STUDY OF THE SOLUBILITY AND RHEOLOGICAL PROPERTIES OF THE $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$-$C_4H_6O_5 \cdot NH_2C_2H_4OH$-$H_2O$ SYSTEM

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ABSTRACT

To obtain the highly effective complex-acting defoliant, the $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$-$C_4H_6O_5 \cdot NH_2C_2H_4OH$-$H_2O$ system was studied using binary systems and ten internal sections, and the visual polythermal solubility diagram was constructed in the range of -24.2°C to 32.0°C. In the diagram, the crystallization areas of ice, $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2 \cdot 2H_2O$ and $C_4H_6O_5 \cdot NH_2C_2H_4OH$ were separated. This system belongs to the simple eutonic type, the components have preserved their individuality and showed good solubility in water. In the [55 % $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$ + 45 % H_2O]-[$C_4H_6O_5 \cdot NH_2C_2H_4OH$] system, when the components are added in different proportions, the pH, crystallization temperature, refractive index, viscosity, and density changes of the solution were determined, and a “composition-property” diagram was constructed.

Keywords: solubility, calcium chlorate two urea, malic acid monoethanolamine, “composition-property”, viscosity, density, crystallization temperature, refractive index, pH, isotherm.

INTRODUCTION

Until now, chemical preparations regulating the growth of plants are widely used to increase the productivity of crops.

Plant growth regulators are monoethanolamine and its derivatives, which play an important role in oxidation-reduction processes. Malic acid (in the tricarboxylic acid cycle) is one of the intermediate products of metabolism in living organisms [1 - 3]. It is known from the literature that monoethanolamine and its derivatives in defoliants enhance the effect of active components, as well as eliminate the negative effects of chemical compounds on plants [4, 5].

Physiologically active substances are widely used to increase plant growth and resistance to various diseases [6]. One of the effective properties of physiologically active substances is the ability to achieve the expected result even in small quantities [7, 8]. Taking this into account, we use monoethanolamine compounds of malic acid of calcium chlorate and two urea’s, while reducing the harsh effect of ClO_3^--chlorate, the malic acid monoethanolamine compounds contained in it act as a physiologically active substance.

Considering the above, to physical-chemically justify the processes of synthesizing highly effective, complex, physiologically active, cheap defoliants, the solubility of components in aqueous systems containing calcium chlorate diurea and malic acid monoethanolamine in a wide temperature and concentration range and physical-chemical properties were studied by visual-polythermal method.

EXPERIMENTAL

The research object is calcium chlorate di urea, malic acid monoethanolamine. Calcium chlorate diurea obtained for research, calcium chlorate diurea was synthesized by interacting calcium chlorate with urea in a 1:2 mol ratio at 80 - 90°C, and the presence of calcium chlorate diurea was determined using chemical and physical-chemical analysis methods [9, 10].

Malic monoethanolammonium was synthesized based on the neutralization of 97.0% malic acid in the presence of 98.0% monoethanolamine obtained in a molar ratio of 1:1 [11]. C4H6O5·NH2C2H4OH is a clear dark brown, slightly dark liquid solution compared with water. The resulting liquid complex salt has a pH of 6.96 and is very soluble in water, poorly soluble in organic solvents.

In the research, from chemical and physical-chemical methods: ClO^{3-}-chlorate ion size was determined by permanganometric method [12, 13], Ca^{2+}-calcium ion was determined by volumetric complexonometric method [14], Cl^{-}-chlorine ion was determined by volumetric argentometric method [15, 16]. Elemental analysis was carried out for the determination of carbon, nitrogen and hydrogen [17, 18], urea-amide-nitrogen-spectrophotocalorimetric methods FEC-56M [19, 20] TN-6 glass mercury thermometer with a measurement range of solutions from -30ºC to 60°C using, also the density of the solution was determined by pycnometric [21, 22], viscosity by VPJ viscometer, pH value of solution by FE 20 METTLER TOLEDO pH meter and refractive index by PAL-BX/RI ATAGO refractometer.

RESULTS AND DISCUSSION

To physical-chemical justify the interaction of $Ca(ClO_3)_2{\cdot}2CO(NH_2)_2$ and $C_4H_6O_5{\cdot}NH_2C_2H_4OH$, H_2O system, it was investigated in a wide temperature and concentration range.

The solubility of the two-component $Ca(ClO_3)_2{\cdot}2CO(NH_2)_2$-$H_2O$ and $C_4H_6O_5{\cdot}NH_2C_2H_4OH$-$H_2O$ systems was studied by the visual-polythermal method [23 - 25] (Fig. 1a, b).

The two-component binary system $Ca(ClO_3)_2{\cdot}2CO(NH_2)_2$-$H_2O$ was studied in the temperature range from 0ºC to 55.0ºC. In the solubility diagram, the areas of crystallization of ice and calcium chlorate dihydrate of diureas, were separated. In this case, when the eutectic point is less than 49.8 % at the temperature of -15.0ºC, crystals of ice are formed, and when it is more, crystals of calcium chlorate two urea two molecules of water crystalline hydrate are formed.

The two-component binary system $C_4H_6O_5{\cdot}NH_2C_2H_4OH$-$H_2O$ was studied in the temperature range from 0ºC to 80.0ºC. In the diagram, the areas of ice and $C_4H_6O_5{\cdot}NH_2C_2H_4OH$ crystallization are identified, where the eutectic point crystallizes together with 38.9 % $C_4H_6O_5{\cdot}NH_2C_2H_4OH$ and 61.1 % H_2O at the temperature of -20.0ºC. The visual-polythermal solubility diagram was constructed in the range from -24.2ºC to 32.0ºC based on the ten internal divisions of the three-component system of $Ca(ClO_3)_2{\cdot}2CO(NH_2)_2$-$C_4H_6O_5{\cdot}NH_2C_2H_4OH$-$H_2O$ and

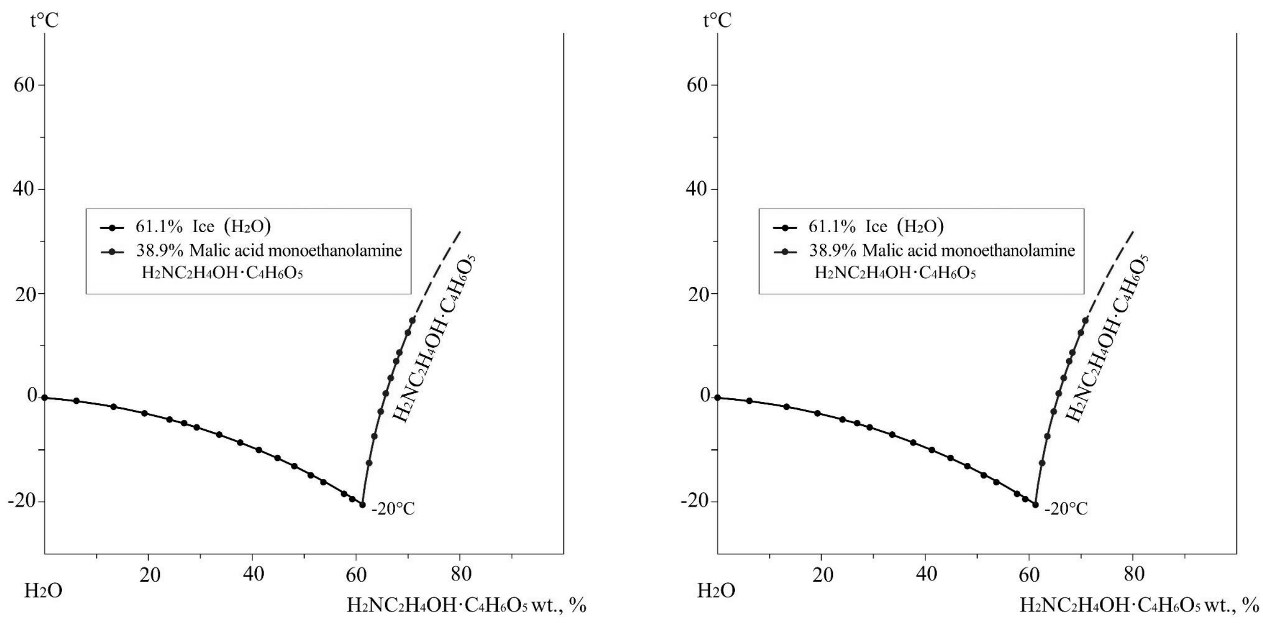

Fig. 1. (a) calcium chlorate diurea-water, (b) malic acid monoethanolamine - water solubility diagrams of two-component systems.

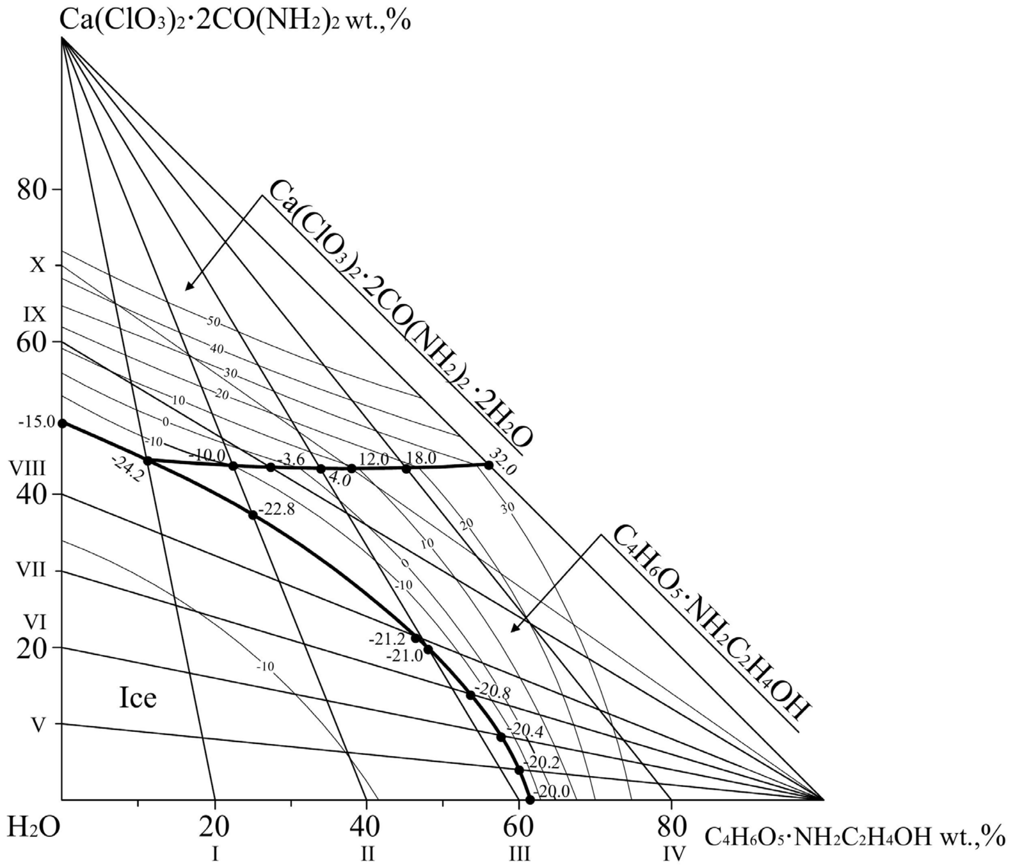

Fig. 2. Polythermal solubility diagram of the $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$-$C_4H_6O_5 \cdot NH_2C_2H_4OH$-$H_2O$ system.

the binary systems (Fig. 2, Table 1).

From them, sections I-IV were transferred from $C_4H_6O_5 \cdot NH_2C_2H_4OH$-$H_2O$ to $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$, sections V-X from $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$-$H_2O$ to $C_4H_6O_5 \cdot NH_2C_2H_4OH$ were studied.

Crystallization areas of ice, calcium chlorate two urea two molecules aqueous crystalline hydrate, and malic acid monoethanolamine were separated in the diagram. These areas meet at a single ternary point, where the crystallization temperature is -24.2ºC with 47.2 % H_2O, 41.2 % $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2 \cdot 2H_2O$, 11.6 % $C_4H_6O_5 \cdot NH_2C_2H_4OH$ and the solid phase composition is calcium chlorate two urea two molecules aqueous crystalline hydrate, malic acid is compatible with monoethanolamine and ice.

At temperatures from -15.0ºC to -24.2ºC, calcium chlorate urea two-molecule aqueous crystalline hydrate and ice co-crystallization, from -22.8ºC to -10.0ºC malic acid monoethanolamine and ice crystallization and in the range from -10.0ºC to 32.0ºC, areas of crystallisation of calcium chlorate two urea two molecules of aqueous crystalline hydrate and malic acid monoethanolamine were observed.

This system belongs to the simple eutonic type, and the components have preserved their individuality.

Based on the projections of the polythermal solubility diagram (Fig. 3), the isotherms were drawn at every 10ºC.

For the development and physical-chemical justification of the process of obtaining highly effective complex-acting defoliants, the dependence of the change in the physicochemical properties of the solutions on the number of components was studied in the "composition-property" diagram of the [55 % $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$ + 45 % H_2O]-$C_4H_6O_5 \cdot NH_2C_2H_4OH$ system. When the components were added in different proportions in the system, the pH, crystallization temperature, refractive index, viscosity and density of the solution changed (Table 2). Based on the obtained results, a "composition-property" diagram of the [55 % $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$ + 45 % H_2O]-

Table 1. Classification of secondary and tertiary points of the $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$-$C_4H_6O_5 \cdot NH_2C_2H_4OH$-$H_2O$ system.

Composition of the liquid phase, wt. %,			Crystallization temperature, T ºC	Solid phase
$Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$	$C_4H_6O_5 \cdot NH_2C_2H_4OH$ H_2O	H_2O		
46.0	-	54.0	-15.0	Ice + $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2 \cdot 2H_2O$
41.2	11.6	47.2	-24.2	Ice + $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2 \cdot 2H_2O$ + + $C_4H_6O_5 \cdot NH_2C_2H_4OH$
34.6	26.2	39.2	-22.8	Ice + $C_4H_6O_5 \cdot NH_2C_2H_4OH$
21.4	46.4	32.2	-21.2	
20.0	47.9	32.1	-21.0	
14.0	53.6	32.4	-20.8	
8.8	57.6	33.6	-20.4	
4.2	60.0	35.8	-20.2	
-	61.6	38.4	-20.0	
42.8	23.2	34.0	-10.0	$Ca(ClO_3)_2 \cdot 2CO(NH_2)_2 \cdot 2H_2O$ + + $C_4H_6O_5 \cdot NH_2C_2H_4OH$
43.2	28.0	28.8	-3.6	
43.4	34.0	22.6	4.0	
43.6	38.0	18.4	12.0	
43.8	44.8	11.4	18.0	
44.0	55.8	0.2	32	

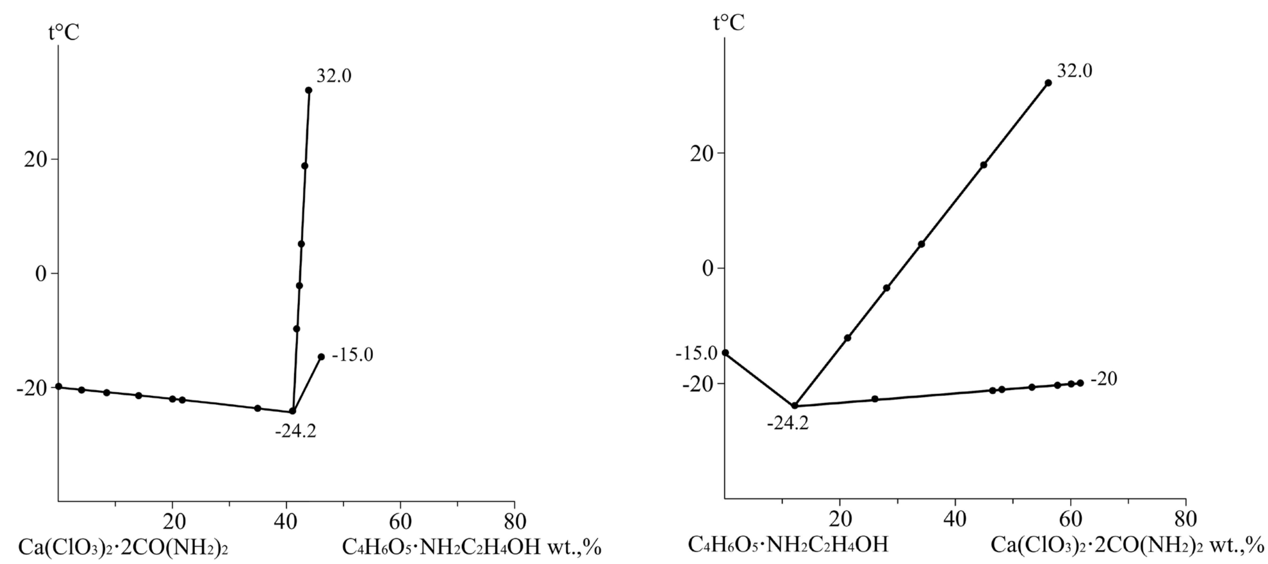

Fig. 3. Projections of $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$-$C_4H_6O_5 \cdot NH_2C_2H_4OH$-$H_2O$ polythermal system.

Table 2. Physical-chemical properties of [55 % $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$ + 45 % H_2O]-$C_4H_6O_5 \cdot NH_2C_2H_4OH$ system.

The composition of the components, %		pH	Crystallization temperature, T °C	Refractive index, n_D	Density, d, g mL^{-1}	Viscosity, η, mm^2 s^{-1}
55 % $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$+ + 45 % H_2O	$C_4H_6O_5 \cdot NH_2C_2H_4OH$					
100	-	7.48	-5	1.4080	1.328	1.482
94.88	5.12	7.24	-8	1.4142	1.332	1.926
89.67	10.33	6.98	-12	1.4181	1.336	2.374
85.08	14.92	6.64	-15	1.4208	1.338	2.726
80.16	19.84	6.28	-20	1.4253	1.340	2.982
75.99	24.01	5.93	-22	1.4287	1.342	3.206
69.93	30.07	5.71	-8	1.4308	1.351	4.294
64.86	35.14	5.52	25	1.4346	1.357	4.867
60.44	39.56	5.34	36	1.4427	1.361	5.254
54.94	45.06	4.97	52	1.4491	1.366	5.862
49.31	50.69	4.62	64	1.4521	1.373	6.312

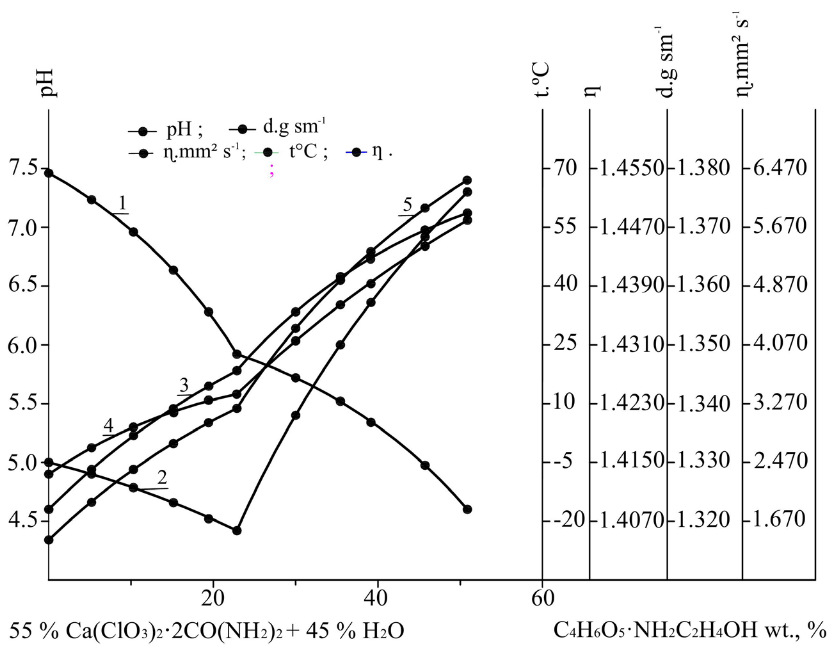

Fig. 4. Physical-chemical and rheological properties of [55 % $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$ + 45 % H_2O]-$C_4H_6O_5 \cdot NH_2C_2H_4OH$ system at 25ºC temperature:1- pH, 2 - crystallization temperature, 3 - refractive index, 4 - density, 5 - viscosity.

$C_4H_6O_5 \cdot NH_2C_2H_4OH$ system was constructed (Fig. 4).

From the diagram "composition-property" when malic acid monoethanolamine is added to a 55 % solution of calcium chlorate diurea, the crystallization temperature ranges from -5.0 to 64.0°C, the refractive index is 1.4080-1.4521 $\eta_{D,}$ the density from 1.328 to 1.373 g mL^{-1} and the viscosity increases from 1.482 to 6.312 $mm^2 s^{-1}$.

The pH value of the solution decreases from 7.48 to 4.62 as the amount of malic acid monoethanolamine increases. In the diagram above (Fig. 4), the "crystallization temperature" curve shows a clear separation into two phases.

The crystallization temperature of the system falls to -22.0ºC until the content of malic acid monoethanolamine in the content is 5.93 %, and this is the space of calcium chlorate dihydrate of diureas.

CONCLUSIONS

The polythermal solubility diagram of the $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$-$C_4H_6O_5 \cdot NH_2C_2H_4OH$-$H_2O$ system in the temperature range from -24.2°C to 32.0°C was constructed using three-component systems and internal sections.

The crystallization areas of ice, calcium chlorate dihydrate of diureas and malic acid monoethanolamine were delimited in the polythermal solubility diagram. It has been established that no new solid phases are formed in the system, and it belongs to a simple eutonic type.

In order to justify the physical-chemical process of obtaining defoliants with physiological activity, the [55 % $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$+45 % H_2O]-$C_4H_6O_5 \cdot NH_2C_2H_4OH$ section was studied, and the "composition-property" diagram was created.

The results obtained are the scientific basis for obtaining high-performance complex-acting defoliants based on calcium chlorate two carbamide and malic acid monoethanolamine.

Authors contributions*: O.O.: Research execution, data analysis, draft manuscript preparation; A.S.: Conceptualization, discussions, proofreading, supervision.*

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