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Interaction of Components in Aqueous Systems Involving Sodium Monourea Chlorate, Monoammonium Phosphate, Diammonium Phosphate, Monoethanolamine, and Diethanolamine

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ABSTRACT:

The solubility of components in systems has been studied $NaClO_3·CO(NH_2)_2$-$NH_4H_2PO_4$-H_2O, $NaClO_3·CO(NH_2)_2$-$(NH_4)_2HPO_4$-H_2O, $NaClO_3·CO(NH_2)_2$-$NH_2C_2H_4OH$-H_2O, $NaClO_3·CO(NH_2)_2$-$NH(C_2H_4OH)_2$-H_2O, from the temperature of complete freezing (respectively -51,9℃, -67,4℃, -32,4℃, -28,2℃) to 18-100℃ respectively. Based on data on the solubility of binary systems and internal sections, their polythermal solubility diagrams were constructed. Systems of a simple eutonic type and a salting-out effect is observed in them $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $NH_2C_2H_4OH$ and $NH(C_2H_4OH)_2$ $NaClO_3·CO(NH_2)_2$ with increasing temperature and increasing concentration of initial components in systems.

Key words: temperature, component, sodium chlorate, monoammonium phosphate, diammonium phosphate, monoethanolamine, diethanolamine, diagram, solubility, concentration, polytherm.

1. INTRODUCTION

With timely and high-quality defoliation with an effective defoliant, as a result of accelerating physiological processes in the plant body and increasing enzyme activity, cotton leaves shed, the bolls ripen and open faster, and this allows 80-90 percent of the cotton crop to be transferred to high varieties in the first harvest.

The introduction of compounds to cotton that accelerate physiological processes during the period of ripening and opening of bolls increases the plant's resistance to the effects of pesticides, accelerates the ripening of bolls and causes leaf fall. To accelerate physiological processes in the plant body, it is desirable to obtain multicomponent defoliants based on chlorate salts, using chemical compounds containing ethylene-forming substances.

It is known from the literature that phosphate salts accelerate the aging process of plants, promoting leaf fall and bringing defoliation closer to the natural processes of leaf fall [1-2].

The introduction of various nitrogen and phosphorus compounds into chlorate-containing defoliants increases their defoliating activity [3-4].

It is known that leaf fall and crop ripening begin when the content of auxins in the plant organism decreases, and the level of ethylene and other antiauxin compounds increases [5-7]. It follows that the main feature of the action of a defoliant and crop ripening accelerator is their ability to increase the level of ethylene and other antiauxin compounds in plant tissues.

One of the possible ways to solve this important problem is to obtain and use chlorate-containing preparations for defoliation, which include compounds containing $-CH_2-CH_2-$ ethylene group. These compounds include ethanolamine, which has a number of valuable physiological and chemical properties. It activates growth processes, increases seed germination [8] and accelerates the ripening and opening of capsules [9].

System $NaClO_3 \cdot CO(NH_2)_2-NH_4H_2PO_4-H_2O$ studied by us visually using the polythermal method [10], from the temperature of complete freezing (-32.4℃) to 100℃.

Sodium monourea chlorate, synthesized by introducing urea and sodium chlorate into the melt in a 1:1 molar ratio, was used as the starting components. After the formation of a homogeneous melt of the components, crystals of the compound were isolated by cooling $NaClO_3 \cdot CO(NH_2)_2$.

Chemical analysis of the synthesized compound gave the following results: found, mass. %:
Na^+ = 13,09; ClO_3^- = 49,80; N_{amid} = 16,75.
For $NaClO_3 \cdot CO(NH_2)$ calculated, mass. %
Na^+ = 13,82; ClO_3^- = 50,168; N_{amid} = 16,82

X-ray phase analysis showed that the diffraction pattern of the compound $NaClO_3 \cdot CO(NH_2)_2$ characterized by its own set of diffraction reflections, uncharacteristic of the initial components (Fig. 1).

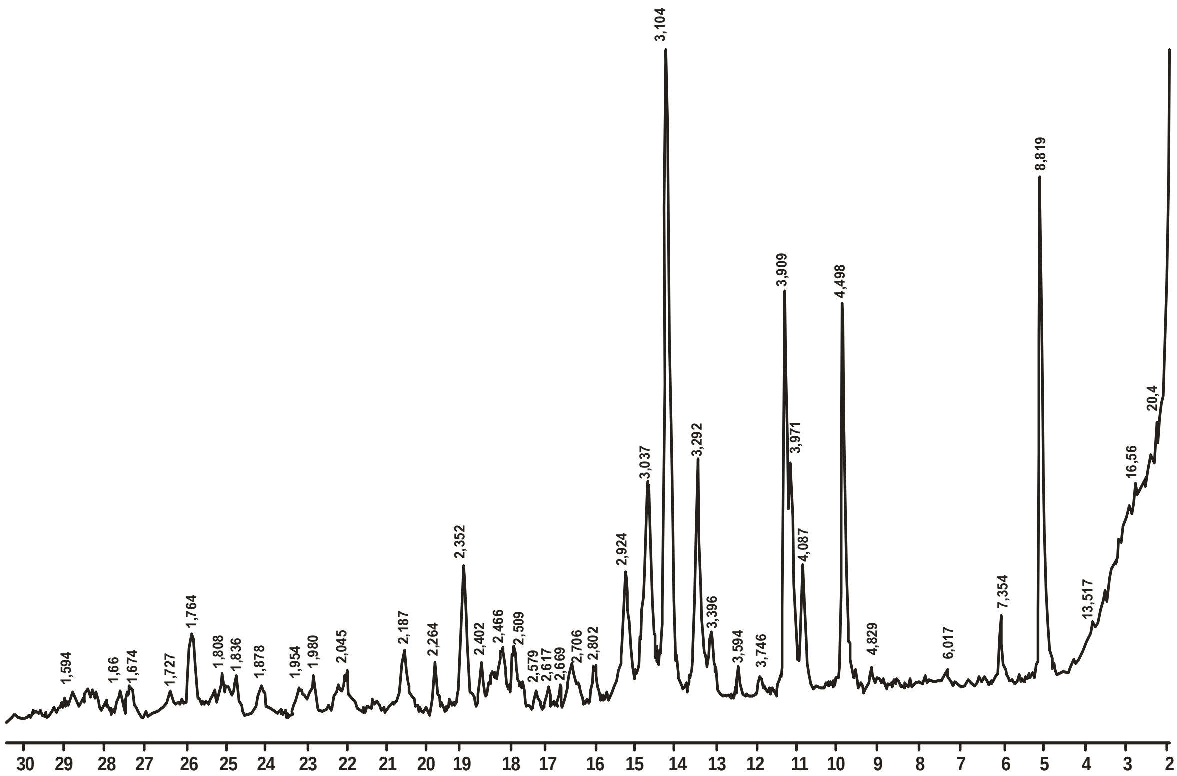


Fig.1. X-ray of the connection $NaClO_3{\cdot}CO(NH_2)_2$.

The heating curve of the compound is characterized by the presence of two temperature effects at 120 and 280℃, the first, endothermic effect corresponds to the melting of the compound, the second, exothermic, corresponds to the decomposition of the compound and its decomposition products (TG = 62.78%) (Fig. 2).

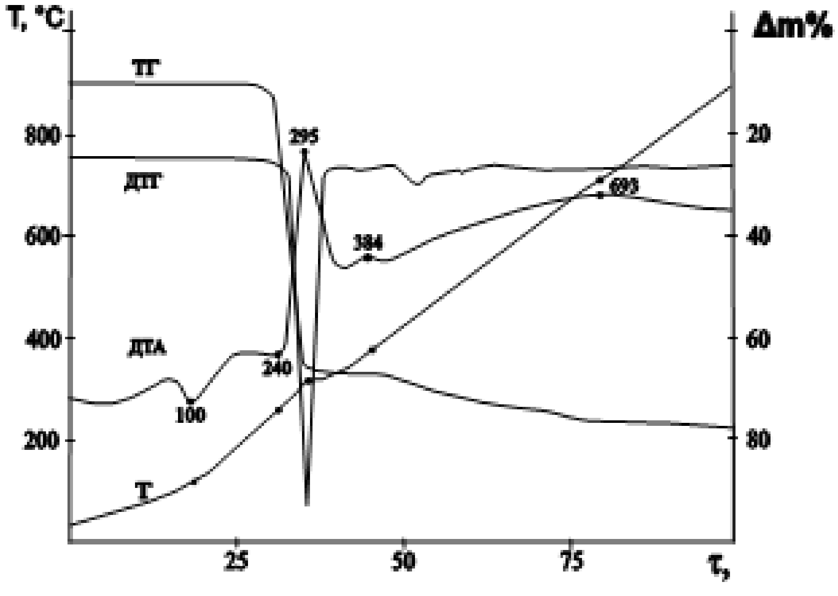


Fig.2. Dervitogram $NaClO_3{\cdot}CO(NH_2)_2$.

The binary system sodium monourea chlorate-water has not been studied previously. Its polythermal solubility diagram reveals branches of crystallization of ice, urea and sodium monourea chlorate (Fig. 3).

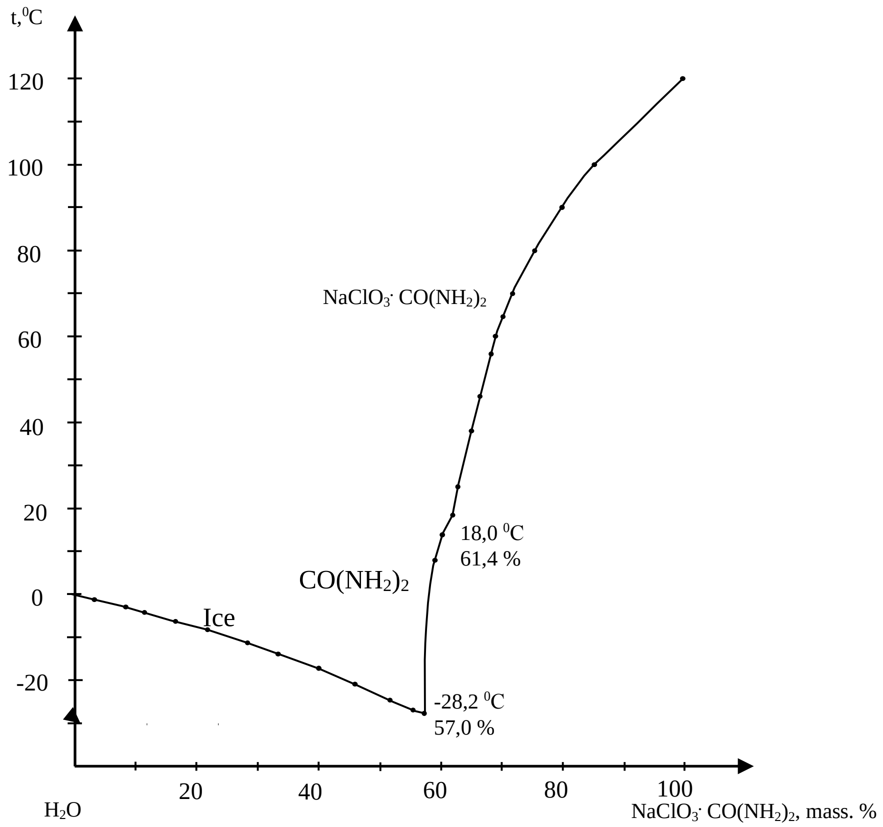


Fig.3. System solubility diagram $NaClO_3{\cdot}CO(NH_2)_2$–H_2O

Ice crystallization continues up to 57.0% sodium monourea chlorate at -28.2℃. From here begins the branch of urea crystallization to 61.4% sodium monourea chlorate at 18.0℃. This point is the transition point where the branch of crystallization of sodium monourea chlorate begins.

System $NaClO_3{\cdot}CO(NH_2)_2$ - $NH_4H_2PO_4$ - H_2O studied by us using eleven internal sections. Of these, sections I-V were examined from the side $NH_4H_2PO_4$-H_2O to the top $NaClO_3{\cdot}CO(NH_2)_2$, VI-XI side cuts $NaClO_3{\cdot}CO(NH_2)_2$-H_2O to the top $NH_4H_2PO_4$.

Based on the results of studying binary systems and internal sections, a polythermal diagram of the solubility of a ternary system from the temperature of complete freezing (-32.4℃) to 100℃ was constructed. The phase diagram of this system delineates the crystallization fields of ice, urea, sodium monourea chlorate and monoammonium phosphate (Fig. 4).

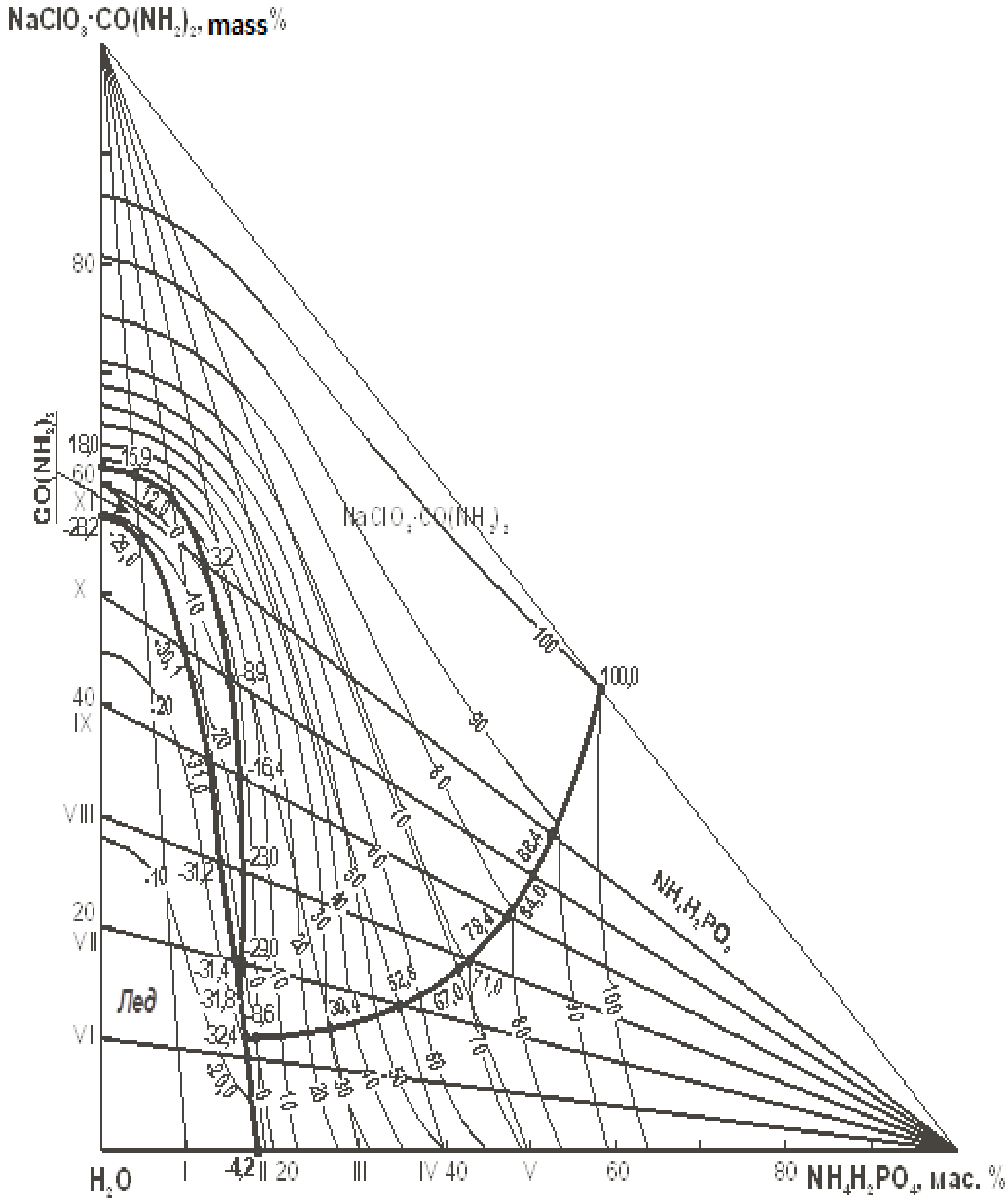


Fig.4. Solubility diagram system $NaClO_3{\cdot}CO(NH_2)_2$-$NH_4H_2PO_4$-H_2O

These fields converge at two triple nodal points of the system, for which the chemical compositions of equilibrium solutions and the corresponding crystallization temperatures are determined (Table 1).

Table 1 Double and triple point systems $NaClO_3{\cdot}CO(NH_2)_2$- $NH_4H_2PO_4$-H_2O

Liquid phase composition, mass.%			Temperature crystal., °C	Solid phase
$NaClO_3{\cdot}CO(NH_2)_2$	$NH_4H_2PO_4$	H_2O		
61,4	-	38,6	18,0	$CO(NH_2)_2$ +$NaClO_3{\cdot}CO(NH_2)_2$
60,8	4,0	35,2	15,9	-//-
59,0	8,0	33,0	12,0	-//-
53,0	11,6	35,4	3,2	-//-
42,8	14,9	42,3	-8,9	-//-

33,9	15,8	50,3	-16,9	-//-
25,0	16,0	59,0	-23,0	-//-
16,9	16,2	66,9	-29,0	-//-
14,1	16,0	69,9	-31,8	Ice $+CO(NH_2)_2+NaClO_3 \cdot CO(NH_2)_2$
10,0	16,4	74,0	-32,4	Ice + $NaClO_3 \cdot CO(NH_2)_2$ $+NH_4H_2PO_4$
8,2	16,8	75,0	-20,0	Ice + $NH_4H_2PO_4$
-	18,0	82,0	-4,2	-//-
57,0	-	43,0	-28,2	Ice + $CO(NH_2)_2$
55,4	4,4	40,2	-29,6	Ice $+CO(NH_2)_2$
45,1	9,8	45,1	-30,1	-//-
35,0	12,8	52,1	-31,0	-//-
25,9	13,7	60,4	-31,2	-//-
17,0	15,1	67,9	-31,4	-//-
11,0	26,8	62,2	30,4	$NH_4H_2PO_4+NaClO_3 \cdot CO(NH_2)_2$
13,0	34,9	52,1	52,8	-//-
16,2	41,8	42,0	67,0	-//-
17,1	42,9	40,0	71,0	-//-
21,5	47,0	31,5	79,4	-//-
24,9	50,0	25,1	84,0	-//-
28,4	52,4	19,2	88,4	-//-
42,0	58,0	-	100,0	-//-

From the data presented it is clear that in the system under study there is no formation of new chemical compounds based on the initial components. The system belongs to the simple eutonic type.

System $NaClO_3 \cdot CO(NH_2)_2$ - $(NH_4)_2HPO_4$ - H_2O We studied it using the visual-polythermal method [10] from the temperature of complete freezing (-28.2℃) to 60℃.

System $NaClO_3 \cdot CO(NH_2)_2$-$(NH_4)_2HPO_4$ -H_2O studied by us using thirteen internal sections. Of these, sections I-VI were examined from the side $(NH_4)_2HPO_4$ -H_2O to the top $NaClO_3 \cdot CO(NH_2)_2$, VII- XIII side cuts $NaClO_3 \cdot CO(NH_2)_2$-H_2O to the top $(NH_4)_2HPO_4$

Based on the results of studying binary systems and internal sections, a polythermal solubility diagram of the ternary system was constructed. The phase diagram of this system delineates the crystallization fields of ice, urea, sodium monourea chlorate, dihydrous and anhydrous ammonium hydrogen phosphate (Figure 5).

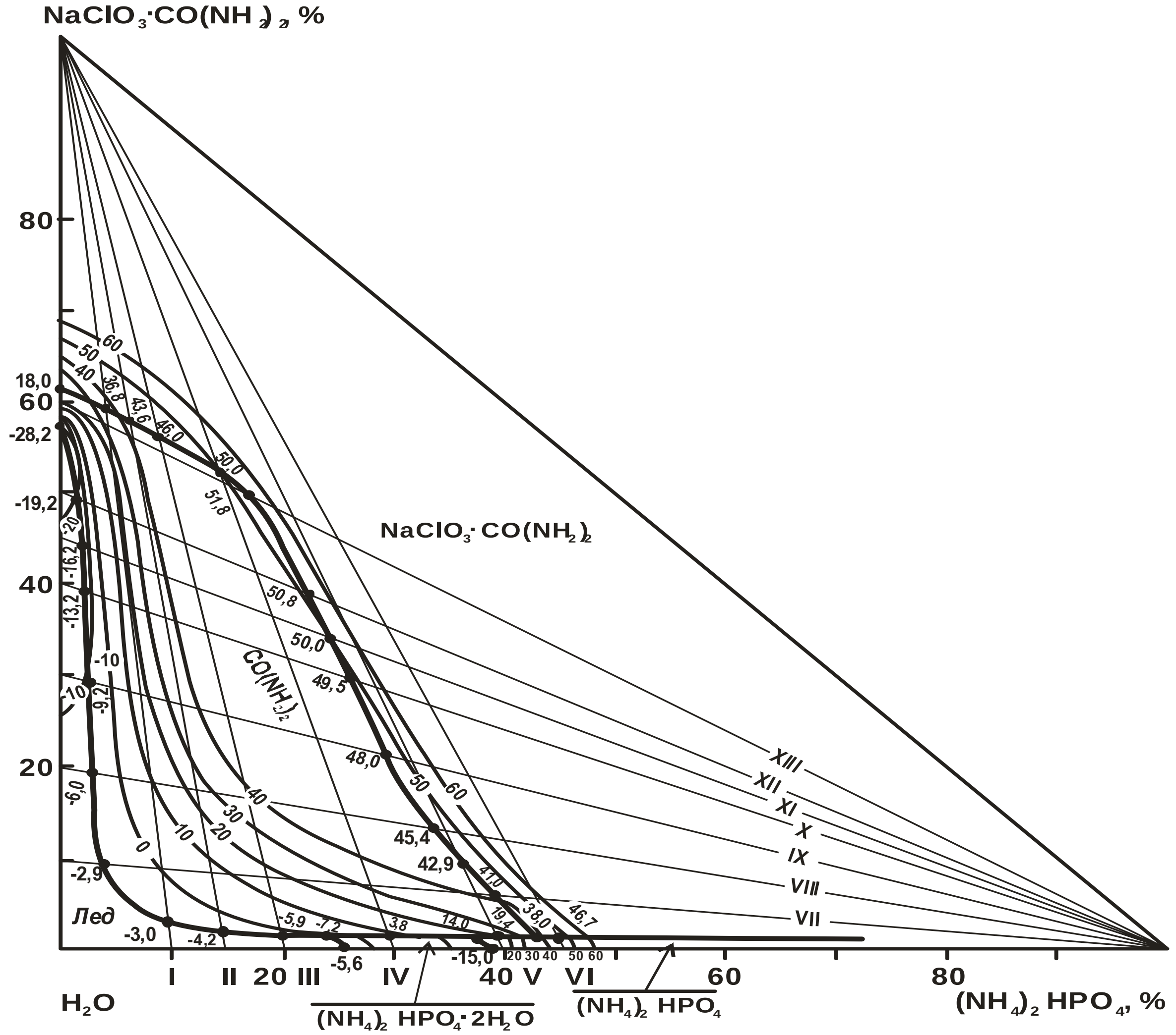


Fig.5. Solubility diagram system $NaClO_3{\cdot}CO(NH_2)_2$-$(NH_4)_2HPO_4$-H_2O

These fields converge at two triple nodal points of the system, for which the chemical compositions of equilibrium solutions and the corresponding crystallization temperatures are determined (Table 2).

Table 2 Double and triple point systems $NaClO_3{\cdot}CO(NH_2)_2$- $(NH_4)_2HPO_4$-H_2O

Composition of the liquid phase, wt.%			Temperature crystal ℃	Solid phase
$NaClO_3{\cdot}CO(NH_2)_2$	$(NH_4)_2HPO_4$	H_2O		
61.4	-	38.6	18.0	$CO(NH_2)_2$ +$NaClO_3{\cdot}CO(NH_2)_2$
59.2	4.0	36.8	36.8	тоже
57.4	6.6	36.0	43.6	-//-
5.8	9.2	85.0	46.0	-//-
49.6	17.2	33.2	51.8	-//-
38.8	22.4	38.8	50.8	-//-
34.0	24.6	41.4	50.0	-//-
29.8	26.0	44.2	49.0	-//-
21.4	29.2	49.4	48.0	-//-
13.2	33.6	53.2	45.4	-//-
9.2	36.4	54.4	42.9	-//-

6.2	39.0	54.8	41.0	-//-
1.2	49.0	49.8	38.0	$CO(NH_2)_2$+ $NaClO_3 \cdot CO(NH_2)_2$+$(NH_4)_2HPO_4$
41.2	45.0	13.8	46.7	$NaClO_3 \cdot CO(NH_2)_2$+$(NH_4)_2HPO_4$
57.0	-	43.0	-28.2	Ice+$CO(NH_2)_2$
49.2	1.4	49.4	-19.2	too
44.2	1.8	54.0	-16.2	-//-
39.4	2.0	58.6	-13.2	-//-
29.4	2.4	68.2	-9.2	-//-
19.4	2.8	77.8	-6.0	-//-
9.6	3.4	87.0	-2.9	-//-
2.6	9.6	87.8	-3.0	-//-
2.0	14.6	83.4	-4.2	-//-
1.4	19.6	79.0	-5.9	-//-
1.2	24.2	74.6	-7.2	Ice + $CO(NH_2)_2$+$(NH_4)_2HPO_4 \cdot 2H_2O$
-	25.6	74.4	-5.6	Ice +$(NH_4)_2HPO_4 \cdot 2H_2O$
1.2	29.6	69.2	3.8	$CO(NH_2)_2$+$(NH_4)_2HPO_4 \cdot 2H_2O$
1.2	37.4	61.4	14.0	$CO(NH_2)_2$+$(NH_4)_2HPO_4 \cdot 2H_2O$+ $(NH_4)_2HPO_4$
1.2	39.4	59.4	19.4	Ice +$(NH_4)_2HPO_4$
-	39.0	61.0	15.0	$(NH_4)_2HPO_4 \cdot 2H_2O$+$(NH_4)_2HPO_4$

From the data presented it is clear that in the system under study there is no formation of new chemical compounds based on the initial components. The system belongs to the simple eutonic type.

The solubility and interaction of components in systems has been studied $NaClO_3 \cdot CO(NH_2)_2$-$NH(C_2H_4OH)_2$-H_2O, from the temperature of complete freezing (-67.4℃) to 18.0℃, using the visual-polythermal method [10]. The starting components were sodium monourea chlorate, synthesized by introducing sodium chlorate urea into the melt at a molar ratio of 1:1. Diethanolamine was used in grade grade, additionally purified by vacuum distillation.

A study of the solubility of the monoethanolamine-water binary system showed that its diagram distinguishes four branches of crystallization; ice, di-, mono- and anhydrous monoethanolamine. The eutectic point of the system corresponds to 52.4% monoethanolamine and 47.6% water at -48.3℃. The data we obtained are in good agreement with the literature [11].

System $NaClO_3 \cdot CO(NH_2)_2$-$NH_2C_2H_4OH$-H_2O studied by us using six internal sections. Of these, incisions I-III were made from the side $NaClO_3 \cdot CO(NH_2)_2$-H_2O to the top $NH_2C_2H_4OH$, IV-VI the incisions were examined from the side $NH_2C_2H_4OH$ - H_2O to the top $NaClO_3 \cdot CO(NH_2)_2$.

Based on the results of studying binary systems and internal sections, a polythermal solubility diagram of the ternary system was constructed. The phase diagram of this system delineates the crystallization fields of ice, urea, sodium monourea chlorate, dihydrate, aqueous and anhydrous monoethanolamine. (Fig. 6).

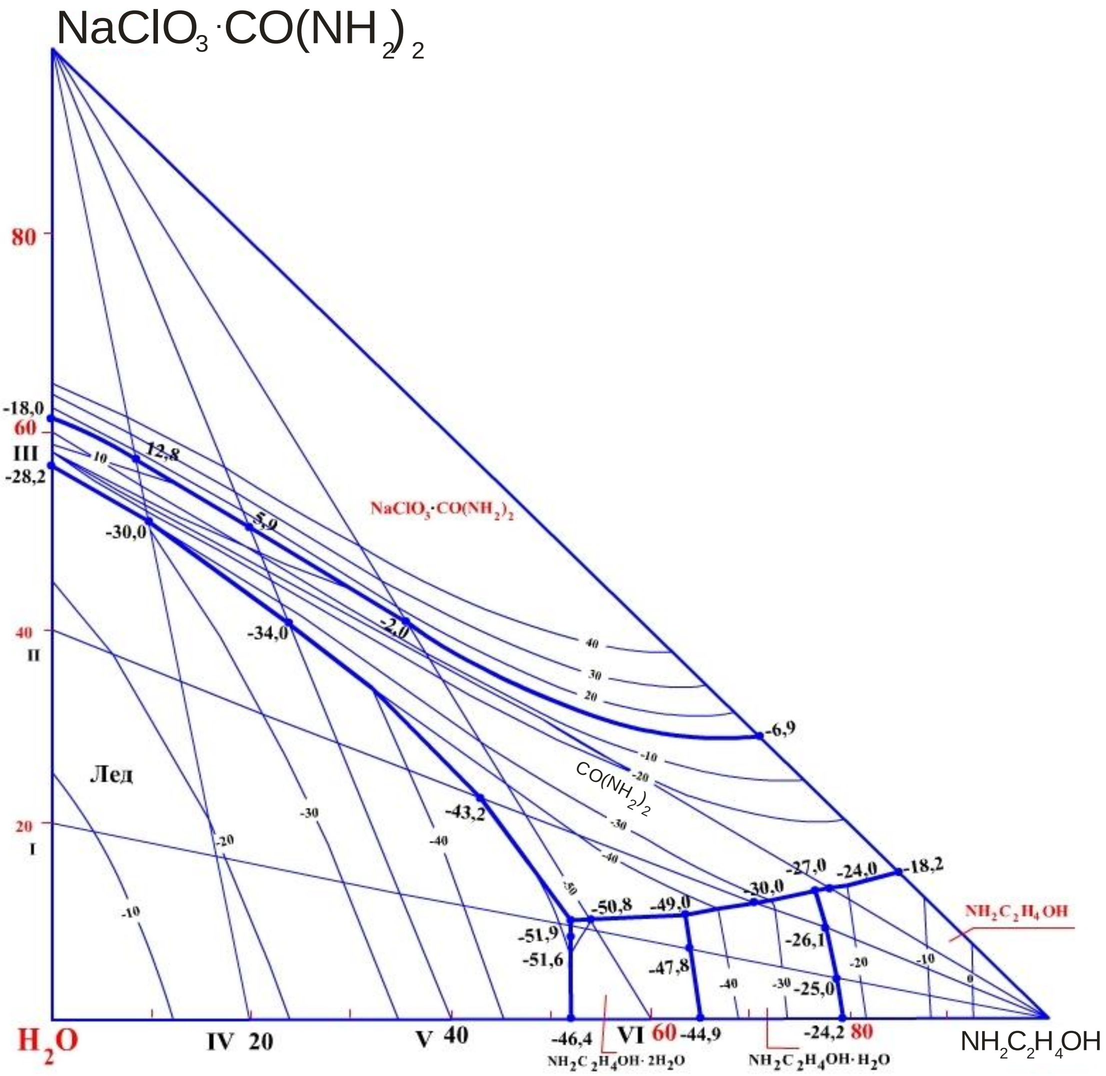


Fig. 6. System solubility diagram $NaClO_3 \cdot CO(NH_2)_2$-$NH_2C_2H_4OH$-H_2O

These fields converge at two triple nodal points of the system, for which the chemical compositions of equilibrium solutions and the corresponding crystallization temperatures are determined (Table 3).

Table 3 Double and triple point systems $NaClO_3 \cdot CO(NH_2)_2$-$NH_2C_2H_4OH$-H_2O

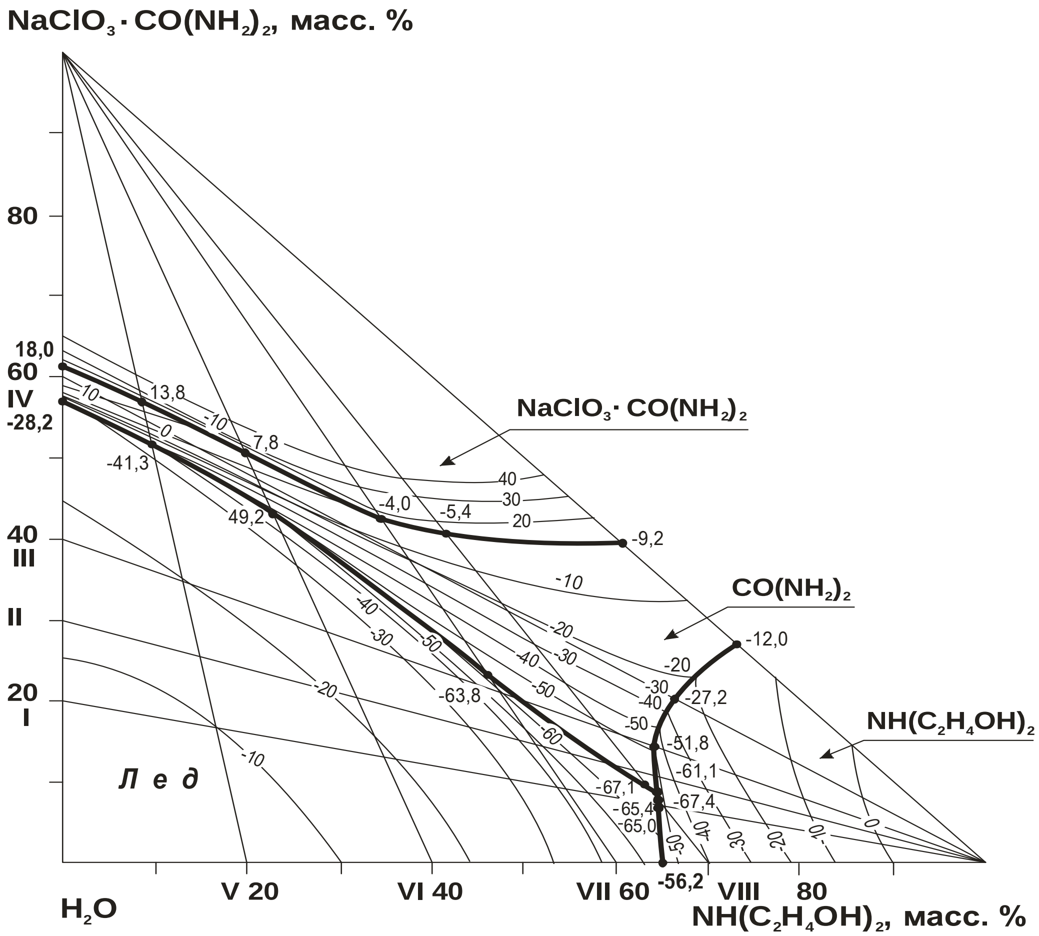
Composition of the liquid phase, wt.%			Temperature crystal.,°C	Solid phase
$NaClO_3 \cdot CO(NH_2)_2$	$NH_2C_2H_4OH$	H_2O		
56,4	-	43,6	-28,2	Ice+ $CO(NH_2)_2$
51,0	9,9	39,1	-30,0	-//-
40,8	23,9	35,3	-34,0	-//-
23,0	43,0	34,0	-43,2	-//-
10,0	52,0	38,0	-51,9	Ice + $CO(NH_2)_2$+ $NH_2C_2H_4OH \cdot 2H_2O$
9,7	52,0	38,3	-51,6	Лед+ $NH_2C_2H_4OH \cdot 2H_2O$
-	52,0	48,0	-46,4	-//-
10,0	54,0	36,0	-50,8	$CO(NH_2)_2$+

				$NH_2C_2H_4OH{\cdot}2H_2O$
10,8	63,9	25,3	-49,0	$CO(NH_2)_2$+ $NH_2C_2H_4OH{\cdot}2H_2O$+ $NH_2C_2H_4OH{\cdot}H_2O$
7,7	64,0	28,3	-47,8	$NH_2C_2H_4OH{\cdot}2H_2O$+ $NH_2C_2H_4OH{\cdot}H_2O$
-	65,0	35,0	-44,9	-//-
12,0	70,6	17,4	-30,0	$CO(NH_2)_2$+ $NH_2C_2H_4OH{\cdot}H_2O$
13,0	76,9	10,1	-27,0	$CO(NH_2)_2$+$NH_2C_2H_4OH{\cdot}H_2O$+ $NH_2C_2H_4OH$
9,0	78,0	13,0	-26,1	$NH_2C_2H_4OH{\cdot}H_2O$+ $NH_2C_2H_4OH$
4,0	79,0	17,0	-25,0	$NH_2C_2H_4OH{\cdot}H_2O$+ $NH_2C_2H_4OH$
-	79,8	20,2	-24,2	$NH_2C_2H_4OH{\cdot}H_2O$+ $NH_2C_2H_4OH$
26,8	78,4	5,2	-24,0	$CO(NH_2)_2$+$NH_2C_2H_4OH$
15,0	85,0	-	-18,2	-//-
61,8	-	38,2	18,0	$CO(NH_2)_2$+$NaClO_3{\cdot}CO(NH_2)_2$
57,8	8,8	33,4	12,8	-//-
50,5	20,0	29,5	5,9	-//-
40,8	35,8	23,4	-2,0	-//-
29,0	71,0	-	-6,9	-//-

From the data presented it is clear that in the system under study there is no formation of new chemical compounds based on the initial components. The system belongs to the simple eutonic type.

System $NaClO_3{\cdot}CO(NH_2)_2$-$NH(C_2H_4OH)_2$ - H_2O We studied it using eight internal sections, from the temperature of complete freezing -67.4℃ to 18.0℃. Of these, I-IV incisions were made from the side $NaClO_3{\cdot}CO(NH_2)_2$-H_2O to the top $NH(C_2H_4OH)_2$, V-VIII the incisions were examined from the side $NH(C_2H_4OH)_2$-H_2O to the top $NaClO_3{\cdot}CO(NH_2)_2$.

Binary system $NH(C_2H_4OH)_2$-H_2O reviewed by a number of authors [12-25]. The results we obtained are in good agreement with the literature. Based on the results of studying binary systems and internal sections, a polythermal solubility diagram of the ternary system was constructed. The phase diagram of this system delineates the crystallization fields of ice, urea, sodium monourea chlorate, and diethanolamine (Fig. 7).



Rice. 7. System solubility diagram $NaClO_3 \cdot CO(NH_2)_2$-$NH(C_2H_4OH)_2$-H_2O.

These fields converge at the triple nodal point of the system, for which the chemical composition of the equilibrium solution and the corresponding crystallization temperature are determined (Table 4).

Table 4 Double and triple point systems $NaClO_3 \cdot CO(NH_2)_2 – NH(C_2H_4OH)_2 – H_2O$

Composition of the liquid phase, %			Crystal temperature., °C	Solid phase
$NaClO_3 \cdot CO(NH_2)_2$	$NH(C_2H_4OH)_2$	H_2O		
61,4	-	38,6	18,0	$NaClO_3 \cdot CO(NH_2)_2 + CO(NH_2)_2$
57,0	8,8	34,2	13,8	-//-
50,9	20,0	29,1	7,8	-//-
42,6	35,0	22,4	-4,0	-//-
41,0	41,8	17,2	-5,4	-//-
39,8	60,2	-	-9,2	-//-
57,0	-	43,0	-28,2	Ice + $CO(NH_2)_2$
51,8	9,9	38,3	-41,3	-//-
43,0	23,0	34,0	-49,2	-//-
23,4	46,0	30,6	-63,8	-//-
9,8	63,0	27,2	-67,1	-//-
8,8	64,5	26,7	-67,4	Ice+ $CO(NH_2)_2$+ $NH(C_2H_4OH)_2$
7,8	64,5	27,7	-65,4	Ice+ $NH(C_2H_4OH)_2$
7,4	64,5	28,1	-65,0	-//-

-	65,0	35,0	-56,2	-//-
11,0	64,3	24,7	-61,1	$CO(NH_2)_2 + NH(C_2H_4OH)_2$
14,5	64,0	21,5	-51,8	-//-
20,2	66,2	13,6	-27,2	-//-
27,0	73,0	-	-12,0	-//-

On the polythermal solubility diagrams of the studied systems, solubility isotherms of the components are plotted every 10℃. To clarify the position of the nodal triple points, projections of polythermal solubility curves onto the corresponding lateral water sides of the concentration triangles were constructed.

From the data presented it is clear that in the systems under study there is no formation of new chemical compounds based on the initial components. The system belongs to the simple eutonic type. In the systems, the salting out effect of ethanolamines and ammonium phosphate salts on sodium monocarbamidochlorate is observed with an increase in temperature and concentration of components within the studied temperatures and concentration limits.

The results of the physical, chemical and agrochemical tests indicate the possibility of obtaining new highly effective multifunctional drugs based on consumable and local raw materials.

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