Section 6. Chemistry

https://doi.org/10.29013/AJT-22-3.4-59-66

Ergashev Dilmurod Adiljonovich,
Associate Professor, Department of Chemical Technology
Fergana Polytechnic Institute,

Khamdamova Shokhida Sherzodovna,
Doctor of Technical Sciences, Professor,
Department of Chemical Technology
Fergana Polytechnic Institute,

Mirzaolimov Akmal Nabiyevich,
Assistant, Department of Chemical Technology
Fergana Polytechnic Institute

Eshpulatova Matluba Boymuradovna,
Junior researcher of the Institute
of General and Inorganic Chemistry of the Academy
of Sciences of the Republic of Uzbekistan

THE SOLUBILITY OF COMPONENTS IN THE SYSTEM {99.7[30 $MgSO_4$+70% H_2O]+0.3%HNO_3 · · $NH_2C_2H_4OH$–$(NH_4)_6Mo_7O_{24}$ · $4H_2O$

Abstract. The heterogeneous phase equilibrium in an aqueous system consisting of magnesium sulfate, monoethanolamine nitrate, and ammonium molybdate has been studied. It has been established that the system, including magnesium sulfate and monoethanolamine nitrate, belongs to a simple eutonic type, where the salting-out effect of the components on each other is observed. The dependence of changes in the physicochemical properties of solutions in a system containing $MgSO_4$, $HNO_3 \cdot NH_2C_2H_4OH$ и $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ depending on the composition of the components was studied. A "composition-property" diagram of this system is constructed.

Keywords: fertilizers, $MgSO_4$, $MgSO_4 \cdot 12H_2O$ and $MgSO_4 \cdot 7H_2O$ $HNO_3 \cdot NH_2C_2H_4OH$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, solubility diagram, the composition-properties diagram.

Introduction. In modern intensive technologies for growing field crops, the fertilizer system provides for the introduction of not only N, P_2O_5, K_2O, but also all the macro-and microelements necessary for the plant. The introduction of sulphur has already become as common as the introduction of nitrogen, phosphorus and potassium. Somewhat less attention in the nutrition system was paid to providing plants with magnesium and calcium. Recently, scientists and agricultural producers have been persistently and convincingly talking about the introduction of calcium as a nutrition element at much lower rates – 200–500 kg/ha.

As for magnesium, theoretically, everyone knows about the need to add it. In the composition of fertilizer mixtures, magnesium is contained in a smaller amount, or its content is lower compared to sulphur. Therefore, it is this, somewhat underestimated, an element that can become a limiting factor in the further growth of field crop yields.

Physiological role magnesium is associated with an effect on the activity of many enzymes. It plays an important role in the process of photosynthesis – it activates an enzyme that catalyzes the participation of CO_2 in photosynthesis. It is directly involved in the synthesis of ATP – the energy carrier in plants. Due to the use of the energy of the ATP molecule, the plant synthesizes glucose from carbon dioxide and water – the first link in the complex chain of photosynthesis. It not only participates in the synthesis of carbohydrates, but also ensures their transportation to the underground part of the plant, due to which a well-developed root system is formed, and in winter crops, the sugar content also increases and frost resistance increases [1].

At present, much attention is paid to the production of complex liquid fertilizers containing N, Ca, P_2O_5, and K_2O, as well as plant protection products, physiologically active substances, etc. Of particular interest is the study of the combined use of liquid fertilizers with physiologically active substances that accelerate the growth and development of plants and increase crop yields. One of such representatives of physiologically active substances is monoethanolammonium nitrate [2; 3].

This article is devoted to research on the production of liquid fertilizer containing Mg, N, Mo, and S and a physiologically active substance. In this regard, the following main research tasks were set and solved:

– Study of solubility in a system consisting of water, magnesium sulfate and monoethanolamine nitrate in a wide temperature and concentration range [4];

– Study of the refractive index, viscosity, density, and pH of the medium at 20 °C in the system [30%$MgSO_4$0,3%$HNO_3 \cdot NH_2C_2H_4OH$] – –$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$;

Objects and methods of research. The following were used in the work: $MgSO_4 \cdot 7H_2O$, $HNO_3 \cdot NH_2C_2H_4OH$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ of analytical grade.

For the study, a 30% aqueous solution of magnesium sulfate was used, which is a transparent solution with a slightly yellowish tint, odourless. The drug dissolves well in water with the formation of homogeneous solutions. Crystallization temperature 19.7–19.9 °C.

The second component is liquid monoethanolamine nitrate (LMEA), which we synthesized based on nitric acid and monoethanolamine [5; 6] at an equimolar ratio of components 1:1. The synthesized compound $HNO_3 \cdot NH_2C_2H_4OH$ is a concentrated solution, slightly cinnamon in colour, and highly soluble in water. Boiling point 145 °C, crystallization point –8.0 °C, pH of aqueous solutions 5.35. The third component is the crystalline salt $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. Ammonium molybdate tetrahydrous (analytically pure) was obtained by mixing ethanol with a concentrated ammonia solution of molybdenum (VI) oxide.

When studying the solubility of phases in physicochemical systems, the visual-polythermal method was used [4]. The viscosity of solutions was measured using a VPZh (ВПЖ)-type viscometer [7] with a capillary diameter of 1.16–1.32 mm. Results accuracy ± 0.0001–10-lm^2/s. The density of the studied compounds and solutions was determined pycnometrically [8]. The pH of solutions was measured according to the procedure [9] on an FE-20 METTLER TOLEDO pH meter.

Results and discussion. To elucidate the behaviour of the components in the process of obtaining a liquid fertilizer based on magnesium sulfate, nitrate monoethanolammonium and ammonium molybdate, the solubility in the $MgSO_4$– – $HNO_3 \cdot NH_2C_2H_4OH–H_2O$ system(Fig. 1., Table 1.) was studied by the visual-polythermal method [4].

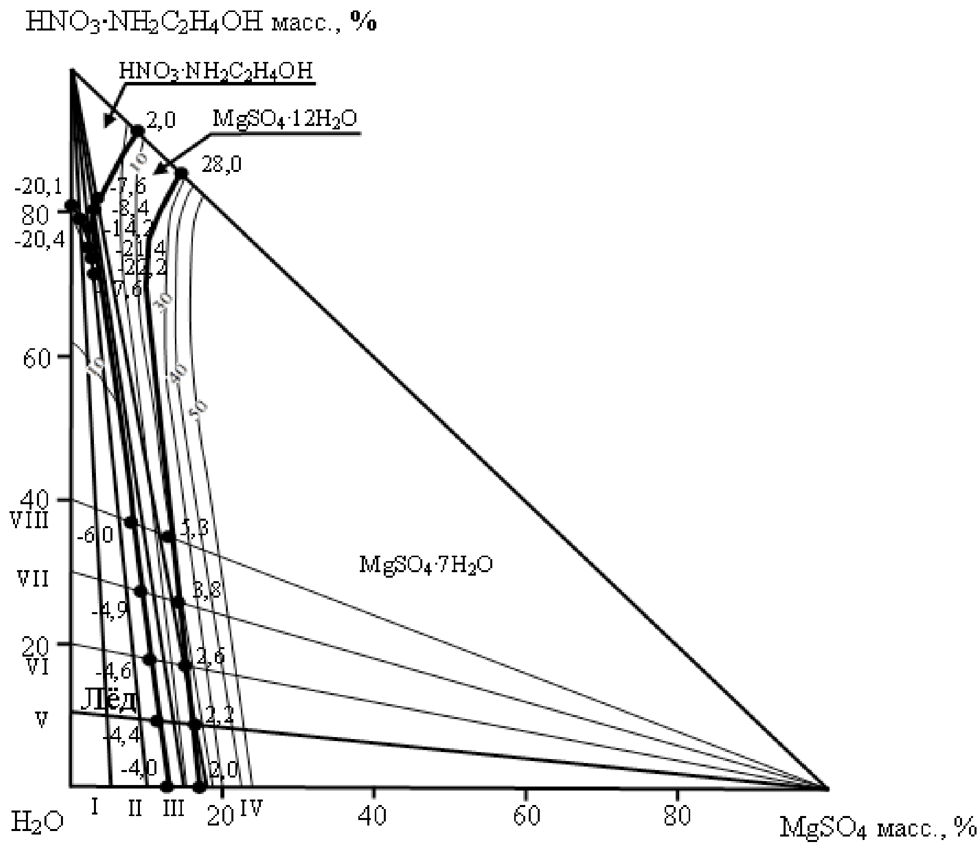

Figure 1. Polythermal solubility diagram of the system $MgSO_4$–$HNO_3 \cdot NH_2C_2H_4OH$–H_2O

Table 1.– Double and triple points of the $MgSO_4$–$HNO_3 \cdot NH_2C_2H_4OH$–H_2O system

The composition of the liquid phase, wt.%			Crystal temperature,°C	solid phase
$MgSO_4$	$HNO_3 \cdot NH_2C_2H_4OH$	H_2O		
1	*2*	*3*	*4*	*5*
12.2	–	87.8	–4.0	Ice + $MgSO_4 \cdot 12H_2O$
11.4	9.2	79.4	–4.4	–
10.2	18.0	71.8	–4.6	–
9.1	27.6	63.3	–4.9	–
8.0	37.0	55.0	–6.0	–
3.0	71.8	25.2	–17.6	–
2.8	74.0	23.2	–22.2	Ice + $MgSO_4 \cdot 12H_2O$+ +$HNO_3 \cdot NH_2C_2H_4OH$
2.0	75.2	21.0	–21.4	Ice + $HNO_3 \cdot NH_2C_2H_4OH$
1.2	79.0	19.8	–20.4	–
–	80.6	19.4	–20.1	Ice + $HNO_3 \cdot NH_2C_2H_4OH$
1.4	78.0	20.6	–14.2	$HNO_3 \cdot NH_2C_2H_4OH$ + $MgSO_4 \cdot$ $\cdot 12H_2O$
3.0	80.4	16.6	–8.4	–

1	2	3	4	5
3.7	81.6	14.7	–7.6	–
8.2	91.8	–	2.0	–
16.5	–	83.5	2.0	$MgSO_4 \cdot 12H_2O + MgSO_4 \cdot 7H_2O$
16.0	9.2	74.8	2.2	–
17.0	9.0	74.0	2.6	–
14.4	23.0	62.6	3.4	–
13.8	26.0	60.2	3.8	–
13.0	35.0	52.0	5.3	–
14.4	85.6	–	28.0	–

On the solubility diagram, the largest field of crystallization belongs to magnesium sulfate heptahydrate, since it has a lower solubility compared to other components of the system. It follows from the given data that no formation of new compounds based on the initial components is observed in the studied system. The system is of a simple type, which means that the components of the system, when presented together, retain their individuality and physiological activity.

The solubility of the binary system of monoethanolammonium nitrate in water was studied from the freezing point of –20.1 to –2.0 °C. Based on the data obtained, the crystallization branches of ice, nitric acid, monoethanolamine and monoethanolamine nitrate were established. The composition and crystallization temperature was determined at figurative points of the system. With the establishment of the quantitative composition of liquid and solid phases, which are given (Table 2., Fig. 2.).

Table 2. – Water solubility data for the $HNO_3 \cdot NH_2C_2H_4OH$-H_2O system

№	Liquid phase composition,%		Tcr., °C	solid phase
	$HNO_3 \cdot H_2NC_2H_4OH$	H_2O		
1	2	3	4	5
1	–	100	0	Ice
2	2.8	97.2	–0.2	Same
3	6.3	93.7	–0.4	–
4	11.1	88.9	–0.8	–
5	16.7	83.3	–1.1	–
6	22.5	77.5	–1.8	–
7	30.6	69.4	–2.4	–
8	37.2	62.8	–3.1	–
9	42.2	57.8	–4.4	–
10	46.9	53.1	–5.7	–
11	51.4	48.6	–7.0	–
12	56.0	44.0	–8.2	
13	61.2	38.8	–10.3	–
14	65.0	35.0	–11.9	–
15	68.2	31.8	–13.2	–
16	72.5	27.5	–15.8	–

1	2	3	4	5
17	76.7	23.3	–17.5	–
18	78.4	21.6	–18.8	–
19	80.57	19.43	–20.1	Ice + $HNO_3 \cdot NH_2C_2H_4OH$
20	81.2	18.8	–18.6	$HNO_3 \cdot NH_2C_2H_4OH$
21	82.1	17.9	–16.8	Same
22	83.9	16.1	–14.0	–
23	86.0	14.0	–11.2	–
24	88.0	12.0	–8.8	–
25	89.8	10.2	–7.4	–
26	92.0	8.0	–5.8	–
27	93.9	6.1	–4.2	–
28	96.1	3.9	–3.5	–
29	98.0	2.0	–2.4	–
30	100	–	–2.0	–

From the above solubility data, it can be seen (Table 1) that monoethanolamine nitrate is very soluble in water. Based on the data obtained, we have constructed a polythermal solubility diagram for the binary system $HNO_3 \cdot NH_2C_2H_4OH–H_2O$.

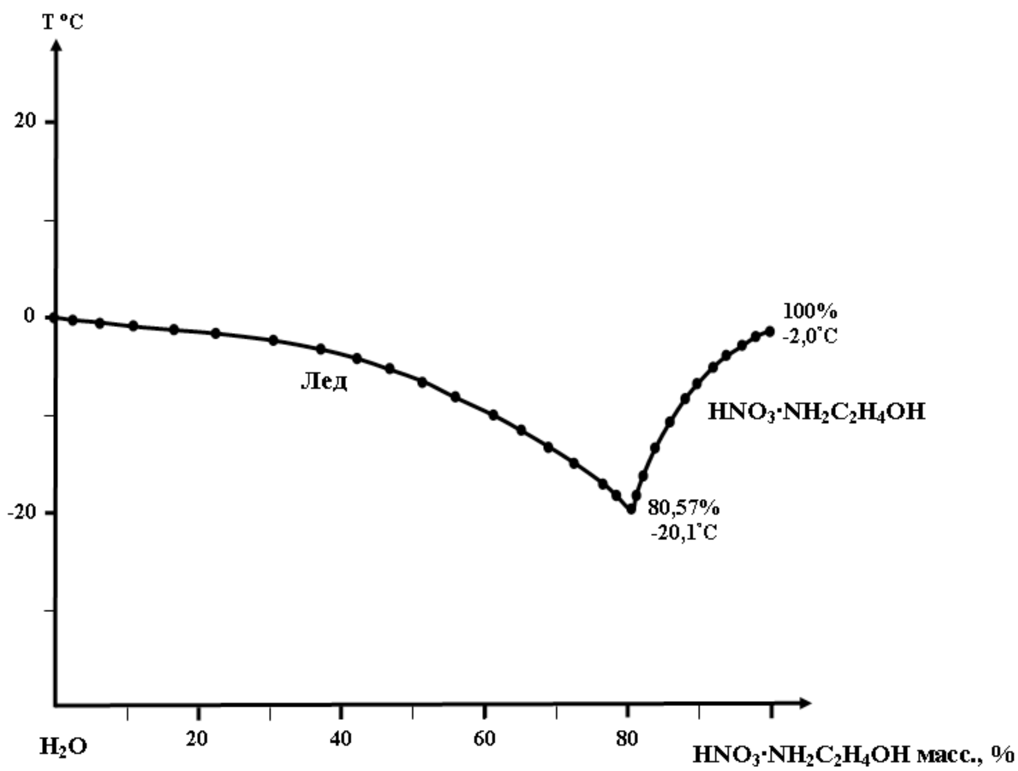

Figure 2. Solubility diagram of the binary system $HNO_3 \cdot NH_2C_2H_4OH-H_2O$

Solubility in binary systems consisting of sodium tricarbamide chlorate and water, $MgSO_4–H_2O$ and $HNO_3 \cdot NH_2C_2H_4OH–H_2O$ has been studied by many authors, our results are in good agreement with the literature [10–20].

For the physicochemical substantiation of the process of obtaining sulfur-containing fertilizer with physiological activity, we studied the $MgSO_4$–$HNO_3 \cdot NH_2C_2H_4OH$ system. On its polythermal solubility diagram, crystallization branches were revealed: $HNO_3 \cdot NH_2C_2H_4OH$, $MgSO_4 \cdot 12H_2O$ and $MgSO_4 \cdot 7H_2O$ (Fig. 3).

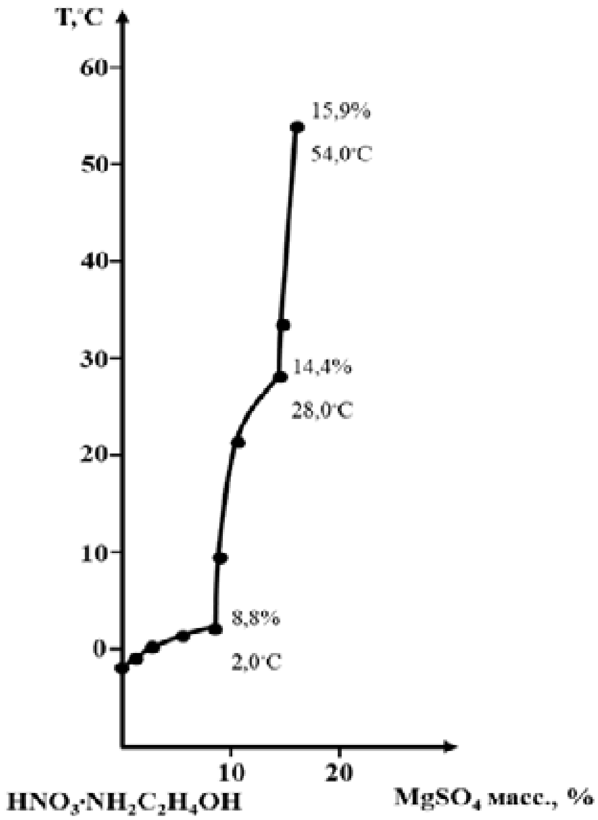

Figure 3. Polythermal solubility diagram of a binary system $HNO_3 \cdot NH_2C_2H_4OH$–$MgSO_4$

To develop technological standards for the process and recommend a technology for obtaining liquid fertilizer based on magnesium sulfate and a physiologically active substance ($HNO_3 \cdot NH_2C_2H_4OH$), the dependence of changes in the rheological properties of solutions on the composition in the $MgSO_4$-$HNO_3 \cdot NH_2C_2H_4OH$-$(NH_4)_6Mo_7O_{24}$ system was studied.

To elucidate the effect of components on the physicochemical properties of solutions of the above system, the dependence of the change in crystallization temperature, medium pH, viscosity and density of solutions on the composition was determined. Based on the data obtained, a "composition-property" diagram of this system was constructed (Fig. 4, Table 3).

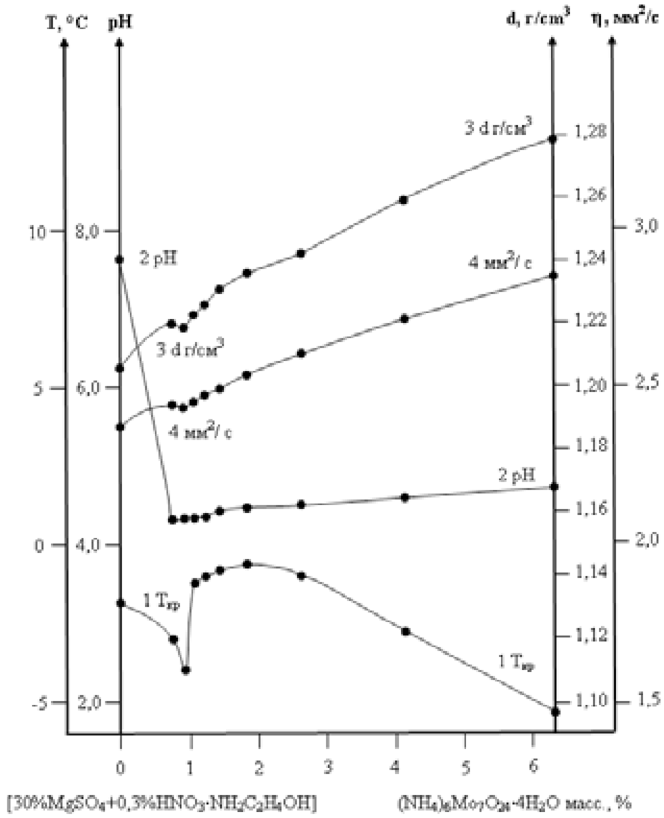

Figure 4. Dependence of the change in crystallization temperature (1), pH (2), density (3) and viscosity (4) of solutions on the composition in the system {99.7%[30%MgSO4+70% H2O]+0.3%HNO3 · NH2C2H4OH} – –(NH4)6Mo7O24 · 4H2O

Table 3. – Dependence of the change in the physicochemical properties of solutions on the composition in the {99,7%[30%$MgSO_4$+70%H_2O]+ 0,3%$HNO_3 \cdot NH_2C_2H_4OH$}–$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ system

№	{99.7%[30%$MgSO_4$+70%H_2O]+ +0,3%$HNO_3 \cdot NH_2C_2H_4OH$}	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Tkr	pH	d g/cm³	mm²/s
1	2	3	4	5	6	7
1	100	–	–1.8	7.65	1.20661	2.37706

1	*2*	*3*	*4*	*5*	*6*	*7*
2	99.22	0.78	–3.0	4.34	1.22100	2.45001
3	99.08	0.92	–4.0	4.35	1.22003	2.44904
4	98.92	1.08	–1.2	4.36	1.22302	2.450825
5	98.78	1.22	–1.0	4.38	1.226541	2.47510
6	98.54	1.46	–0.8	4.42	1.231830	2.49890
7	98.14	1.86	–0.6	4.47	1.23656	2.54545
8	97.37	2.63	–1.0	4.50	1.24297	2.61480
9	95.85	4.15	–2.8	4.60	1.25954	2.72533
10	93.69	6.31	–5.3	4.74	1.27933	2.85267

Figure 4 shows that in the process of dissolution {99,7%[30%$MgSO_4$+70%H_2O]+0.3% $HNO_3 \cdot NH_2C_2H_4OH$} in $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ sharp breaks are observed on the curves of crystallization temperature and pH again formed solutions at content 0.92% $t_{кр}$ –4.0 °C; pH 4.35; d g/cm^3 1.22003; mm^2/s 2,44904. On the curves of density (3) and viscosity (4), the break is not so obvious due to the very small amount of additives. This is explained by the fact that within the studied ranges of component concentrations at breakpoints in the system there is a phase transition from ice to mixtures of salts of magnesium sulfate, monoethanolamine nitrate and ammonium molybdate.

Conclusion. Thus, the mutual influence of the components in the {99.7%[30% $MgSO_4$+70%H_2O]+ +0.3% $HNO_3 \cdot NH_2C_2H_4OH$}–$(NH_4)_6Mo_7O_{24}$ system was studied and the composition of a new liquid fertilizer based on monoethanolammonium nitrate and ammonium molybdate was recommended.

To select the optimal ratio of components in the fertilizer composition based on magnesium sulfate and monoethanolammonium nitrate, preliminary agrochemical tests of various compositions on cotton were carried out. The results showed that the composition of the fertilizer, in which the ratio of the components [30% $MgSO_4$+70%H_2O] and $HNO_3 \cdot$ $\cdot NH_2C_2H_4OH$ equal to 1.0 : 0.006 ÷0.008 has a high agrochemical activity, and also has a positive effect on accelerating the ripening and opening of cotton bolls.

The obtained research results serve as a scientific basis for the development of a technology for obtaining liquid fertilizers of complex action.

Acknowledgements

The authors acknowledge the immense help received from the scholars whose articles are cited and included in references to this manuscript. The authors are also grateful to the authors/ editors/publishers of all those articles, journals and books from where the literature for this article has been reviewed and discussed.

In addition, the authors express gratitude to the head of the Fergana Polytechnic Institute and the scientific community of the Department of Chemical Technology for their assistance in carrying out this research work.

The authors report no conflicts of interest.

The Source of funding is nil.

References:

1. Галынская Надежда. Роль кальция в жизни растений. URL: / 2018.– С. 9–10.
2. Тогашаров А. С., Нарходжаев А. Х., Тухтаев С. Изучение растворимости и реологических свойств системы $NaClO_3 \cdot 3CO(NH_2)$-$HN_2C_2H_4OH \cdot HNO_3$– H_2O // Химический журнал Казахстана. – Алматы, 2009. – №2. – С. 59–66.
3. Саибова М. Т. Применение этаноламинов в сельском хозяйстве // Узбекский химический журнал.– № 1. 1983.– С. 58–64.

4. Трунин А. С. Петрова Д. Г. Визуально-политермический метод / Куйбышевский политехн. Инс-т.– Куйбышев. 1977.– 94 с.
5. Киргинцев А. Н., Трушникова Л. Н., Лаврентьева В. Г. Растворимость неорганических веществ в воде. Справочник. Изд-во «Химия», л. 1972.– С. 111–112.
6. Абдуллаева М. Т. Взаимодействие моноэтаноламина с уксусной кислотой. Узб. хим. журн. – № 3. 2008.– С. 50–54.
7. Фролов Ю. Г Курс коллоидной химии // Поверхностное явление и дисперсные системы.– М.: 1982.– С. 117–124.
8. Здановский А. Б., Галлургия: – Л.: Химия. 1972.– 572 с.
9. Горбачев С. В. Практикум по физической химии –М.: Высшая школа. 1974.– 310 с.
10. Эргашев Д. А., Аскарова М. К., Эшпулатова М. Б., Махаматова Г. Б., Омонбоева Г. Б. изучение взаимного влияния компонентов в системах, обосновывающих процесс получения жидкого удобрения // Евразийский союз ученых. 2019.– № . 9–1.– С. 33–37.
11. Эргашев Д. А., Аскарова М. К., Исабаев З., Эшпулатова М. Б., Махаматова Г. Б., Исабаев Д. З. Исследование систем, обосновывающих процесс получения жидкого удобрения комплексного действия // Евразийский Союз Ученых.– № . 5–1 (62). 2019.– С. 25–30.
12. Эргашев Д. А., Аскарова М. К., Эшпулатова М. Б., Исабаев З., Исабаев Д. З. Растворимость компонентов в системе $Ca(NO_3)_2$-$HNO_3 \cdot NH_2C_2H_4OH$-H_2O // Universum: технические науки.– № 7. – (52). 2018.– С. 61–68.
13. Эргашев Д. А., Тураев Т. Т., Мирзаолимов А. Н., Аминбоев А. Ғ., Хамдамова Ш. Ш. Физико-химическое обоснование процесса получения нового дефолианта // Universum: технические науки.– № . 2 (59). 2019.
14. Эргашев Д. А., Адилов З. Х., Тожиев Р. Р., Хамдамова Ш. Ш. Получение хлоратсодержащих дефолиантов, обладающих инсектицидными свойствами олучение хлоратсодержащих дефолиантов, обладающих инсектицидными свойствами // Монография European Scientific Platform, – Фергана-Винница, 2021 г.
15. Изучение физико-химических свойств растворов в системе {[19, 37% Ca (ClO3) 2+ 15, 06% Mg (ClO3) 2 + 3, 72% CaCl2+ 2, 68% MgCl2+ 45, 17% H2O]+ 10, 0% Co (NH2) 2+ 4, 0% C2H5OH}–CH3COOH· · NH2C2H4OH // Universum: технические науки.2018.– № 4. – (49).– С. 2–2.
16. Эргашев Д. А., Эшпулатова М. Б., Тураев Т. Т., Хамракулов З. А., Аскарова М. К. Диаграмма растворимости системы $Ca(ClO_3)_2$–$CH_3COOH \cdot NH_2C_2H_4OH$–$H_2O$ при 25 °C // Universum: технические науки.– – №4. – (49). 2018.– С. 1–1.
17. Эргашев Д. А., Хамдамова Ш. Ш., Мирзаолимов А. Н., Мухаммедов С. Б. Получение хлоридов кальция и магния из доломита месторождения «Навбахор» // Universum: технические науки.– №11–2. – (68). 2019.– С. 69–74.
18. Кодирова Д. Т., Мирсалимова С. Р., Умаралиева М. Ж., Абидова М. А., Нурматова З. Н. Изучение процесса получения азотно-фосфорных удобрений разложением кызылкумских фосфоритов азотной кислотой // Universum: технические науки.– № 3–2. – (72). 2020.– С. 57–59.