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# *Synthesis Of Related Compounds Of Ethylidenediamine-Tetraacetic Acid And Their Applications*

Sevara Jasurovna KHALIKOVA, Doniyor Rakhmonalievich ANORKULOV and Khasan Irgashevich KADIROV

Tashkent chemical-technological institute



**Abstract – The development purpose is to study the urea interaction reaction with monochloroacetic acid, obtaining tetracarboxymethylene-related urea by the ethylidene diamine tetraacetic acid structure. The regularities of the tetracarboxymethylene urea formation from urea and chloroacetic acid have been established.It was studied the senergic efficacy of the resulting product in a composition with industrial scale inhibitors in waters of hardness 4- 14 mg/eq·l, which efficiency was in of 80.0 - 98.0% range.**

**Keywords – Chelating Agents, Polydentate Compounds, Urea, Monochloroacetic Acid, Inhibitors Of Mineral Salt Deposition.**

## I. INTRODUCTION

Currently the complexones chemistry is going through an intensive development period. If in the middle of the 20th century has been described and studied in detail only two classes of connections: nitrilotriacetic and ethylenediaminetetraacetic acids, then already today several dozen chelants are known and the number of complexones mentioned in the literature exceeded 200 items and continues to grow. Even greater dynamism is distinguished by the information accumulating process about the composition, structure and properties of complexonates, conditions of their existence, potential and real areas of practical use [1-4].

Much attention is paid to the obtaining methods, complexon technology, in particular, original methods of waste-free production. Complexones - organic ligands of the polyamino-polyacetic acids group containing iminodiacetate fragments associated with various aliphatic and aromatic radicals - have been developed and are being produced. Relying on the complexonates production a large number of similar compounds have been synthesized, including other acid groups instead of acetate – alkylphosphonic, arylarsonic and alkylsulfonic, instead of nitrogen -(III) – phosphorus (III), sulfur (II), selenium (II), tellurium (II).

The main properties of complexon is the ability to form complexonates with most metal ions in aqueous solutions, which stability, as a rule, is so high that the corresponding cation cannot be detected using classical analytical methods. Synthetic availability and wide possibilities for modifying the molecular structure of complexones and complexes based on them open up large promising connections with a predefined set of properties to solve both theoretical problems of coordination chemistry, and envelope national economic tasks.

Enterprises of chemical, petrochemical, gas, metallurgical and other industries, as well as communication water treatment systems are the main water consumers. As a result, the increasing water sources mineralization, a also multiple use of limited water volumes and wastewater use cause the equipment contamination of heat exchange systems with low-soluble salts and corrosion products deposits.

**Corresponding Author:** Sevara Jasurovna KHALIKOVA

The protecting technological equipment problem from scale deposits and internal corrosion invariably remains relevant. One of the most effective approaches solving it, recommended by a number of normative documents [5], is the use of scale and corrosion inhibitors.

The most effective scale and corrosion inhibitors are organophosphonic acids complexes with transition metals, of which, as noted above, OEDP and NTP complexes with zinc received the greatest practical application, stable in the sodium or potassium salts form [6]. Modern scientific research [7] has fully established the mechanism of these inhibitors action. High efficiency of phosphonate zincate corrosion inhibitors noted by IPCE RAS specialists [8] and confirmed in practice by VTI (All-Russian thermal engineering institute) [9] specialists.

In this regard, the new highly effective, stable, economic means development to prevent abnormal phenomena and the water supply systems improvement is a very urgent task.

Methods for the carboxyl-containing complexones synthesis are quite diverse and are widely used in these practically important compounds obtaining technology.

Carboxyl-containing complexones of the aliphatic series are the most common ligands, which synthesis ways are still attracting the researchers' attention. Currently, more than a thousand polydentate compounds have been synthesized and studied mainly by amines carboxylation reaction with haloalkylcarboxylic acids and cyanomethylation followed by obtained nitriles hydrolysis.

Among the considered polydentate compounds the most characteristic and thoroughly studied are nitrilotriacetic and ethylenediaminetetraacetic acids [3].

Nitrilotriacetic acid (NTA, complexon I, trildon A, chelaton 1) is a crystalline powder; poorly soluble in water: at 5 °C 0.1338 g dissolves in 100 ml of water. NTA is a tribasic acid with a zwitterionic structure [4].

A typical method for the nitrilotriacetic acid preparation consists in the aqueous ammonia solution interaction with chlorine or bromine acetic acids. The reaction proceeds sequentially according to the $S_N2$ mechanism, maximum speed is reached at pH=10 – 11.

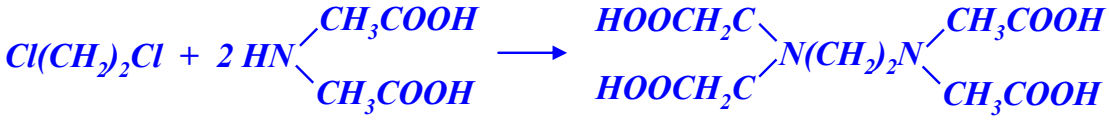
$$NH_3 + 3\,HalCH_2COOH \longrightarrow N(CH_2COOH)_3 + 3HHal$$

It is noted that glycine reacts with monochloroacetic acid about 10 times more actively.

Ethylenediaminetetraacetic acid (EDTA, ethylenediamine-N,N,N',N'- tetraacetic acid, complexone II, chelaton II) due to the successful combination and mutual arrangement of donor centers in the molecule proved to be one of the most effective universal chelates, found the widest application in various fields of technology, analytical chemistry, medicine [4].

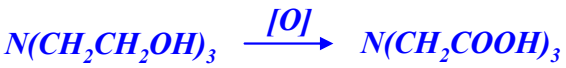
The proposed method for producing ethylenediaminetetraacetic acid is the ethylenediamine carboxyalkylation with monochloroacetic acid. Ethylenediaminetetraacetic acid is also synthesized by an amine cyanomethylation in acidic or alkaline media. It is noted that, in this case, nitrilotriacetic acid is formed as a by-product.

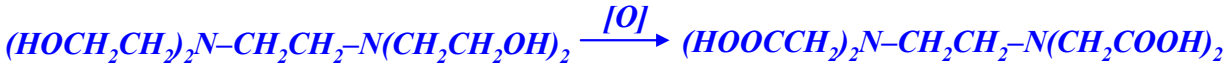
The ethylenediaminetetraacetic acid preparation by the introduction of iminodiacetic acid into the nucleophilic substitution reaction of halogen in dihaloethane is described:



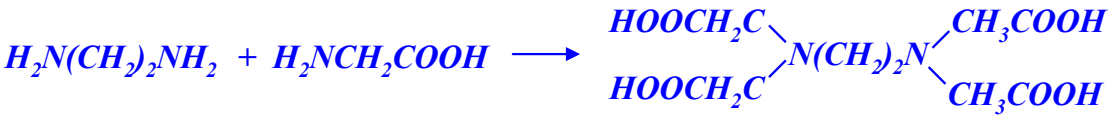
The reaction is carried out in an alkaline environment (pH=8,5 - 9) at 80 - 100°C.

NTA, EDTA and its analogs can be obtained by oxidation of N-hydroxyethyl derivatives of amines. The reaction is proposed to be carried out in the alkali presence under rather harsh conditions at 200 - 260°C, under pressure, for a long time (~90 ч). The use of catalysts activates the process:





It is proposed to obtain EDTA homologues by the α-amino acids interaction with amines. The reaction is recommended to be carried out in an aqueous-alkaline medium without air access, with the removal of the formed ammonia.

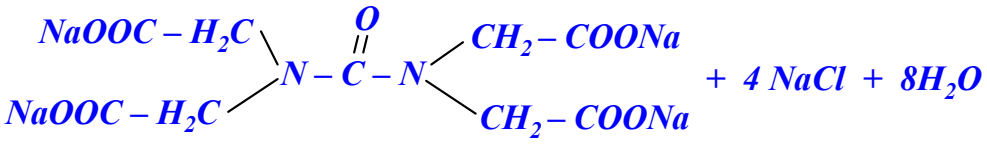


## II. Experimental part

It is known that carboxyalkylated amines such as iminodiacetic acid, ethylenedialinotetraacetic acid, and etc. are of significant theoretical and practical interest and are widely used in various national economy sectors.

In these compounds, the effect on the resulting complexes strength, an increase in dentition due to the introduction of additional iminoacetate groups, as well as the steric factors influence, is quite evident.

With the aim of expanding the amino polyacids range and their practical application finding areas, we have studied the condensation reaction of carbamide with monochloroacetic acid. Condensation of urea with monochloroacetic acid in an alkaline medium (pH = 8-10), at 45-80°C temperature range, leads to the formation of carboxymethyl derivatives according to the scheme:



Product yield up to 51.0%.

We have studied two methods of carbamide carboxymethylation with monochloroacetic acid. The first of them is based on the urea interaction with monochloroacetic acid in an alkaline medium pH = 10-12. Condensation was carried out in a three-necked flask equipped with a mechanical stirrer, thermometer, and dropping funnel.

100 g (0.42 mol) of monochloroacetic acid was dissolved in 50 ml water and while cooling, add 20% sodium hydroxide to the set environment. At the same time, the temperature was controlled so that it did not exceed 40°C. Then, 6 g (0.1 mol) of urea was added to the reaction medium and heated to 70°C with vigorous stirring. To maintain the pH of the medium, at regular intervals, 20% NaOH was added to the reaction mass from a dropping funnel in an amount of 12-14 ml. The solution cooled to 20°C was neutralized with HCl. The formed NaCl from the finished product was isolated by repeated washing with cold water.

New possibilities in the complexones synthesis are opened by the use of corresponding esters instead of haloalkylcarboxylic acids. This allows the reaction to be carried out in a non-aqueous medium in the alkalis absence. The esterified derivatives of chelating agents thus obtained are converted into the corresponding chelating agents by saponification.

The second method is based on the ethyl ester interaction of monochloroacetic acid with urea. For this, 32 g of ethyl alcohol was added to the calculated amount (108 g 4 mol) of chloroacetic acid, the reaction proceeds with decreasing temperature, the reaction is endothermic. After complete dissolution of monochoroacetic acid, 3 g of urea was added with vigorous stirring. The temperature was maintained in the 50-55°C range. The reaction time is 5-6 hours. Then the mass was cooled to room temperature and neutralized by saponification, adding 50% aqueous NaOH solution. Since the finished product, carboxymethylene carbamide,

is insoluble in organic solvents, including alcohol, during neutralization and cooling, a white precipitate begins to form. The precipitated finished product was filtered using a Nutsch filter and washed with alcohol. The product yield is 80% of theoretical.

## III. THE RESULTS DISCUSSION

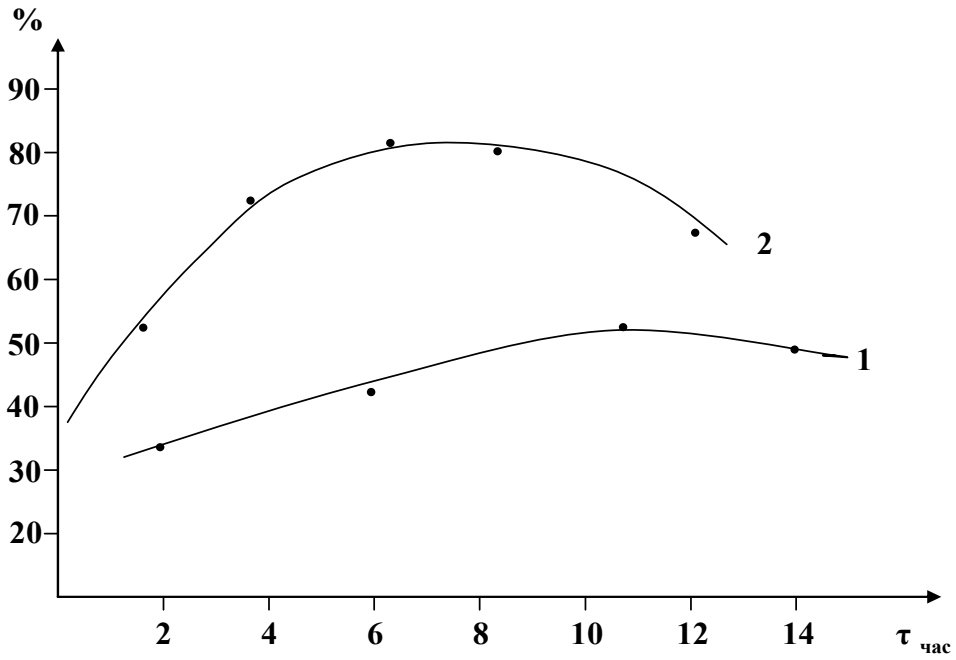
As a research result, the temperature, reaction time, components ratio and product isolation method influence the optimal conditions for the carboxymethylene carbamide derivatives yield and quality were determined.

Table 1. The temperature effect on the carboxymethylene carbamide derivatives yield

| № | Temperature, °C | Product yield, % | |
|---|---|---|---|
| | | 1- method | 2- method |
| 1 | 45-50 | 43,0 | 46,0 |
| 2 | 50-55 | 47,0 | 53,0 |
| 3 | 55-60 | 51,0 | 64,0 |
| 4 | 60-65 | 56,0 | 70,0 |
| 5 | 65-70 | 59,0 | 74,0 |
| 6 | 70-75 | 64,0 | 81,0 |
| 7 | 75-80 | 60,0 | 76,0 |

Comparative data in Table 1 show that at 45-50°C temperature the tetracarboxymethylene carbamide derivatives yield remains minimal and is 43.0% when using the alkaline method and 46.0% when using the esterification method. As the temperature rises, the product yield smoothly increases in the temperature range 70-75°C and reaches a maximum of 64.0 and 81.0%, respectively, thus proving the esterification method advantages.

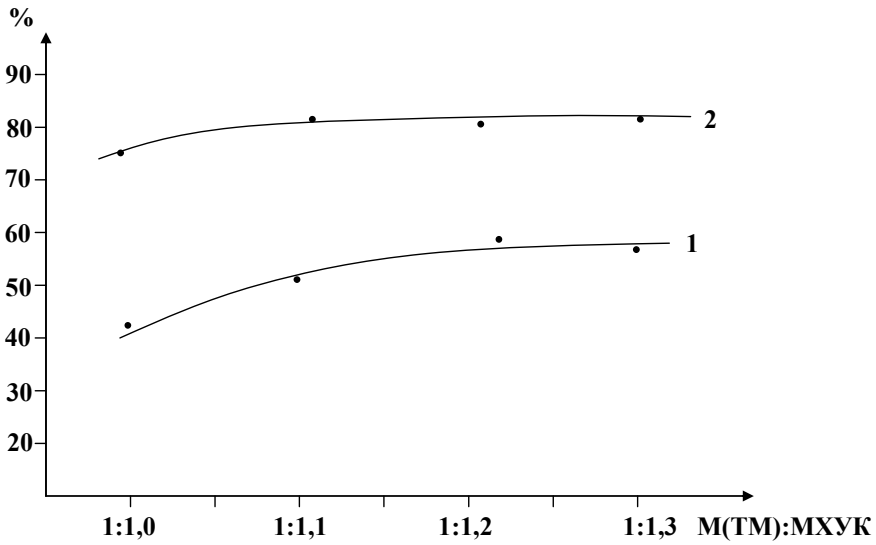
To determine the finished product yield effect depending on the reaction time, the urea interaction with monochloroacetic acid was carried out for 2-14 hours (Fig. 2).




1- alkaline method; 2- esterification method.

Fig. 2. Dependence of the product yield on the reaction time

As can be seen from Fig. 2, when using the esterification method, the finished product can be obtained with the maximum yield (more than 80 %) with a reaction duration of 6-8 hours, at the same time, with the alkaline method, the maximum yield is achieved with the interaction of the starting products in the time interval of 10-12 hours and is less than 55%.




1- alkaline method; 2- esterification method

Fig. 3. Dependence of the components ratio on the carboxymethylene carbamide derivatives yield

As can be seen from Fig. 3, the ratio of the initial components of urea can be considered optimal: monochloroacetic acid 1: 1.2 mol, at which the products yield is more than 80%.

The IR spectrum of the resulting product has characteristic bands for the dimeric form of acids, containing hydrogen bonds, stretching vibrations of the COO–H bond in the 2500-3000 $cm^{-1}$ range; stretching vibration of OH - groups give an intense broad band in the region of 3600-3400 $cm^{-1}$, stretching vibrations for C=O in the range 1530-1550 $cm^{-1}$, also detected C–O–H vibrations at about 3640 $cm^{-1}$.

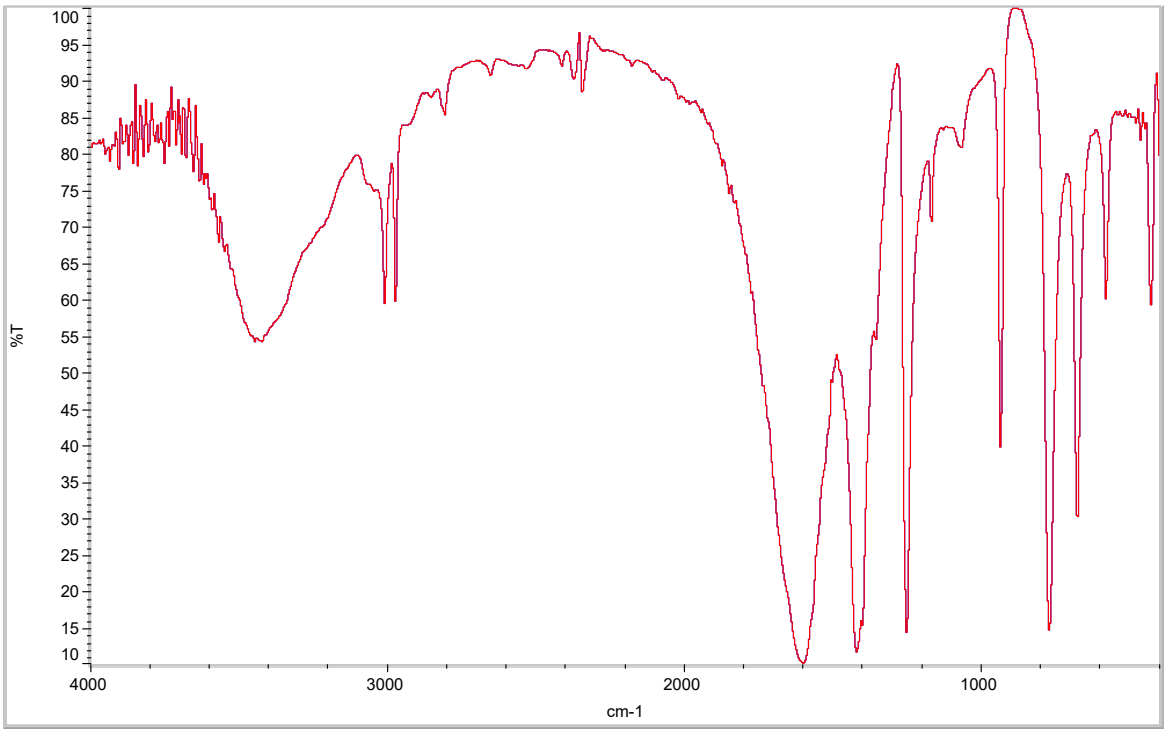



Fig. 4. IR spectrum of the condensation product of monochloroacetic acid with urea, cm-1

COO–H OH C=O C–O–H

| | | | |
|---|---|---|---|
| 2500-3000 | 3600-3400 | 1530-1550 | 3640 |

ПМР spectra of the obtained products show absorption in a weak field (τ from – 2 to – 0,5; δ – 10,5-12) of the proton of the carboxyl groups. The finished product quality is regulated by the following technological indicators.

1. Appearance - white powder.
2. The main substance content is up to 80%.

The water-insoluble substances content is not more than 0.1%.

In order to obtain highly effective inhibitors of the deposition of mineral salts compositions prepared based on our carboxymethylene urea derivatives (CUD) and thiourea (CMTU) with the addition of bases of industrial scale inhibitors OEDP and ИОМС-1 in 1 : 1 ratio and tested in real waters of Kokand, Yangiyul, Navoi (the results are shown in Table 2).

Table 2. Effectiveness of mineral salt inhibitors
(85 - 90 °C temperature)

| Components | Inhibitor dose mg/l | Efficiency with test water hardness, mg·eq/l | | |
|---|---|---|---|---|
| | | 4-5 | 7-8 | 8-11 |
| CUD + ОЭФК | 2,0 | 88,0 | 82,0 | 81,0 |
| | 4,0 | 91,0 | 89,0 | 84,0 |
| | 6,0 | 99,0 | 98,0 | 96,0 |
| | 8,0 | 98,0 | 95,0 | 91,0 |
| CMTU + ОЭФК | 2,0 | 85,0 | 81,0 | 76,0 |
| | 4,0 | 89,0 | 84,0 | 79,0 |
| | 6,0 | 91,0 | 90,0 | 91,0 |
| | 8,0 | 98,0 | 97,0 | 96,0 |
| CUD + ИОМС-1 | 2,0 | 86,0 | 83,0 | 70,0 |
| | 4,0 | 90,0 | 87,0 | 71,0 |
| | 6,0 | 93,0 | 80,0 | 85,0 |
| | 8,0 | 93,5 | 81,0 | 85,0 |
| CMTU + ИОМС-1 | 2,0 | 81,0 | 78,0 | 76,0 |
| | 4,0 | 87,0 | 81,0 | 78,0 |
| | 6,0 | 82,0 | 88,0 | 82,0 |
| | 8,0 | 81,0 | 81,0 | 89,0 |
| ИОМС-1 | 4,0 | 93,0 | 92,0 | 90,0 |
| OEDP | 4,0 | 90,0 | 88,0 | 90,0 |

As can be seen from the data in Table 3, the effectiveness of inhibitors CUD + ОЭФК and CMTU + ОЭФК is much higher, than the original products and reaches up to 98 - 99%.

## IV. Conclusion

Purposeful research has been carried out to develop, study the properties of new improved methods for obtaining complexones based on amines and amides with monochloroacetic acid in an alkaline medium and by the esterification method.

It was studied the carboxymethylation of urea (thiourea) and aniline reaction at 50 – 95°C temperature range. It was found that in the synthesis of carboxymethyl derivatives of urea (thiourea), the optimal temperature is with alkaline method 75 - 80 °C and when synthesizing from esters of the corresponding acids 50 - 65 °C.

The inhibiting properties of the synthesized CUD and CMTU were studied in waters with hardness in the 4-11 mg·eq/l range. It has been shown that with an increase in the inhibitor concentration, its selectivity and effect increase. In the water of Nukus, this has the highest hardness, at 8.0 mg/l - 96.0% concentration.

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