 °C, the reaction becomes deeper as illustrated in Figures 1 and 2. The results of the study show that the reaction rate increases by 1.13-1.32 times every 10 ºC. In order to obtain high yields diglitsidylcarbamide and diglitsidylthiocar- bamide require reagents, namely urea (thiocarbamide): epixlorgidrin at 1 (1): 2, as shown in Table 1. Figures 1 and 2 show the reaction duration and reaction temperature dependence of the reaction products of urea and thiocarbamide with epixlorgidrin at different temperatures. It has been suggested that the best product for the formation of diglitsidylcarbamide and diglitsidylthiocarbamide is the temperature of 40-45 °C and the reaction product with the highest yield at 6-6.5 hours is longer.

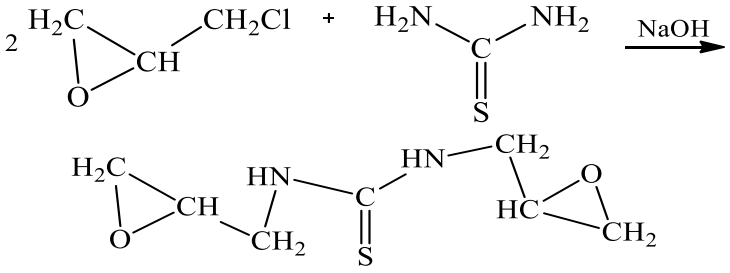
Thiocarbamide interacts with epoxylorgidrin at room temperature with intense heat excretion. Condensation reaction is carried out in the presence of solvent to maintain the same reaction rate of epixlorgidrin with thiocarbamide and to reduce exothermicity. As solvent, ethyl, isoamyl alcohols, dimethylformamide, toluene are used.

High polymer absorption is achieved using isoamyl alcohol and dimethylformamide. The reaction rate and the polymer yield depends on the amount of solvent used. The duration of the condensation reaction, the effects of thiocarbamide and soluble mass ratios (0.5: 1.0: 1.5: 2.0: 2.5) on the anionite property were studied in detail. When a mass fraction of 0.5-0.6 to thiocarbamide is used in a mass fraction of 0.5-0.6, the condensation reaction is intensified with a brittle polymer with low mechanical strength. An increase in solvent content by 1.5 to 2.5 mass fraction results in prolongation of reaction mass hardening time (100-120 h). With the use of one bulk solvent and one mass fraction thiocarbamide, the condensation process is stable and the mechanical strength of the resulting product is good and sufficient replacement capacity (Turaev *et al.*, 2012, Eshkurbonov *et al.*, 2020). The

results of the experiment are shown in Figure 3. The reaction of the change in epixlorgidrin concentration was calculated as the velocity constant, and the product formation was assumed to be due to the interaction of the chlorine atom in the epixlorgidrin with the hydrogen atoms in the thiocarbamide amino group. In the first step of the reaction, glycidyl derivatives are formed:



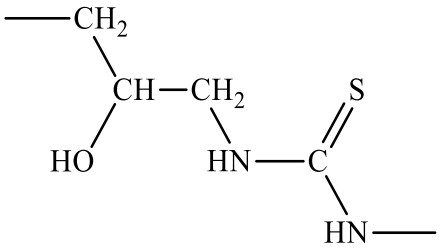
Glycidyl derivatives can also be formed by the substitution of two hydrogen atoms in the amide:



At the same time, glycidyl derivatives are formed by the amino group at the expense of the opening of the epoxide group and separate polyamine molecules form a transverse bridge due to the release of the hydrogen atom.

In order to study the structure of the resulting product, the initial substances and the IR spectra of the product were compared. The reaction was carried out at different temperatures and environments. The IR spectra of the condensation products of thiocarbamide and epixlorgidrin in the base, neutral, and acidic environments are presented. At the same time, the absorption of epoxide group-specific absorption was not observed in the area 1278 cm^{-1} in the absorption line of products obtained in neutral and acidic environments. In the swallow line, the CCl garden is shown in areas 760 cm^{-1} and aminogroups 1619-1661, 3328 cm^{-1}. In the specified frequency spectra, the valence vibration of the S - C bond 990-1076 cm^{-1}, CH and CH_2 is observed in areas 2845-2918 and 1247 cm^{-1}, with the presence of C - C absorption lines (1300-1450 cm^{-1}) and in addition 2051, 2185 cm^{-1} exhibits valent vibration frequencies specific to the azometyl group (Eshkurbonov *et al.*, 2014, 2018, 2020).

In the IR spectrum of products obtained in a strong acidic and neutral environment, there was virtually no absorption line corresponding to the epoxide group, the interaction of thiocarbamide with epixlorgidrin is due to the release of chlorine at epixlorgidrin and the amino group of thiocarbamide (Turaev *et al.*, 2013).



The condensation reaction rate of thiocarbamide and epixlorgidrin at a constant ratio of 1: 2 was studied at 80, 90, 100, and 110 °C (Table 2).

Table 2. Influence of temperature of polycondensation reaction on physical and chemical properties of products

Reaction temperature, °C	Reaction duration, hours	Water solubility, %	Characteristic viscosity, η_{xv}
80	13	45	2.2
90	11	40	2.5
100	8	15	1.9
110	6	10	1.81
120	2	8	1.0

As can be seen from the data in Table 2, the duration of the polycondensation reaction at 80 °C is 13 hours and the product viscosity is 2.2. As the temperature of the reaction medium increases, viscosity gradually increases, but at 110 °C the viscosity decreased slightly to 1.81. At 120 °C, the process is shortened almost three times, but the characteristic viscosity decreases by 1.0. Therefore, based on the experimental results, the optimal temperature for the reaction of thiocarbamide with epixlorgidrin was 100 °C. At the same time, the product, formed as a result of rhythmic reaction for 8 hours, is characterized by good physical and chemical properties and mechanical properties (Eshkurbonov, 2013, 2022).

The effect of epixlorgidrin concentration on polycondensation was studied at 100 ° C with 10, 20, 30% thiocarbamide relative to the mass of epixlorgidrin. Figure 3 shows the degree of completion of epoxlorgidrin and thiocarbamide polycondensation in different proportions depending on the reaction duration (t) and degree of completion (A) (Izzatillaev *et al.*, 2013).

As can be seen in Figure 3, the velocity constant increases with increasing thiocarbamide concentration at 100 ° C. In the synthesis of a product, the concentration of initial substances is an important factor influencing its physico-chemical properties.

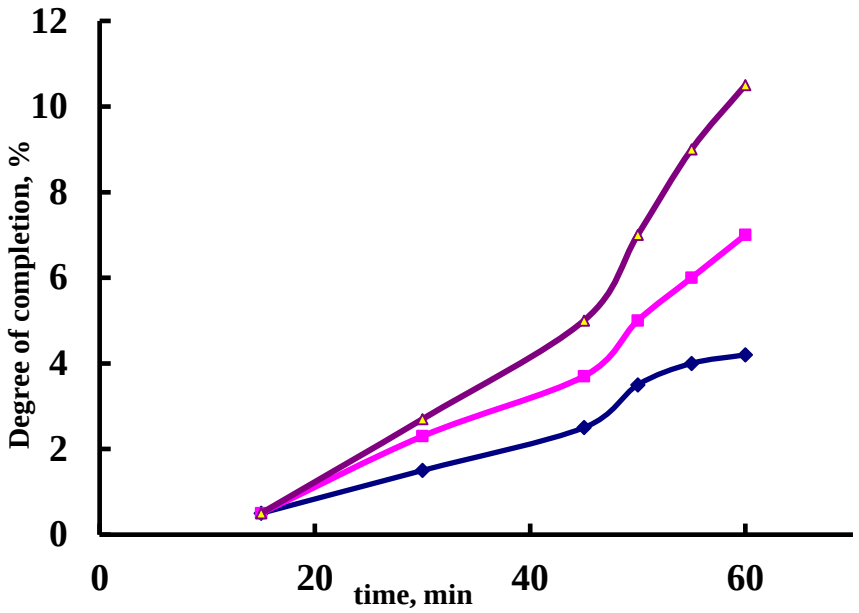


Fig. 3. Completion rate of polycondensation of thiocarbamide and epixlorgidrin at 100 °C (1. 10% ( ), 2. 20% ( ), 3. 30% ( ) epixlorgidrin content)

Epixlorgidrin is a dissociating agent in the production of this product, so its concentration in the reaction mixture affects not only the dissection but also the quantitative ratio of the active groups (Table 3).

Table 3. Dependence of the properties of the resulting product on the reaction phase epixlorgidrin and thiocarbamide concentrations

The amount of epoxlorgidrin in the reaction mixture	Characteristic viscosity, $\eta_{xв}$	Water solubility, %	Reaction potential, %
1.0	2.2	35	64.0
1.5	2.3	45	76.0
2	2.7	55	92.0

4. Conclusions

The hydrogen atoms of the thiocarbamide aminogroup interact with the epoxide group of epixlorgidrin, resulting in primary primary aminogroups secondary to secondary and secondary to tertiary. With the increase of epixlorgidrin content, the viscosity of the product also increases and its solubility decreases. When using 1.5 mol and 20% thiocarbamide in relation to the mass of epixlorgidrin, the viscosity of the product is high, but in acid solution there is a change in color of the product. This can be explained by partial melting of the product. Studies have shown that epixlorgidrin is not fully affected by the excess of thiocarbamide. As can be seen from Table 2.5, the optimal ratio of epixlorgidrin is 2 mol.

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