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Study of solubility in systems chlorate-chloride of magnesium and ammonium salts of chloroethylphosphonic acid

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ABSTRACT: The influence of components in a complex system consisting of magnesium chlorate-chloride and ammonium salt of chloroethylphosphonic acid in a wide range of concentration and temperature from -39,3 to 34,9 ℃ was studied. A polythermal solubility diagram has been constructed. It has been established that the system belongs to a simple eutotic type, that is, the components of the system retain their individual properties.

KEYWORDS: cotton plant, system, solubility, polytherm, abscission, defoliant, ethylene, chlorate, phosphoric acid, composition, properties, preparation “Najot”.

I. INTRODUCTION

Cotton growing is one of the most important sectors of the national economy of the Republic of Uzbekistan. By now, the primary task of the technological process in cotton growing is mechanized harvesting, in the implementation of which the pre-harvest chemical deleafing of cotton with the help of defoliants plays an extremely important role. The existing range of defoliants used in the Republic today does not meet modern requirements for agriculture [1,2] Leaf fall, natural aging and maturation of cotton begins when the level of anti-auxin compounds such as ethylene and abscisic acid prevails over auxin compounds in the plant organism. In this regard, it seems more promising to use compounds capable of decomposing in plants with the formation of ethylene as defoliants and accelerators of cotton maturation. These ethylene producers include 2-chloroethylphosphonic acid and its derivatives [3] This work is a continuation of our systematic studies on the interaction of magnesium chlorate-chloride with the preparation “Najot” [4]. The presence in their composition of molecules of the ethylene -CH_2-CH_2- group exhibit retardant properties [5,6], increasing the content of ethylene in the zone of leaf fall [7]. Ammonium salts of 2-chloroethylphosphonic acid are part of the active ingredients of a number of plant growth and development stimulants, they are effective synergists for chlorate-containing defoliants, enhancing their defoliating activity [8].

II. MATERIALS AND METHODS.

The objects of study are magnesium chlorate chloride, ammonium and diammonium chloroethylphosphonates. To study the solubility of the system, the visual-polythermal method was used [9]. The amount of 2-chloroethylphosphonic acid was determined according to the method [10], amide nitrogen was determined by spectrophotometric method on FEK-56M (GOST 20851), elemental analysis for carbon, nitrogen, hydrogen was carried out according to [11] on the pH-meter FE20 METTLER TOLEDO, the refractive index on the refractometer IRF 454 model BM.

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III. RESULTS AND DISCUSSION.

Solubility in the system $[21\%ClCH_2CH_2PO(OH)_2*NH_3+11\%ClCH_2CH_2PO(OH)_2*2NH_3+12\%NH_4H_2PO_4+56\%H_2O]$–$\{55\%[79\%Mg(ClO_3)_2+21\%MgCl_2]+45\%H_2O\}$-$H_2O$ was studied by us by the visual-polythermal method in the temperature range from -39,3 to 34,9°C. On its polythermal solubility diagram, the fields of crystallization of ice, hexahydrate magnesium chlorate and chloride, and ammonium salts of chloroethylphosphonic acid are delimited (Fig.1).

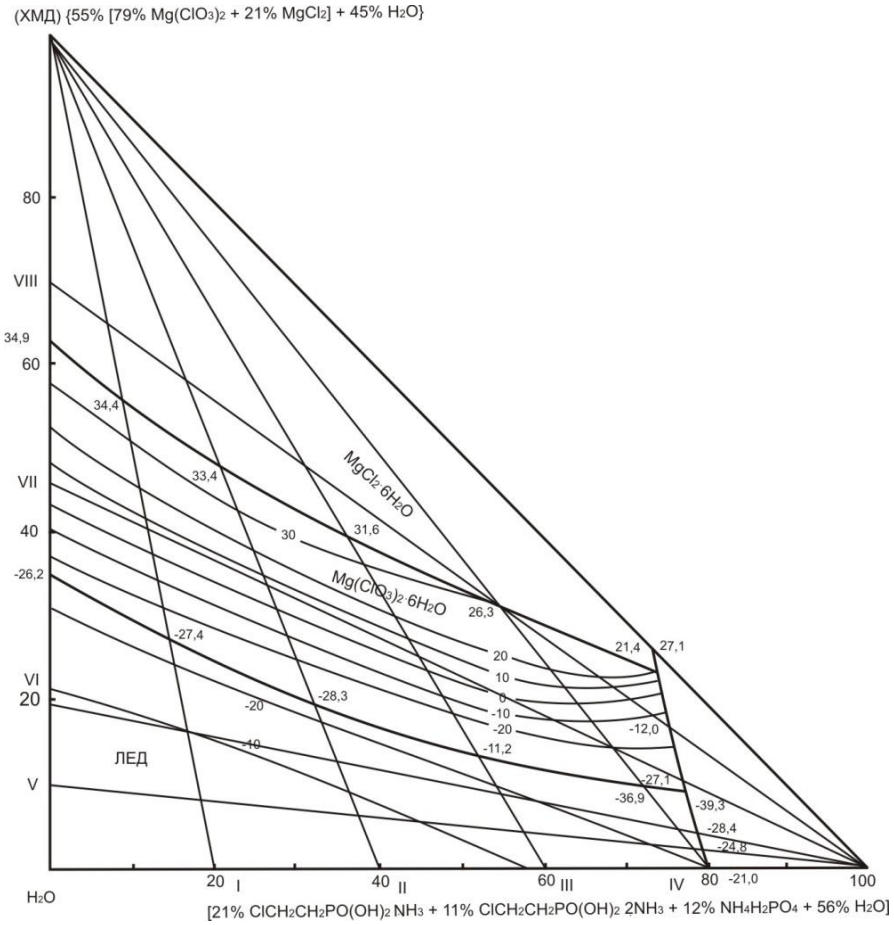

Fig.1. System solubility diagram

$[21\%ClCH_2CH_2PO(OH)_2*NH_3+11\%\ ClCH_2CH_2PO(OH)_2*2NH_3+12\%NH_4H_2PO_4+56\%H_2O]$–
$\{55\%[79\%Mg(ClO_3)_2+21\%MgCl_2]+45\%H_2O\}$–$H_2O$

Two triple points of the system are established, for which the crystallization temperatures and compositions of equilibrium solutions are determined (Table 1).

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Table 1.

Double and triple system nodes

[21%$ClCH_2CH_2PO(OH)_2$*NH_3+11%$ClCH_2CH_2PO(OH)_2$*2NH_3+12%$NH_4H_2PO_4$+56% H_2O]–{55% [79% $Mg(ClO_3)_2$+21%$MgCl_2$]+45% H_2O}–H_2O

Liquid phase composition, %			Crystallization temperature, ℃	solid phase
(Magnesium Chloride Chloride)	(Najot)	H_2O		
-	80,0	20,0	-21,0	Ice +“ Najot”.
2,0	79,6	18,4	-24,8	Ice +“Najot”.
4,2	79,0	16,8	-28,4	Same
9,2	77,8	13,0	-39,3	Ice+“Najot”+$Mg(ClO_3)_2$*$6H_2O$
10,6	77,0	12,4	-27,1	$Mg(ClO_3)_2$*$6H_2O$+ “Najot”
17,0	75,6	7,4	-12,0	$Mg(ClO_3)_2$*$6H_2O$+ “Najot”
23,4	74,0	2,6	21,4	$Mg(ClO_3)_2$*$6H_2O$+ $MgCl_2$*$6H_2O$+“Najot”
26,2	73,8	-	27,1	$MgCl_2$*$6H_2O$+“Najot”
35,6	-	64,4	-26,2	Ice+$Mg(ClO_3)_2$*$6H_2O$
27,4	14,5	58,1	-27,4	Ice +$Mg(ClO_3)_2$*$6H_2O$
20,0	31,8	48,2	-28,3	Ice +$Mg(ClO_3)_2$*$6H_2O$
13,8	51,4	34,8	-31,2	Ice +$Mg(ClO_3)_2$*$6H_2O$
10,2	71,5	18,3	-36,5	Ice +$Mg(ClO_3)_2$*$6H_2O$
63,0	-	37,0	34,9	$Mg(ClO_3)_2$*$6H_2O$+ $MgCl_2$*$6H_2O$
56,2	9,0	34,8	34,4	$Mg(ClO_3)_2$*$6H_2O$+ $MgCl_2$*$6H_2O$
48,0	21,0	31	33,4	$Mg(ClO_3)_2$*$6H_2O$+ $MgCl_2$*$6H_2O$
39,8	36,0	24,2	31,6	$Mg(ClO_3)_2$*$6H_2O$+ $MgCl_2$*$6H_2O$
31,6	54,3	14,1	26,3	$Mg(ClO_3)_2$*$6H_2O$+ $MgCl_2$*$6H_2O$

These fields converge at two triple nodal points, corresponding to: 9,2% magnesium chlorate-chloride, 77,8% Najot and 13% water at -39,3°C; 23,4% magnesium chlorate chloride, 74,0% Najot and 2,6% water at 21,4°C. On the polythermal solubility diagram, isotherms are plotted every 10°C. To refine the nodal triple points, the projections of the polythermal solubility curves onto the corresponding lateral sides of the system were constructed. In the temperature range (-21,0°C÷24,8°C), ice crystallizes from the equilibrium solution and [21%$ClCH_2CH_2PO(OH)_2$*NH_3 +11%$ClCH_2CH_2PO(OH)_2$*2NH_3 +12%$NH_4H_2PO_4$ + 56% H_2O] , and in the temperature range -27,1÷-12,0°C magnesium chlorate hexahydrate and [21%$ClCH_2CH_2PO(OH)_2$*NH_3+11%$ClCH_2CH_2PO(OH)_2$*2NH_3+12%$NH_4H_2PO_4$+56%H_2O]. Magnesium chloride hexahydrate and magnesium chlorate hexahydrate co-crystallize in the temperature range of 34,9 ÷ 26,3°C, ice and magnesium chlorate hexahydrate co-crystallize in the temperature range of -26,2 ÷ -36,5°C. In order to substantiate the process of obtaining an effective defoliant with physiological activity based on magnesium chlorate chloride and ammonium salts of chloroethylphosphonic acid, we studied the solubility and rheological properties of the components. As follows from the solubility diagrams of the systems, the initial components, both individually and in the joint presence, are highly soluble in water with the formation of concentrated solutions having crystallization temperatures below 20ºC. This indicates the possibility of obtaining, on the basis of liquid magnesium chlorate chloride and ammonium salts of chloroethylphosphonic acid, effective complex-acting liquid defoliants. Liquid magnesium chlorate defoliant is commercially produced in the domestic industry in accordance with TSH 88.16-29-2001 in the form of an aqueous solution containing 40,0-43,0% $Mg(ClO_3)_2$, not more than 10,0% $MgCl_2$ and 1,0% NaCl according to technology recommended by the French company Krebs. The average content of components in the resulting product is 35,0% magnesium chlorate, 9% magnesium chloride and 1,0% sodium chloride. With the introduction of ammonium salts of 2-chloroethylphosphonic acid into the liquid magnesium chlorate defoliant, a decrease in the crystallization temperature of solutions from 11 to 8,0 °C is observed, then with an increase in the concentration of ammonium salts of chloroethylphosphonic acid, a sharp increase in the crystallization temperature is observed from 8,0 to 26,0°C . The viscosity and density of the newly formed solutions practically do not change, and is in the range of 4,785-5,466 mm2/s and 1,446-1,470 g/cm^3. The pH of the solution medium decreases sharply with an increase in the concentration of ammonium salts of chloroethylphosphonic acid.

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Table 2

Physico-chemical properties of the system {55%[79%$Mg(ClO_3)_2$+21% $MgCl_2$]+45%H_2O}-[21%$ClCH_2CH_2PO(OH)_2$*NH_3+11%$ClCH_2CH_2PO(OH)_2$ *2NH_3 +12%$NH_4H_2PO_4$ +56% H_2O]-H_2O

Liquid phase composition, %		Crystallization temperature, ℃	Viscosity, mm^2/s	Density, g/cm^3	Index refraction	pH
Liquid 55 % KHMD,%	[21%$ClCH_2CH_2PO(OH)_2$*NH_3+11%Cl $CH_2CH_2PO(OH_2$*2NH_3+12%$NH_4H_2PO_4$ +56%H_2O], %					
55,0	-	11,0	4,785	1,4700	1,4203	5,81
54,5	0,5	10,0	4,729	1,4704	1,4198	4,06
54,4	0,6	9,2	4,6834	1,4720	1,4199	3,72
54,25	0,75	9,5	4,5982	1,4710	1,4202	3,08
54,0	1,0	9,0	4,7107	1,4708	1,4200	2,70
53,5	1,5	8,5	4,8421	1,4704	1,4199	2,15
53,0	2,0	8,0	4,8983	1,4698	1,4197	2,03
49,0	6,0	12,0	4,4981	1,4587	1,4184	1,23
43,0	12,0	26,0	5,4668	1,4468	1,4169	1,02

With an increase in the concentration of [21%$ClCH_2CH_2PO(OH)_2$*NH_3+11%$ClCH_2CH_2PO(OH)_2$*2NH_3+12%$NH_4H_2PO_4$+56%H_2O] in the system, fluctuations in density, viscosity, crystallization temperature, refractive index, and a decrease in solution pH were observed. A noticeable change in all curves confirms the phase transition.

IV. CONCLUSION

Thus, from the results of the study, it was established that the components of the system, both individually and in the joint presence, are highly soluble in water with the formation of concentrated solutions with a low crystallization temperature. This shows the possibility of obtaining liquid stimulants for leaf fall, maturation and opening of cotton bolls and defoliants based on them.

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