



SOLUBILITY POLYTHERM OF THE SYSTEM: GUANIDINE CARBONATE -2-CHLOROETHYL PHOSPHONIC ACID - WATER

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ABSTRACT: The mutual solubility in the heterogeneous system 2 - chloroethylphosphonic acid - guanidine carbonate - water was studied visually – by polythermic method, and a polythermic solubility diagram of the system was constructed. The fields of formation of guanidine chloroethylphosphonate are delimited. On the basis of the data of chemical and physico - chemical methods of analysis, the selected compound was proposed a structural formula.

KEYWORDS: polythermic diagram, guanidine carbonate, 2-chloroethylphosphonic acid, visual- polythermic method, defoliant.

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INTRODUCTION

Among the existing assortment of defoliants used in cotton production, magnesium chlorate and 2-chloroethyl phosphonic acid (2-CEPA) are the most accessible from the point of view of production and ease of use. However, they are used in large doses and have desiccating properties [1,2]. Promising is the improvement and expansion of their assortment. In this aspect, of particular interest is the development of defoliants based on magnesium chlorate, 2-CEPA and auxin antagonists - salts of guanidine and its derivatives, the presence of the latter in the composition of the defolating mixture significantly enhances their activity, reduces the consumption rate, the “hardness” of influence of the main preparations on the leaves of the plant and prevents the second growth of cotton leaves, which is important for high-quality mechanized harvesting of raw cotton [3,4].

PURPOSE OF THE RESEARCH

In available scientific literature [5], there is no information on solubility and interaction in the aquatic environment of the carbonate salt of guanidine and 2 - CEPA. The study of the mutual dissolution of these components represent a certain theoretical and practical interest. Since it allows to know the

chemistry of the interaction of the reacting components, to judge their stability in the technological process, to find out the optimal parameters for obtaining the target product based on these compounds.

MATERIALS AND METHODS OF THE RESEARCH

The study of the phase equilibria of a three - component system was carried out by visual - polythermal method [6].

The construction of polythermic solubility diagrams of the studied system was carried out by us in the form of a right-angled triangle. The isotherms are plotted on the polythermic diagram every 10°C. Determination of the composition and crystallization temperatures of nodal nonvariant points was carried out by constructing a projection of polythermal solubility curves on the corresponding lateral water sides of the system. The concentration of the solutions is expressed in mass percent.

2 - CEPA and guanidine carbonate of the “p” and “pfa” qualifications were used in carrying out the research.

THE RESULTS AND THEIR DISCUSSION

In the system of guanidine carbonate $\text{NH}_2\text{CNHNH}_2 \cdot \text{H}_2\text{CO}_3$, 2-CEPA $\text{ClCH}_2\text{CH}_2\text{PO}(\text{OH})_2$ and water the solubility was studied in the temperature range from - 52.8 to +70°C (table 1).

Table 1

Double and triple points of the system
2 - chloroethylphosphonic acid - guanidine carbonate – water

Liquid phase composition, wt. %			Crystallization temperature, °C	Solid phase
$\text{ClCH}_2\text{CH}_2\text{PO}(\text{OH})_2$	$[\text{NH}_2\text{CNHNH}_2]_2 \cdot \text{H}_2\text{CO}_3$	H_2O		
1	2	3	4	5
50,5	-	49,6	-47,0	Ice + $\text{ClCH}_2\text{CH}_2\text{PO}(\text{OH})_2$
43,3	15,8	40,9	-51,6	Same
45,9	10,8	43,3	-49,9	Same
-	24,0	76,0	-4,6	Ice + $[\text{NH}_2\text{CNHNH}_2]_2 \cdot \text{H}_2\text{CO}_3$
7,0	30,0	63,0	-7,5	Same
15,8	21,2	63,0	-7,6	Ice + $\text{NH}_2\text{CNHNH}_2 \cdot \text{H}_2\text{CO}_3$ $\text{ClCH}_2\text{CH}_2\text{PO}(\text{OH})_2$
31,1	19,3	49,6	-22,4	Same
10,6	25,0	64,4	-7,0	Same
32,2	19,2	48,6	-23,8	Same
13,2	35,3	51,7	12,0	Ice + $\text{NH}_2\text{CNHNH}_2 \cdot \text{H}_2\text{CO}_3$ $\text{ClCH}_2\text{CH}_2\text{PO}(\text{OH})_2$ $[\text{NH}_2\text{CNHNH}_2]_2 \cdot \text{H}_2\text{CO}_3$
24,1	39,6	36,3	39,6	Same
32,8	41,0	26,2	49,2	$\text{NH}_2\text{CNHNH}_2 \cdot \text{H}_2\text{CO}_3$ $\text{ClCH}_2\text{CH}_2\text{PO}(\text{OH})_2$ $[\text{NH}_2\text{CNHNH}_2]_2 \cdot \text{H}_2\text{CO}_3$
40,4	42,0	17,6	56,0	Same
48,3	42,8	8,9	61,8	Same
56,5	43,2	0,3	67,0	Same

45,6	18,3	36,1	-31,8	$ClCH_2CH_2PO(OH)_2^*$ $NH_2CNHNNH_2^*$ $ClCH_2CH_2PO(OH)_2$
57,2	17,9	24,9	3,2	Same
76,0	17,6	12,4	33,2	Same
82,7	17,2	0,1	46,2	Same
42,0	18,4	39,6	-52,8	Ice+ $ClCH_2CH_2PO(OH)_2$ + $NH_2CNHNNH_2^*$ $ClCH_2CH_2PO(OH)_2$
9,2	32,0	58,8	-8,9	Ice+ $NH_2CNHNNH_2^*$ $ClCH_2CH_2PO(OH)_2$ + $[NH_2CNHNNH_2]_2^*H_2CO_3$

On the constructed polythermic solubility diagram (Fig. 1), the field of crystallization of ice, 2 – CEPA, guanidine carbonate and the new compound $ClCH_2CH_2PO(OH)_2 \cdot NH_2CNHNNH_2$ are delimited, for which the temperature and concentration limits of existence have been determined. The fields converge at two nodal points corresponding to the crystallization of three different solid phases.

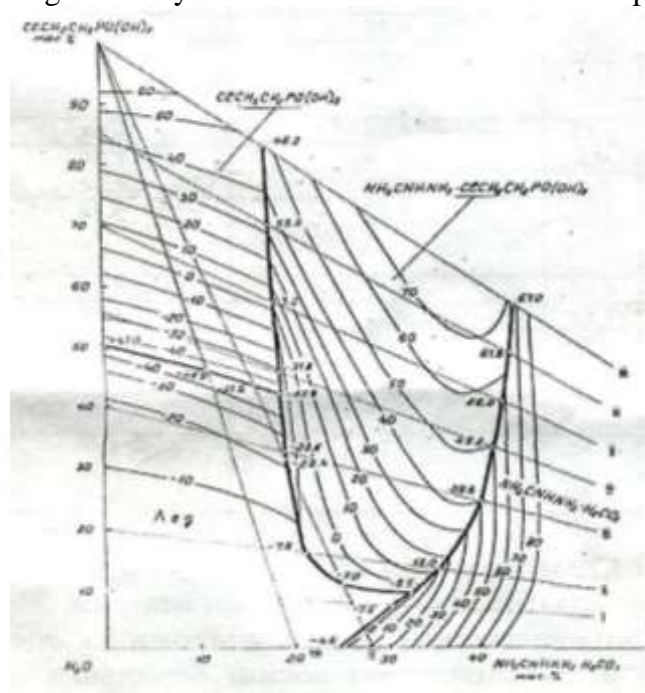


Figure 1: Solubility diagram of the system
 $ClCH_2CH_2PO(OH)_2 - [NH_2CNHNNH_2]_2 \cdot H_2CO_3 - H_2O$

An analysis of the solubility diagram showed that the detected 2 – CEPA compounds with guanidine are congruently soluble in water, since the crystallization rays of 2 - guanidine chloroethylphosphonate, connecting the poles of the compounds to the beginning of coordinates cross its crystallization fields in a wide temperature range.

The compounds were isolated in crystalline form and identified by the results of X-ray phase and chemical methods of analysis.

By X-ray phase analysis, it was found that for the $ClCH_2CH_2PO(OH)_2 \cdot NH_2CNHNNH_2$ compound, the following set of diffractolines with interplanar spacing (d) are characteristic:

11,28, 7,34, 4,91, 4,69, 4,61, 3,86, 3,75, 3,67, 3,52, 3,44,

3,17, 3,08, 3,01, 2,84, 2,72, 2,60, 2,51, 2,46, 2,42, 2,34,
2,26, 2,21, 2,10, 2,06, 2,02, 1,95, 1,89, 1,86, 1,80, 1,78 Å⁰.

This indicates that the isolated compound is individual and does not contain admixture of the initial components.

Chemical analysis of the isolated compound from its intended crystallization region gave the following results, in wt. %:

Found: $ClCH_2CH_2PO(OH)_2$ – 70,98; NH_2CNHNH_2 – 29,02.

Calculated: $ClCH_2CH_2PO(OH)_2$ – 71,01; NH_2CNHNH_2 – 28,99.

To clarify the nature of the relationship between the components, an IR spectroscopic study of the isolated compound was carried out. In the IR spectrum of guanidine 2-chloroethylphosphonate, intense absorption bands disappear in the region of 1590, 1400 cm⁻¹, assigned respectively to the valence vibrations of $\nu(C = N)$ and the deformation vibrations $\delta(C = O)$ of guanidine.

This circumstance indicates that protonation proceeds precisely in this group due to which delocalization of the electron density of C = N double bond occurs. In addition, in the spectrum of the compound, the moderate absorption band in the region of 3000-3400 cm⁻¹ is shifted by 90-60 cm⁻¹ to the higher frequency region, which indicates the appearance of a signal of the free OH - group of the chloroethylphosphonic complex, the absorption band $\nu(NH_2)$ was found in the region of frequencies 3480 and 3390 cm⁻¹ [7].

Based on abovementioned for guanidine 2-chloroethylphosphonate, the following formula can be assumed:



CONCLUSIONS

As a result of the conducted research, it was established that in 2- CEPA – guanidine carbonate – water system, formation of the compound with the composition $ClCH_2CH_2PO(OH)_2 \cdot NH_2CNHNH_2$ occurs, for which the concentration and temperature limits of formation has been determined. The compound was isolated in crystalline form and identified by X-ray phase and chemical methods of analysis. The obtained data can be used to develop highly effective and mildly influencing cotton defoliant.

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