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Polytherm of Solubility System K₂SO₄ –CH₃COOH•H₂NC₂H₄OH–H₂O

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ABSTRACT.The solubility polytherm for the K_2SO_4 -CH₃COOH•H₂NC₂H₄OH-H₂O system was studied using eight internal sections. On the basis of the solubility polytherm of binary systems and internal sections, a polythermal diagram of the solubility of this system is constructed. It was found that the system belongs to a simple eutonictype, the components of the system in the studied intervals retain their individuality and physiological activity.

KEYWORDS.Physiologically active substances, binary system, liquid fertilizers, potassium sulfate, monoethanol ammonium mono-acetic acid mono-ethanol.

I. INTRODUCTION

Liquid fertilizers have a number of advantages over solid fertilizers. They do not generate dust, do not cake, are characterized by free fluidity, and unfavorable climatic conditions do not significantly affect their quality indicators. Together with liquid fertilizers, it is possible to effectively use trace elements, herbicides and insecticides, which are introduced directly into solutions. Liquid fertilizers are equivalent to solid fertilizers in terms of their agrochemical efficiency. They provide the possibility of complete mechanization of all application processes during soil cultivation (plowing, cultivation and other methods). At the same time, their production is much simpler and cheaper, since energy-intensive stages of evaporation, drying and granulation are excluded [1-3]. For normal growth, development and creation of high yields of plants, along with nitrogen-phosphorus fertilizers, potash fertilizers are needed, which contribute to the normal course of vital processes in the plant organism. The lack of mobile forms of potassium in the soil will reduce the yield and impair the assimilation of nitrogen and phosphorus fertilizers [4]. Among the chlorinefree forms of potash fertilizers, potassium sulfate, which feeds plants with potassium and sulfur, has the greatest prospects for production and use. Potassium sulfate is a valuable chlorine-free fertilizer. Potassium sulfate has a much more effective effect on the size of the crop and its quality if it is used in combination with nitrogen and phosphorus fertilizers. After the use of potassium sulfate in the grown fruits, vegetables and berries, the content of sugars and vitamins increases noticeably, the resistance of plants to various diseases increases, and the percentage of damage to finished products by heart and gray rot decreases. Potassium sulfate as a fertilizer must be used to provide perennial plants with a successful winter. By feeding fruit trees and shrubs with potassium sulfate in autumn, one can expect that they will survive even the most severe frosts with insignificant losses [5]. One promising, agrochemically and economically feasible way to increase the efficiency of mineral fertilizers, increase crop yields and improve the quality of agricultural products is the combined use of physiologically active substances with basic mineral fertilizers. The introduction of physiologically active substances increases the efficiency (efficiency) of the applied mineral fertilizers. Physiologically active substances are plant growth regulators capable of causing various changes in the process of plant growth and development in small quantities. They are strong biostimulants, i.e. increase immunity, rooting of cuttings, increase germination and accelerate seed germination, reduce the negative impact of adverse external factors such as cold weather or drought, stimulate the formation of ovaries, accelerate fruit ripening, stimulate flowering [6]. To obtain high yields with good qualities, physiologically active substances (auxins, kinins, gibbelens, succinic acid, monoethanolamine, thiocarbamide, and others) are widely used today. One of them is monoethanolammonium monoacetic acid monoethanolammonium (MEA), which is physiologically active substances. Monoethanolamine and its derivatives in the composition of drugs enhance the effect of active components, while eliminating the negative effect of drugs on plants [7, 8]. It has been established that monoethanolamine interacts with acetic acid to form monoethanolammonium mono-acetic acid [7, 8]. For the physicochemical substantiation of the process of obtaining liquid fertilizers with physiologically active substances, it is necessary, first of all, to know the solubility of salts in



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systems that include the components under study and the interaction of the initial components in a wide range of temperatures and concentrations.

II. SIGNIFICANCE OF THE SYSTEM

The solubility polytherm for the K_2SO_4 -CH₃COOH•H₂NC₂H₄OH-H₂O system was studied using eight internal sections. 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.

III. METHODOLOGY

For the study, potassium sulfate recrystallized from an aqueous solution, mono-substituted monoethanolammonium acetic acid synthesized on the basis of acetic acid and monoethanolamine taken in a molar ratio of 1:1 [8, 9] were used as starting components. The study of phase equilibria in physicochemical systems was carried out by the visual-polythermal solubility method [10]. The essence of the visual-polythermal method is to visually observe the temperature of the appearance of the first crystals with uniform cooling or the disappearance of the last crystals with slow heating and continuous stirring of solutions. The instrument for determining the solubility is a test tube closed with a stopper through which a platinum or glass stirrer passes, as well as a thermometer with a graduation of 0,10 C. For uniform cooling, the test tube is placed in an outer test tube - a sleeve, which is in the cooling mixture. Heating is also carried out through a sleeve. Cooling is carried out in Dewar vessels with liquid nitrogen or dry ice

IV. EXPERIMENTAL RESULTS

In this regard, in order to substantiate the process of obtaining a liquid fertilizer with physiological activity, we studied the mutual influence of the components in the K_2SO_4 -CH₃COOH • H₂NC₂H₄OH-H₂O system by a visual – polythermal research method. The binary system K_2SO_4 - H₂O was studied by us in the temperature range from -1.8 °C to 30°C.On the solubility diagram, the branches of crystallization are revealed: ice, potassium sulfate monohydrate and anhydrous potassium sulfates.That is, the data obtained by us are in good agreement with the literature [9] (Fig. 1).



Fig. 1.Solubility diagram of the potassium sulfate - water binary system.

By studying the binary system $CH_3COOH \cdot H_2NC_2H_4OH-H_2O$ from the freezing point of -50,3 to 10°C, it was found that the crystallization fields of ice, acetic acid and monoethanolammonium acetic acid are distinguished on the solubility diagram. The first eutectic point of the system corresponds to 55,8% $CH_3COOH \cdot$ at a temperature of -50,3°C, the second eutectic point is 78% $CH_3COOH \cdot H_2NC_2H_4OH$, at a temperature of -26,1°C and that is in good agreement with the data given in [8](fig. 2)



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Fig. 2.Diagram of the solubility of the binary system monoethanolammonium acetic acid - water

The solubility polytherm of the system potassium sulfate - monoethanolammonium mono-acetic acid - water was investigated from the freezing point of -60,0 to 10,0 °C using eight internal sections. Sections I through III are drawn from the K_2SO_4 -H₂O side to the top at CH₃COOH•NH₂C₂H₄OH, and from IV to VIII — from the CH₃COOH•NH₂C₂H₄OH-H₂O side to the K₂SO₄ top (Fig. 3). The diagram of the solubility of the system is characterized by the presence of fields of crystallization of ice, aqueous potassium sulfate, and potassium sulfate, acetic acid, monoethanolammonium mono-acetic acid mono-substituted monoethanol.



Figure:3. Polytherm of solubility of the system potassium sulfate - mono-acetic acid monoethanolammonium - water.

It follows from the solubility diagram of this system that it belongs to the simple eutonic type. The indicated fields converge at two triple points of the studied system. The compositions and crystallization temperatures of the double and triple points of the system are shown in Table 1.

 Table 1. Double and triple nodal points of the system of potassium sulfate - monoethanolammonium acetic acid - water.

Liquid phase composition, wt%			Tom Chris	
CH ₃ COOH·NH ₂	K-SO	H.O	°C	Solid phases
C ₂ H ₄ OH	R ₂ 50 ₄	1120	C	
—	6,5	93,5	-1,6	Ice $+K_2SO_4 \cdot H_2O$
9,6	5,2	85,2	-11,0	Also
19,7	4,0	76,3	-34,0	////
28,0	3,6	68,4	-38,0	////



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35,0	3,3	61,4	-40,0	$Ice+ K_2SO_4 \cdot H_2O + K_2SO_4$
_	8,4	91,6	9,7	$K_2SO_4 \cdot H_2O + K_2SO_4$
9,2	8,2	82,6	-3,2	Also
19,4	5,6	75	-20,0	////
28,3	4,4	67,3	-30,4	////
55,8		44,2	-50,3	$Ice + CH_3COOH$
55,1	1,2	43,7	-52,5	Also
54,0	2,4	43,6	-55,1	Ice+CH ₃ COOH+ K ₂ SO ₄
48,8	2,7	48,5	-50,4	$Ice + K_2SO_4$
58,9	1,9	39,2	-30,0	$CH_3COOH + K_2SO_4$
78,0	_	22,0	-26,1	CH ₃ COOH+ CH ₃ COOH·NH ₂ C ₂ H ₄ OH
77,6	0,8	21,6	-26,8	Also
77,4	1,2	21,4	-27,2	$CH_{3}COOH+CH_{3}COOH\cdot NH_{2}C_{2}H_{4}OH+K_{2}SO_{4}$

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On the basis of the data of polythermal sections, by means of interpolation, the isotherms of the solubility of the system were drawn every 10 °C. The projections of the polytherm of the system onto the lateral sides of K_2SO_4 - H_2O and $CH_3COOH \cdot NH_2C_2H_4OH - H_2O$ were constructed. According to the data presented, no new chemical compounds are formed in the studied system. In the system, there is a mutual salting-out effect of the components on each other. As the results of studying the system at different temperatures show, the salting-out effect of monoethanolammonium acetic acid on potassium sulfate increases with increasing temperature, while the latter on monoethanolammonium mono-acetic acid has a large salting-out effect on potassium sulfate. From the results of studying the K_2SO_4 - $CH_3COOH \cdot NH_2C_2H_4OH$ - H_2O system, it follows that in the joint presence of the initial components, the formation of their concentrated solutions with a low crystallization temperature is observed. This indicates the possibility of obtaining liquid fertilizers based on initial components at relatively low temperature conditions.

V. CONCLUSION AND FUTURE WORK

Thus, it was found that in the studied temperature and concentration range, the components of the system in the studied temperature and concentration range retain their individuality, and, consequently, their physiological activity. The results indicate the possibility of joint use of monoethanolammonium mono-acetic acid with potassium sulfate to obtain a fertilizer with physiological activity

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