Western European Journal of Modern Experiments and Scientific Methods
Volume 1, Issue 3, November, 2023
https://westerneuropeanstudies.com/index.php/1
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STUDY OF SOLUBILITY OF SYSTEMS: POTASSIUM SALT- MONOSUBSTITUTED ACETIC ACID ETHANOLAMMONIUM-WATER.

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Abstract: The solubility polymeter in the system K_2SO_4–$CH_3COOH \cdot H_2NC_2H_4OH$–$H_2O$ was studied using eight internal sections. A diagram was constructed based on the solubility polymeter of binary systems and eight internal sections. The mutual influence of components in the system $CH_3COOH \cdot H_2NC_2H_4OH$–KCI–$H_2O$, studied by the method of isomolar series, revealed branches of the existence of initial components and new chemical compounds on the temperature crystallization isotherms, viscosity, density, and pH of the medium.
The studied system belongs to the simple eutonic type with the preservation of the individuality of the constituent components.

Keywords: Physiologically active substances, binary system, liquid fertilizers, potassium sulfate, potassium chloride, monosubstituted acetic acid ethanolamine.

The growth of the world population leads to an increase in demand for basic food products, while at the same time, the resource of free global arable land per capita is decreasing, which necessitates the intensification of agriculture, the development, and implementation of new technologies. As a result, the needs of agricultural producers for mineral fertilizers are growing, and their qualitative characteristics are changing [1].

Liquid fertilizers have several advantages over solid ones. They do not dust or clump, have free-flowing properties, and adverse weather conditions do not significantly affect their quality. Microelements, herbicides, and insecticides can be effectively applied together with liquid fertilizers, as they are introduced directly into the solutions. Liquid fertilizers are equivalent to solid ones in their agrochemical effectiveness. They provide the possibility of fully mechanizing all processes of soil application (plowing, cultivation, and other methods). At the same time, their production is significantly simpler and cheaper, as energy-intensive stages of evaporation, drying, and granulation are excluded [2-4].

In addition to nitrogen-phosphorus fertilizers, potassium fertilizers are necessary for normal plant growth, development, and high yields, promoting the normal flow of vital processes in the plant organism. A lack of mobile forms of potassium in the soil will reduce crop yields and worsen the absorption of nitrogen and phosphorus fertilizers [5].

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Among the non-chlorine forms of potassium fertilizers, potassium sulfate has the greatest prospects for production and use, nourishing plants with potassium and sulfur. Potassium sulfate is a valuable non-chlorine fertilizer. The use of potassium sulfate in combination with nitrogen and phosphorus fertilizers has a much more effective impact on the yield and its quality. After the application of potassium sulfate, the content of sugars and vitamins in cultivated fruits, vegetables, and berries noticeably increases, the resistance of plants to various diseases increases, and the percentage of core and sulfur rot in the finished product decreases. The use of potassium sulfate as a fertilizer has the advantage of ensuring a successful wintering of perennial plants. By fertilizing fruit and berry trees and bushes with potassium sulfate in the fall, it is possible to expect that they will survive even the strongest frosts with minimal losses [6].

Potassium chloride is one of the most popular primary fertilizers in private households. This is due to its availability and quick migration in the soil compared to other potassium fertilizers, allowing for timely feeding of annuals during the season with potassium chloride. However, the same quick migration and the presence of chloride ions, which are contraindicated for many garden crops, require careful use of potassium chloride. Potassium chloride can be used to feed plants that do not tolerate chloride, such as potatoes, carrots, pumpkins, and others, as long as you know how and when to use it. At the same time, potassium chloride is used as a source of potassium in most industrially produced complex fertilizers, which contain up to 47% chloride [7].

As it is known, the utilization coefficient of nutrients by plants for phosphorus does not exceed 15-20%, for nitrogen and potassium - 40-50%. One of the ways to increase the yield of agricultural crops and the efficiency of fertilizers is to introduce physiologically active substances into their composition [7,8].

One of the promising and agrochemical and economically feasible ways to increase the efficiency of mineral fertilizers, increase the yield of agricultural crops 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 contributes to an increase in the efficiency of the applied mineral fertilizers.

Physiologically active substances are plant growth regulators that are capable of causing various changes in the growth and development process of plants in small quantities. They are powerful biostimulants, i.e. they increase immunity, rooting of cuttings, increase germination and accelerate seed germination, reduce the negative impact of adverse external factors such as cold or drought, stimulate the formation of ovaries, accelerate fruit ripening, stimulate flowering [9].

To obtain high yields with good quality, physiologically active substances (auxins, cytokinins, gibberellins, succinic acid, monoethanolamine, thiocarbamide, and others) are widely used nowadays. One of these physiologically active substances is monosubstituted acetic acid monoethanolamine (MAMEA). As noted in the literature review,

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monoethanolamine and its derivatives in the composition of preparations enhance the action of active components, simultaneously eliminating the negative effect of preparations on plants [10,11]. It has been established that when monoethanolamine interacts with acetic acid, monosubstituted acetic acid monoethanolamine is formed [12,13].

To provide a physico-chemical basis for the process of obtaining liquid fertilizer with physiologically active substances, it is necessary to have knowledge of the solubility of salts in systems that include the studied components, as well as the interaction of initial components over a wide range of temperatures and concentrations.

In this regard, to justify the process of obtaining liquid fertilizer with physiological activity, we studied the mutual influence of components in the K2SO4 – CH3COOH · H2NC2H4OH – H2O system using a visually-polythermic method of investigation.

For the study, potassium sulfate, recrystallized from an aqueous solution, grade "ch", and monosubstituted acetic acid monoethanolamine, synthesized based on acetic acid and monoethanolamine taken in a molar ratio of 1:1 [12], were used as initial components.

In order to theoretically justify the process of obtaining fertilizer based on potassium chloride containing physiologically active substances, the mutual influence of components in the $CH_3COOH \cdot H_2NC_2H_4OH$–KCI–$H_2O$ system was studied over a wide range of temperatures and concentrations using the isomolar series method [8].

The binary system K_2SO_4 – H_2O was studied by us in the temperature range from -1,8°C до 30°C. The crystallization branches were identified on the solubility diagram: ice, potassium sulfate monohydrate, and anhydrous potassium sulfates. Thus, the data obtained by us are in good agreement with the literature [14] (Fig. 1).

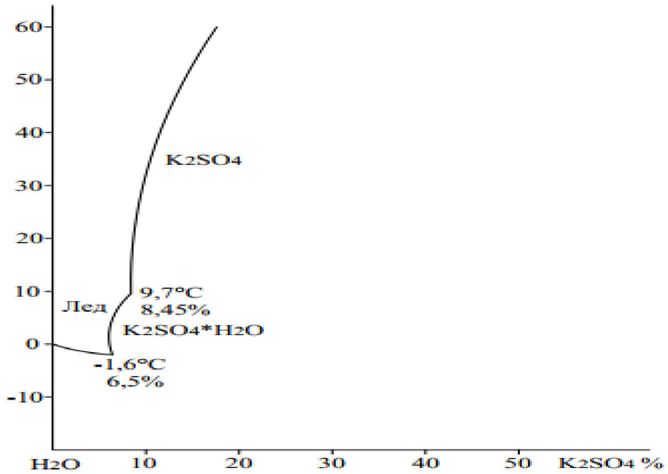

Fig. 1. Solubility diagram of the binary potassium sulfate -water system.

The solubility of the binary system $CH_3COOH \cdot H_2NC_2H_4OH$–$H_2O$ was studied in the temperature range from the temperature of complete freezing -50.3 to 10°C. It was found that the solubility diagram separates the fields of crystallization of ice, acetic acid, and

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monosubstituted acetic acid monoethanolamine. The first eutectic point of the binary system corresponds to 55.8% CH_3COOH at a temperature of -50.3°C, and the second eutectic point corresponds to 78% $CH_3COOH \cdot H_2NC_2H_4OH$, at a temperature of -26.1°C, which is in good agreement with the data presented in [12] (Fig. 2).

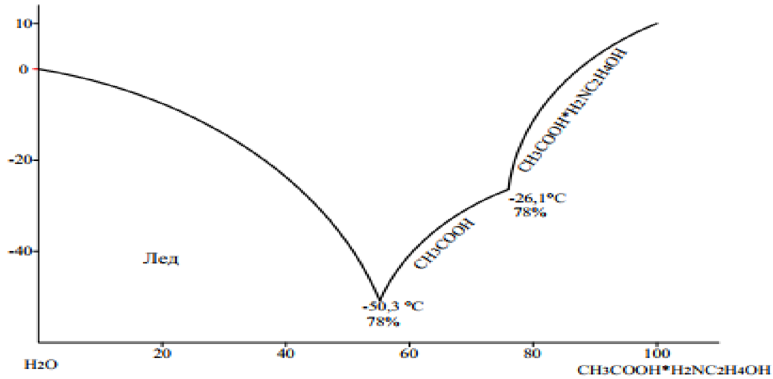

Fig. 2. Solubility diagram of the binary system monosubstituted acetic acid monoethanolamine - water.

The polytherm of solubility of the potassium-sulfate monosubstituted acetic acid monoethanolamine - water system was studied in the range from the temperature of complete freezing -60.0 to 10.0 °C using eight internal sections. Sections I to III were conducted from the K_2SO_4- H2O side towards the top of CH3COOH · NH2C2H4OH, and sections IV to VIII were conducted from the $CH_3COOH \cdot NH_2C_2H_4OH$ side towards the top of K_2SO_4 (Fig. 3).

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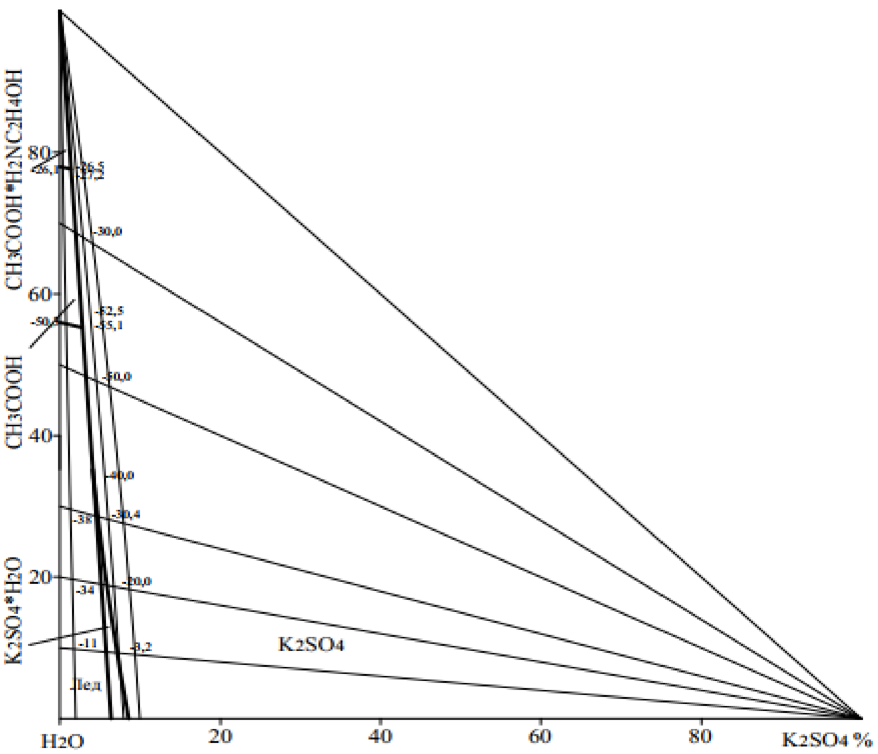

Fig. 3. Polytherm of solubility of the binary system potassium sulfate monosubstituted acetic acid monoethanolamine - water.

The solubility diagram of the system is characterized by the presence of fields of crystallization of ice, potassium sulfate crystal hydrate, anhydrous potassium sulfate, acetic acid, and monosubstituted acetic acid monoethanolamine. From the solubility diagram of this system, it can be concluded that it belongs to a simple eutonic type. The indicated fields converge at two triple points of the studied system. The compositions and temperatures of crystallization of the double and triple points of the system are given in Table 1.

Table 1.

Double and triple nodal points of the system potassium sulfate monosubstituted acetic acid monoethanolamine-water.

Composition of the liquid phase, mass%			Temperature of crystallization ºC	Solid phases
$CH_3COOH \cdot NH_2C_2H_4OH$	K_2SO_4	H_2O		
–	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_3COOH+ K_2SO_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_3COOH+ $CH_3COOH \cdot NH_2C_2H_4OH$
77,6	0,8	21,6	-26,8	То же
77,4	1,2	21,4	-27,2	CH_3COOH+ $CH_3COOH \cdot NH_2C_2H_4OH$ + K_2SO_4

Based on the data of polythermal sections, isotherms of the system were constructed by interpolation through every 10°C of the temperature range. Projections of the polytherm of the system were also made on the lateral sides of K_2SO_4-H_2O and $CH_3COOH \cdot NH_2C_2H_4OH$-$H_2O$. It was established that the components of the system retain their individuality in the studied temperature and concentration range. The studied system belongs to a simple eutonic type.

To determine the mechanism of interaction between potassium chloride and monosubstituted acetic acid monoethanolamine, the system potassium chloride - monosubstituted acetic acid monoethanolamine - water was studied using the isomolar series method. For this, the concentration of aqueous solutions of potassium chloride and monosubstituted acetic acid monoethanolamine was 2 mol/l. All measurements were carried out in a water bath at (20±0.1)°C [8].

The kinematic viscosity of the solutions was determined using a capillary viscometer VPZh-2 with a capillary diameter of 1.16-2.75 mm. The accuracy of the results was ±0.0001·10-1 m^2/s [9].

Определены температуры кристаллизации, вязкость, плотность и pH среды растворов данной системы в зависимости от соотношения компонентов (Табл.1)

The relative density was determined by the pycnometer method. To determine the density, the pycnometers were filled with distilled water, thermostated at 20°C, and weighed. Knowing the weight of the dry pycnometer, the density of water at 20°C, and the weight of the filled pycnometer, its volume was calculated. Weighing was carried out with an accuracy of ±0.00005 g. The results are presented with an accuracy of ±0.1 kg/m^3 [10].

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The pH of the solution was measured using the METTLER TOLEDO FE 20/FG pH meter according to the methodology [11].

The temperatures of crystallization, viscosity, density, and pH of the solutions of this system were determined depending on the ratio of the components (Table 1).

Table 1

Change in system properties depending on molar principles

The ratio of monosubstituted acetic acid monoethanolamine to potassium chloride.	pH medium	d, g/cm^3	ŋ, мм^2/c	Temperature of crystallization °C.
100	7,00	1,0256	13,00	-1,8
90:10	7,00	1,0280	12,70	-1,8
80:20	6,98	1,0300	12,36	-1,9
70:30	7,00	1,0328	11,95	-1,9
60:40	7,05	1,0352	11,52	-2,0
50:50	7,05	1,0378	11,19	-2,0
40:60	7,10	1,040	10,62	-2,1
30:70	6,98	1,410	10,52	-2,2
20:80	6,98	1,439	10,31	-2,2
10:90	7,00	1,462	10,02	-2,2
100	7,00	1,483	9,050	-2,3

Based on the obtained data, a "composition-property" diagram was constructed for the $CH_3COOH·H_2NC_2H_4OH$-KCl-H_2O system, with the properties of density, pH of the solution, viscosity, and crystallization temperature plotted on the ordinate axis and the solution compositions plotted on the abscissa axis. It was found that no new compounds were formed in the isomolar solutions. The isotherms of refractive index, density, viscosity, and pH in the "composition-property" diagram of the studied system show only one bend, corresponding to the branches of existence of the initial components. The diagram shows that in the concentration range of 70.0-30.0% $CH_3COOH·H_2NC_2H_4OH$ and KCl, the substances are present together.

Conclusion. The components of the system in the studied temperature and concentration range maintain their individuality, and hence their physiological activity. The results indicate the

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possibility of using monosubstituted acetic acid monoethanolamine together with potassium sulfate to produce a fertilizer with physiological activity.

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