ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 9, Issue 4 , April 2022

Study of the Polythermal Solubility of Components in the System $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$-$CH_2ClCOONa$-$H_2O$

K.A. Turaev, D.U. Kuyliyeva, A.A. Sidikov, Zh.S. Shukurov and A.S. Toghasharov

PhD doctoral student of The Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan
Junior researcher of The Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan
Chief researcher of The Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan,
Chief researcher of The Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan

ABSTRACT: The solubility of the $NaClO_3 \cdot CO(NH_2)_2$-$N(C_2H_4OH)_3 \cdot HNO_3$-$H_2O$ system from the freezing point (-44.2) to 60.0 °C was studied. A polythermal solubility diagram was constructed, on which the crystallization fields of ice, $NaClO_3 \cdot CO(NH_2)_2$, $CO(NH_2)_2$, and $N(C_2H_4OH)_3 \cdot HNO_3$, are demarcated. The system belongs to a simple eutonic type. The physicochemical properties of the system $[60\%NaClO_3 \cdot CO(NH_2)_2 + 40\%H_2O]$-$N(C_2H_4OH)_3 \cdot HNO_3$ were also studied and a "composition-properties" diagram was constructed based on the obtained data.

KEY WORDS: Solubility diagram, Calcium dicarbamidochlorate, Sodium monochloroacetate, Crystallization temperature, Compound.

I.INTRODUCTION

Currently, to obtain high yields of cotton with good qualities, calcium chlorate-containing, mildly and complex-acting defoliants with physiologically active substances are used [1-5]. One of the most promising, agrochemical and economically feasible ways to increase the efficiency of the applied defoliants, increase crop yields and improve the quality of agricultural products is the combined use of defoliants with ethylene producers and mineral fertilizers [6–10]. There is insufficient data in the literature to substantiate the physicochemical bases and technology for obtaining complex defoliants based on calcium chlorate containing physiologically active substances and nutrients.

In the synthesis of new effective defoliants, the use of sodium monochloroacetate, which is an intermediate for chemical production, is of considerable interest. It has defoliating and herbicidal activity [8].

For the physico-chemical substantiation of the processes of obtaining soft-acting defoliants, it is necessary to know the solubility of salts in systems including the studied components and the interaction of the initial components in a wide range of temperatures and concentrations [5].

Based on the foregoing, we studied the interaction of components in a water system with the participation of calcium dicarbamidochlorate and sodium monochloroacetate in a wide range of temperatures and concentrations by the visual-polythermal method.

II. SIGNIFICANCE OF THE SYSTEM

The article focuses on the study of the interaction of various salts in a multicomponent system by the visual polythermal method. The study of literature survey is presented in section III, Methodology is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and Conclusion.

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III. LITERATURE SURVEY

Kucharov X. et al [5] clarified the interaction of components in the system of sodium chlorate, triethanolamine and water. The system has been studied over a wide temperature range. It is established that the system belongs to a simple eutonic type.

Authors Hamdamova Sh.Sh. and Mirzaev N.A. [6] investigated the solubility of the magnesium chlorate-tetranolamine-water system using the visual-polythermal method at temperatures from -56.0 to 31.2 °C. The polythermic diagramme of solubility was built, on which bordered the fields of crystallization of an ice, sixteen, twelve and six-aqua magnesium chlorate, treethanolamin and new substances with the structure $MgOHClO_3 \cdot N(C_2H_4OH)_3 \cdot 2H_2O$ and $(C_2H_4OH)_3 \cdot HClO_3$ are established. The compounds were identified by chemical and physical chemical methods of analysis.

Khudoyberdiev F.I. [7] studied the solubility in the $NaClO_3 \cdot 3CO(NH_2)_2$-$N(C_2H_4OH)_3 \cdot C_4H_4N_2O_2$-$H_2O$ system by using a visual polythermal method. The solubility diagram of the system is constructed in the temperature range (-23.9) to 60 ºC in order to justify the conditions for the synthesis of a new compound based on the starting components.

IV. METHODOLOGY

The objects of study are sodium monochloroacetate and calcium dicarbamidochlorate. Sodium chloroacetate forms colorless crystals. Sodium chloroacetate is soluble in water, poorly soluble in methanol, insoluble in acetone, benzene, diethyl ether, carbon tetrachloride [11].
Calcium dicarbamide chlorate was obtained by the interaction of melting carbamide with calcium chlorate at a molar ratio of components 2:1 $2CO(NH_2)_2$:$Ca(ClO_3)_2$ [12].
For quantitative chemical analysis, conventional methods of analytical chemistry were used, in particular, the amount of chlorate ion was determined by volumetric permanganometric [13] and calcium by volumetric complexometric methods [14]. The content of elemental carbon and hydrogen was determined according to the method [15]. The concentrations of sodium monochloroacetate were determined by the photometric method [16]. The visual-polythermal method was used to study the solubility of the components [17-18]. Crystallization temperatures were determined using glass mercurial thermometers TP-6 with a measurement range of -30 to +60 °C and LT-15 with a measurement range of -100 to +20 °C. The pycnometric method was used to determine the density [19]. The viscosity of the solutions using a VTL viscometer, the pH of the solutions by FE20 METTLER TOLEDO pH meter and the refractive indices of the solutions using a digital refractometer (model PAL-BX/RI, ATAGO refractometer) were measured at a temperature of 20 °C [20]. The IR absorption spectra of the initial components and the studied compounds were recorded in the frequency range 4000 – 400 cm^{-1} on a FT-IR SHIMADZU MIRacle10 [21–24].

V. EXPERIMENTAL RESULTS

The binary system $H_2ClCOONa$-H_2O was studied in the temperature range from -29.0 °C to 70.0 °C. The polythermal solubility diagram is characterized by the presence of crystallization branches of ice and monochloroacetic acid sodium salt at a temperature of -29.0 °C and a concentration of 58.0% $CH_2ClCOONa$ and 42.0% H_2O [25].
The binary system $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$-$H_2O$ is characterized by crystallization branches of ice and calcium dicarbamide chlorate with a transition point at 15 °C, in which the concentration of $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$ is 46.1%. The results are in good agreement with the literature data [5, 26].
Solubility in the $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$- $CH_2ClCOONa$ - H_2O system was studied using eight internal incisions. Based on the results of studying the sides of the system and internal incisions, a complete polythermal diagram of the $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$ - $CH_2ClCOONa$ - H_2O system was constructed in the temperature range from -36.2 °C to 44.8 °C (Fig. 1).
On the polythermal solubility diagram of the $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$ - $CH_2ClCOONa$ - H_2O system, the fields of crystallization are delimited: ice, $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2 \cdot 2H_2O$, $C_2H_2ClO_2Na$ and as a new phase $(C_2H_2ClO_2)CaOH \cdot H_2O$.

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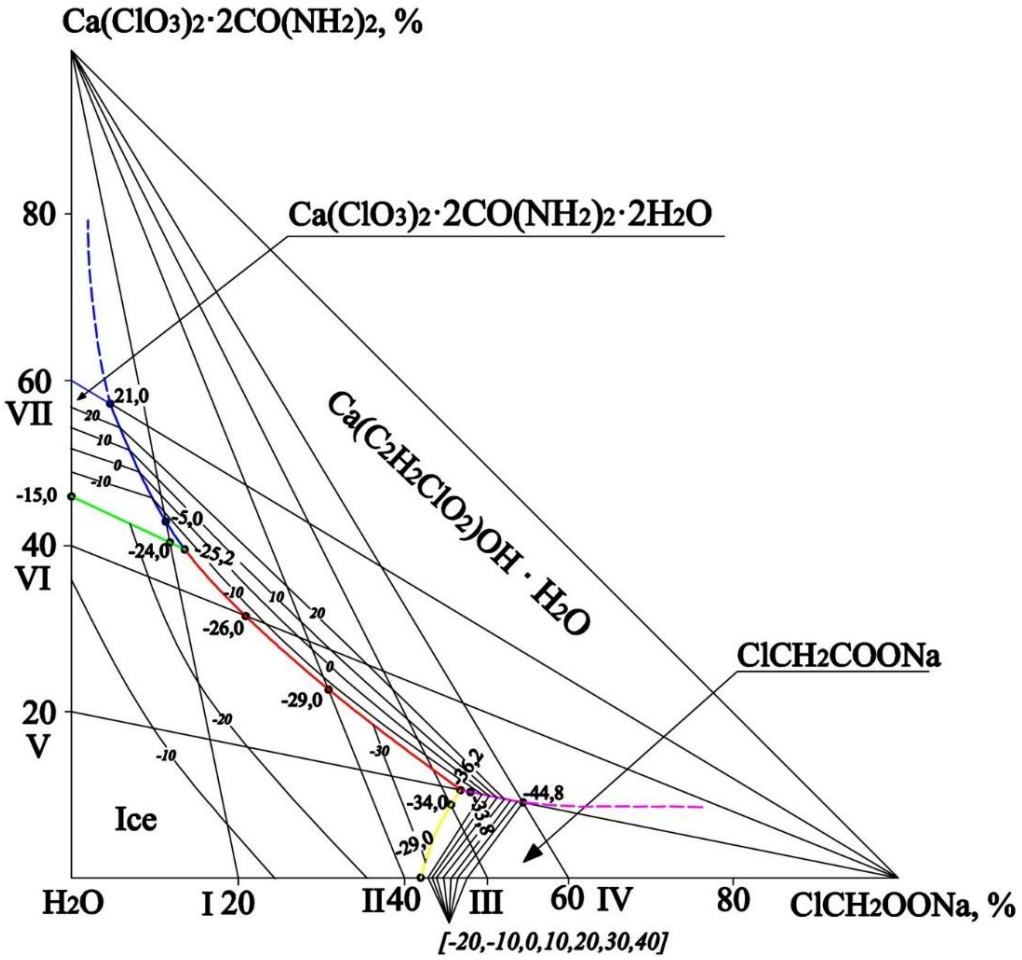

Fig. 1. Polythermal diagram of the solubility of the $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$- $CH_2ClCOONa$ - H_2O system.

The boundaries of the $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2 \cdot 2H_2O$, $(C_2H_2ClO_2)CaOH \cdot H_2O$ and $C_2H_2ClO_2Na$ crystallization fields adjacent to the ice crystallization region are highlighted in green, red, and yellow, respectively. The crystallization fields of $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2 \cdot 2H_2O$ and $(C_2H_2ClO_2)CaOH \cdot H_2O$ are bounded by a blue line, and $C_2H_2ClO_2Na$ and $(C_2H_2ClO_2)CaOH \cdot H_2O$ regions are bounded by a purple line. These fields converge at two triple nodal points of the system, for which the compositions of the equilibrium solution and the corresponding crystallization temperatures are determined (Table 1). Solubility isotherms at temperatures of -20, -10, 0, 10, 20, 30, 40 °C are plotted on the polythermal state diagram of the system.

The new phase was isolated in crystalline form and identified by chemical and physico-chemical analysis methods.

Table 1. Double and triple points of system $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$- $CH_2ClCOONa$ - H_2O.

Composition of the liquid phase (%)			T_c (°C)	Solid phase
$Ca(ClO_3)_2 \cdot 2CO(NH_2)_2$	$NaC_2H_2ClO_2$	H_2O		
46.0	-	53.0	-15.0	Ice +$Ca(ClO_3)_2 \cdot 2CO(NH_2)_2 \cdot 2H_2O$
43.0	11.6	45.4	-24.0	The same
42.3	15.0	42.8	-25.2	Ice + $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2 \cdot 2H_2O$ + $(C_2H_2ClO_2)CaOH \cdot H_2O$

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31.8	21.0	47.2	-26.0	Ice + $(C_2H_2ClO_2)CaOH{\cdot}H_2O$
21.0	32.0	47.0	-29.0	The same
11.6	44.2		-34.4	-//-
11.0	46.0	43.0	-36.2	Ice + $(C_2H_2ClO_2)CaOH{\cdot}H_2O$ + $NaC_2H_2ClO_2$
8.2	45.9	45.9	-34.0	Ice + $NaC_2H_2ClO_2$
-	41.8	58.2	-29.0	The same
45.0	11.2	43.8	-5.0	$Ca(ClO_3)_2{\cdot}2CO(NH_2)_2{\cdot}2H_2O$ + $(C_2H_2ClO_2)CaOH{\cdot}H_2O$
57.6	4.8	37.6	21.0	The same
10.4	47.8	41.8	-33.8	$(C_2H_2ClO_2)CaOH{\cdot}H_2O$ + $NaC_2H_2ClO_2$
9.8	54.2	36.0	44.8	The same

The chemical composition of the solid phase isolated from the assumed crystallization area $(C_2H_2ClO_2)CaOH{\cdot}H_2O$ corresponds to the following results:

Found (wt %): Ca^{2+}-23.66; Cl-20.82; H-2.96.

Anal. calcd. (wt %): Ca^{2+}-23.73; Cl-21.06; H-2.96.

The solubility of the obtained new substance in water (in%): 22.76 at 10°, 29.62 at 20°, 32.62 at 30°, 34.02 at 40° and 35.81 at 50°C. It is insoluble in organic solvents such as ethylene, toluene, benzene, acetone and chloroform.

Comparing the data of X-ray phase analysis of the initial compounds $CH_2ClCOONa$ and $(C_2H_2ClO_2)CaOH{\cdot}H_2O$, it can be noted that all reflections on diffraction patterns, as a rule, are characterized by their own reflection angles, a set of interplanar distances and diffraction line intensities (Fig. 2). This indicates the individuality of the crystal lattice $(C_2H_2ClO_2)CaOH{\cdot}H_2O$.

Fig. 2. X-ray phase analysis of monochloroacetic acid sodium (a) and double aqueous monochloroacetic hydroxycalcium (b).

According to IR-spectroscopic studies, it can be seen that the vibrations of $NaC_2H_2ClO_2$ and the new compound $(C_2H_2ClO_2)CaOH{\cdot}H_2O$ contain all the bands of stretching and bending vibrations inherent in them (Fig. 3).

The IR spectrum of $NaC_2H_2ClO_2$ is characterized by absorption bands at 667.4 and 763.81 cm^{-1} conditioned to antisymmetric and symmetric stretching vibrations of the C-Cl group. The bands at 929.69 cm^{-1} are caused by a non-planar, deformational vibrations of the OH-bond of the carboxyl group, and the stretching vibrations ν_{as}(C=O) and

ISSN: 2350-0328

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ν_s(C=O) of the carboxyl group are attributed to to absorption bands in the frequency range of 1593.20, 1396.46 and 1247.94 cm^{-1}.

The IR spectra of $(C_2H_2ClO_2)CaOH{\cdot}H_2O$ differ from the spectra of free monochloroacetic acid sodium salt by the presence of new absorption bands in the frequency range of 3363.86 and 3537.45 cm^{-1}. They are characteristic of asymmetric and symmetric to OH stretching vibration groups, in which it is related with the formation of a hydrogen bond in crystallized water.

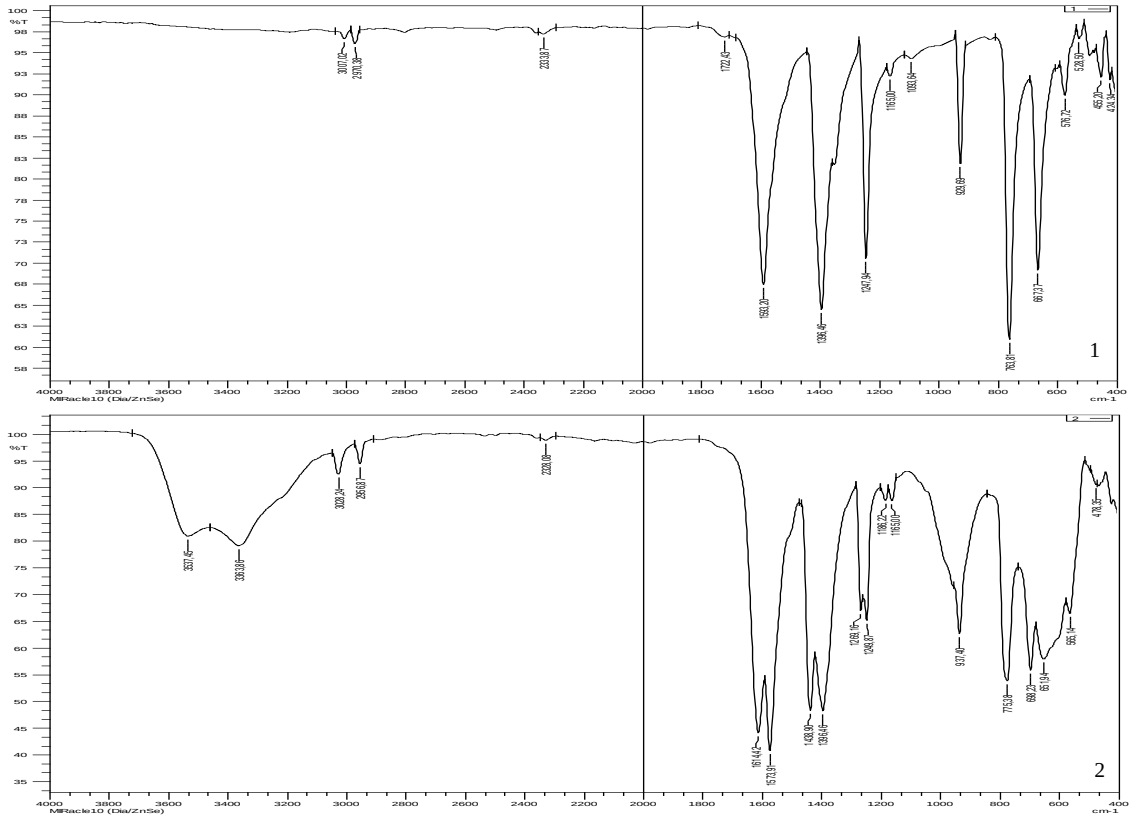

Fig. 3. IR spectra: monochloroacetic acid sodium (a) and double aqueous monochloroacetic hydroxycalcium (b).

In order to substantiate the process of obtaining an effective defoliant based on calcium dicarbamidochlorate and sodium salt monochloroacetic acid, the solubility and rheological properties of the components in the $[55\%Ca(ClO_3)_2{\cdot}CO(NH_2)_2{+}45\%H_2O]$-$C_2H_2ClONa$ system were studied, the results of which are shown in table 2.

Table 2. Physicochemical and rheological properties of the $[55\%Ca(ClO_3)_2{\cdot}CO(NH_2)_2{+}45\%H_2O]$-$C_2H_2ClONa$ system.

Components content, %		Cryst. temperature., t. °C	Density, d, g/cm^3	Viscosity, η.mm^2/s	pH	Refractive index, n	Solid phase
$55\%Ca(ClO_3)_2{\cdot}2CO(NH_2)_2{+}45\%H_2O$	$NaC_2H_2ClO_2$						
100	0	15.0	1.365	1.500	7.42	1.4088	$Ca(ClO_3)_2{\cdot}2CO(NH_2)_2{\cdot}2H_2O$
99.5	0.5	14.5	1.372	1.540	7.26	1.4096	The same
98.5	1.5	14.0	1.383	1.620	7.0	1.4110	-//-

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98.0	2.0	13.5	1.391	1.660	6.84	1.4122	-//-
96.0	4.0	12.0	1.398	1.800	6.4	1.4136	-//-
94.0	6.0	10.0	1.408	1.920	6.0	1.4154	-//-
92.5	7.8	8.0	1.415	1.960	5.68	1.4160	$Ca(ClO_3)_2 \cdot 2CO(NH_2)_2 \cdot 2H_2O$ + $(C_2H_2ClO_2)CaOH \cdot H_2O$
90.5	9.5	12.2	1.428	2.300	5.4	1.4192	$(C_2H_2ClO_2)CaOH \cdot H_2O$
88.5	11.5	15.2	1.439	2.620	5.16	1.4216	The same
86.5	13.5	17.8	1.449	2.900	4.98	1.4240	-//-
83.5	16.5	20.7	1.459	3.240	4.74	1.4268	-//-
81.1	18.9	22.8	1.466	3.440	4.56	1.4284	-//-

Based on the results of studying the physicochemical and rheological properties, a composition-properties diagram of the $[55\%Ca(ClO_3)_2 \cdot CO(NH_2)_2 + 45\%H_2O]$-$C_2H_2ClONa$ system was constructed (Fig. 4).

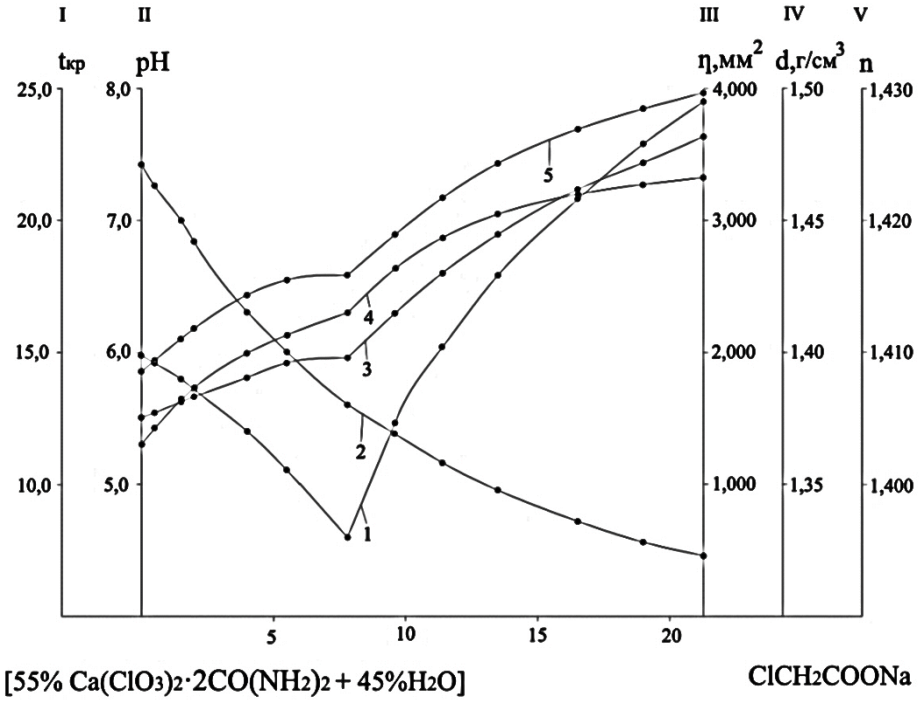

Fig. 4. The "composition-properties" diagram of the system $[55\%Ca(ClO_3)_2 \cdot CO(NH_2)_2 + 45\%H_2O]$-$C_2H_2ClONa$ at 20 °C, depending on the amount of addition of $H_2NC_2H_4OH \cdot HNO_3$. crystallization temperature (1) density (2); viscosity (3); pH of the medium (4); refractive index (5).

The results of the study show that when the sodium salt of monochloroacetic acid is added to a 55% saturated solution of calcium dicarbamidochlorate, the crystallization temperature initially decreases from 15.0 °C to 8.0 °C and then rises again to 22.8 °C, an eutectic point is formed when the concentration reaches 7.8%. At the eutectic point, $Ca(ClO_3)_2 \cdot 2CO(NH_2)_2 \cdot 2H_2O$ and $(C_2H_2ClO_2)CaOH \cdot H_2O$ crystallize together. Further addition of the sodium salt of

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monochloroacetic acid leads to increase temperature and changing indicators of composition and properties. This indicates that a new phase $(C_2H_2ClO_2)CaOH{\cdot}H_2O$ is formed in the system.
A further increase in the concentration of the sodium salt of monochloroacetic acid in the solution of the system leads to an increase in density from 1365 to 1466 g/cm^3, viscosity from 1500 to 3440 mm^2/s, refractive index from 1.4088 to 1.4284, and a decrease in the pH of the solution from 7.42 to 4.56 were observed with an increase in concentration to 7.8 %. A sharp change in all curves confirms the phase transition.

VI. CONCLUSION AND FUTURE WORK

The solubility of the components in the $Ca(ClO_3)_2{\cdot}CO(NH_2)_2$-$C_2H_2ClONa$-$H_2O$ system was studied for the first time by a visual polythermal method. The phase diagram demarcates the crystallization fields of the starting substances and the new compound $Ca(C_2H_2ClO_2)OH{\cdot}H_2O$. The formation of a new compound is confirmed by chemical and physical-chemical analysis methods. The results of the study of the composition-properties of the system $[55\%Ca(ClO_3)_2{\cdot}CO(NH_2)_2+45\%H_2O]$-$C_2H_2ClONa$ show that an effective defoliant can be obtained on the basis of calcium dicarbamidochlorate and sodium salt monochloroacetic acid.

REFERENCES

[1] Bobozhonov Z.S., Shukurov Z.S., Togasharov, A.S. *et al. Russ. J. Inorg. Chem.* **66,** 1031–1035 (2021). https://doi.org/10.1134/S0036023621070032
[2] Umarov A.A., Kutyanin L.I. New defoliants: search, properties, applications. M.: Chemistry. 2000.
[3] Shukurov Zh.S., Togasharov A.S., Askarova M.K., Tukhtaev S. Complex defoliants with physiologically active and insecticidal properties // Tashkent, ed. "Navruz", 2019, -136 p.
[4] Shukurov Z.S., Askarova M.K., Tukhtaev S. // Russ. J. Inorg. Chem. 2018. V. 63. № 2. P. 275. https://doi.org/10.1134/S0036023618020201
[5] Khamdamova Sh.Sh. [and etc.]. Univ. tech. sc.: elec. sc. j. 2019. No. 10(67). https://7universum.com/ru/tech/archive/item/7938
[6] Shukurov Z.S., Khusanov E.S., Mukhitdinova M.S. *et al. Russ. J. Inorg. Chem.* **66,** 902–908 (2021). https://doi.org/10.1134/S0036023621060176
[7] Sidikov A.A., Toghasharov A.S., Shukurov J.S. et al. Russ. J. Inorg. Chem. 66, 1554–1560 (2021). https://doi.org/10.1134/S003602362110017X
[8] Kodirova D.T., Abidova M.A. Univ. tech. sc.: elec. sc. j. 2019. No. 11 (68). https://7universum.com/ru/tech/archive/item/8127
[9] Miyassarov I.M. etc. (ESU) Ezh. scientific zhur. 2020, part 1. No. 6 (75) p. 60-64. doi:10.31618/ESU.2413-9335.2020.1.75.825
[10] Teshaev F., Khaitov B. J. Cott. R. and Dev. (CRDA). –India, 2015. -№1. pp. 57-60. http://www.crdaindia.com/past-issue.php
[11] Patent 2344118 C2 Russian Federation No. 2007104912. Appl. 02/08/2007; publ. 20.01.2009 Bull. The method of obtaining sodium salt of monochloroacetic acid / V.N. Anikeev, Yu.N. Zhukov, A.A. Lobanova and others. (Russia) Bulletin No. 2. - 2009.
[12] Khamdamova Sh. [i dr.]. Univ. tech. sc.: elec. sc. j. 2018. No. 10 (55). https://7universum.com/ru/tech/archive/item/6412
[13] Ts 00203855-43:2019. Defoliant "UzDEF". organization standard. -T .: Publishing house of standards, 2019. -12 p.
[14] A.L. Podkorytov, [i dr.]. Yekaterinburg Ural University Press - 2015, 19p. http://hdl.handle.net/10995/30960
[15] Klimova V.A. Basic micromethods for the analysis of organic compounds M.: Chemistry, 1975.-224 p.
[16] MU 4921-88 Guidelines for photometric measurement of the concentration of sodium monochloroacetate in the air of the working area.
[17] Trunin A.S. Petrova D.G. Visual-polythermal method / Kuibyshev Polytechnic. Inst. Kuibyshev.: 1977.
[18] E. A. Frolova [i dr.]. J. Inorg. Chem. 2021 T 66 No. 4 S. 531-533 DOI: 10.31857/S0044457X21040115
[19] Zdanovsky A.B. Gallurgia / L.: Chemistry, 1972.
[20] TO 34.15.051 Technical description and operating instructions.
[21] Nedoma I. Interpretation of X-ray powders. -M.: Metallurgy, 1975. -423 p.
[22] Zinyuk R.Yu., Balykov A.G., Gavrilenko I.B., Shevyakov A.M. IR spectroscopy in inorganic technology - L.: Chemistry, 1983. -160 p.
[23] Smith A. Applied IR spectroscopy. –M.: Mir, 1982. -319 p.
[24] Sapozhnikov Yu.E. [and etc.]. Bash. Chem. j. 2015. Volume 22. No. 1 pp. 40-43. https://cyberleninka.ru/article/n/issledovanie-termicheskoy-stabilnosti-natrievoy-soli-monohloruksusnoy-kisloty-1
[25] K.A. Turaev, A.S. Togasharov, S. Tukhtaev. "Improvement and implementation of innovative ideas in the field of chemistry and chemical technology" // Collection of reports and abstracts October 23-24, 2020 144-145 P.
[26] Khamdamova Sh.Sh. Izvestiya Universities. Applied chemistry and biotechnology. 2017;7(2):9-15. https://doi.org/10.21285/2227-2925-2017-7-2-9-15