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Study of liquid fertilizer production through complex systems

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Annotation: Currently, all over the world, with intensive population growth, a reduction in suitable land resources and water reserves, the role of the production of new types of fertilizers is increasing to fully satisfy the population's needs for quality products. One of the effective ways to produce mineral fertilizers is to obtain them in liquid form. The production of such fertilizers leads to a reduction in a number of processes and, compared to solid fertilizers, to a noticeable reduction in costs.

Keywords: solid fertilizers, production of new types of fertilizers

Currently, all over the world, with intensive population growth, a reduction in suitable land resources and water reserves, the role of the production of new types of fertilizers is increasing to fully satisfy the population's needs for quality products.

One of the effective ways to produce mineral fertilizers is to obtain them in liquid form. The production of such fertilizers leads to a reduction in a number of processes and, compared to solid fertilizers, to a noticeable reduction in costs.

Today, one of the important tasks is the development and improvement of technologies for producing new complex fertilizers based on local raw materials.

To solve this problem, it is relevant to use the products of nitric acid decomposition of dolomite (a solution of calcium and magnesium nitrates) as feedstock, followed by its enrichment with nitrogen fertilizer components, physiologically active substances and microelements.

Feedstock, i.e. The product of nitric acid decomposition of dolomite was obtained by us by decomposing dolomite with a 40% solution of nitric acid at a temperature of 30÷40°C and a process duration of -60 minutes. It contains 41÷42.0% of the sum of calcium and magnesium nitrates and has the following physical and chemical properties: crystallization temperature -11.0°C, density 1.3961 g/cm^3, viscosity 3.013 mm^2/s and pH 1.15.

This solution can be used to obtain a complex liquid fertilizer containing both calcium nitrate and magnesium nitrate.

Since calcium and magnesium nitrates are components of the nitric acid decomposition product of dolomite, it was interesting to study their mutual influence when present together.

This system was previously studied by the authors of [1] using the isothermal method at 0, 25 and 100°C. In the phase diagram of the system, the authors identified crystallization regions of $Ca(NO_3)_2{\cdot}4H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, but the crystallization region of $Ca(NO_3)_2{\cdot}3H_2O$ was not detected .

The solubility of the components in the system $Ca(NO_3)_2$- $Mg(NO_3)_2$- H_2O was studied by us in a wide range of temperatures and concentrations using the polythermal method [2].

By studying the binary system calcium nitrate - water, we established the presence of four branches of crystallization on its solubility diagram: ice, four-, three- and two-aqueous calcium nitrate. The eutectic freezing point of the binary system corresponds to -26.7°C at 43.36% calcium nitrate content.

A study of the binary system magnesium nitrate - water showed that its solubility diagram revealed branches of crystallization: ice, nine- and six-hydrate magnesium nitrate. The data obtained on the position of the eutectic and the regions of existence of crystalline hydrates of magnesium nitrate are consistent with the literature [3].

The calcium nitrate–magnesium nitrate–water system was studied using eleven internal sections.

Based on data on the solubility of binary systems and internal sections, projections and a polythermal diagram of the solubility of the system from the eutectic freezing point (-34.0 ° C) to 50 ° C were constructed,

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where the presence of crystallization fields was established: ice, four-, three- and two-water calcium nitrate, nine- and six-aqueous magnesium nitrate (Fig. 1, 2).

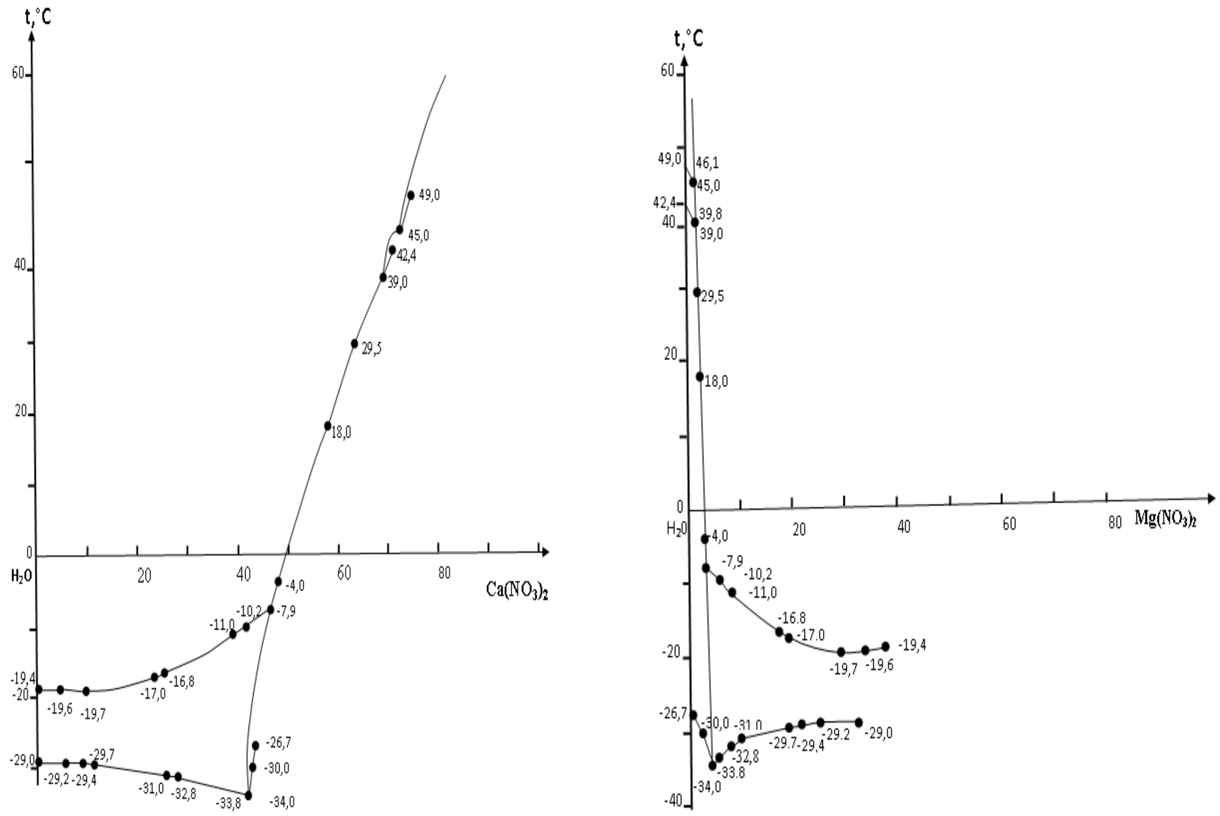

Fig.1. Polythermal projections of the calcium nitrate - magnesium nitrate - water system

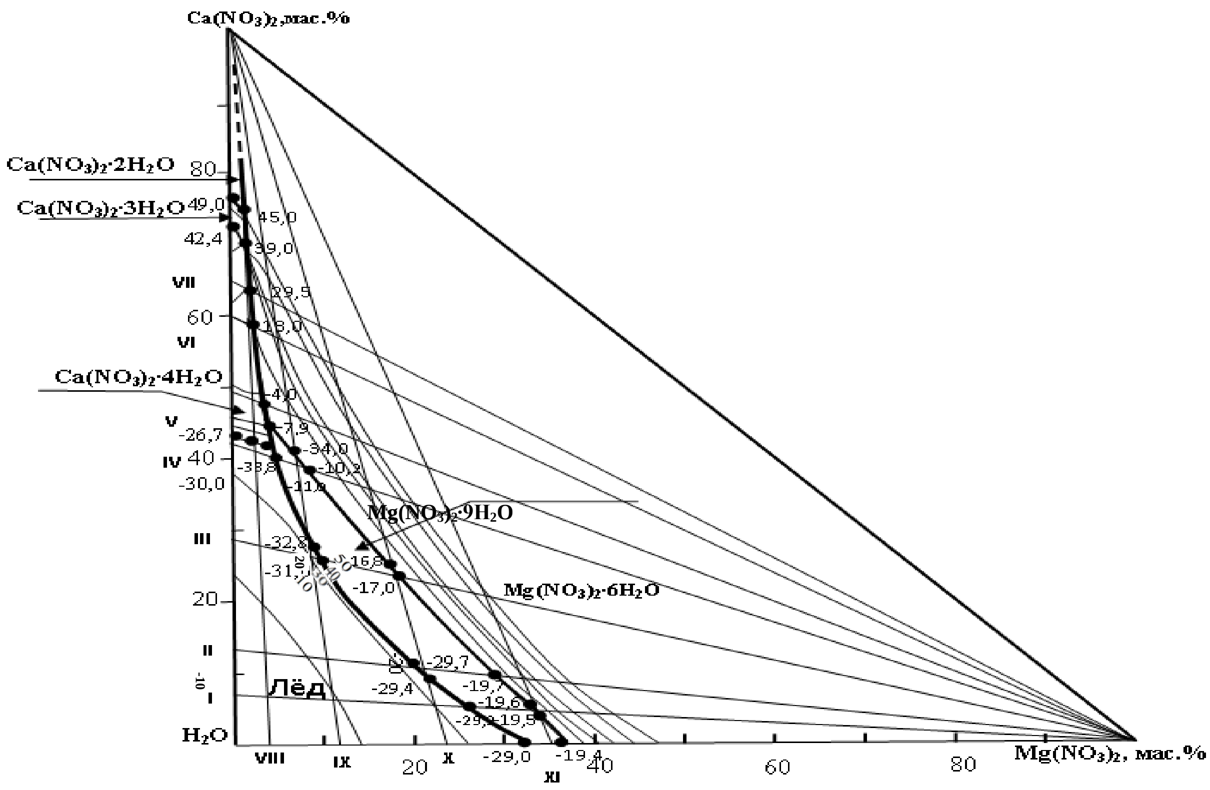

Fig. 2. Polythermal diagram of the solubility of the system

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$Ca(NO_3)_2 - Mg(NO_3)_2 - H_2O$

These fields converge at four triple nodal points, the characteristics of which are given in Table 1.

Table 1.

Triple node points of the system $Ca(NO_3)_2 - Mg(NO_3)_2 - H_2O$

Composition of the liquid phase, m.%			tcr , ^{0}C	Solid phase
$Ca(NO_3)_2$	$Mg(NO_3)_2$	H_2O		
73.7	1.4	24.8	45.0	$Ca(NO_3)_2 \cdot 3H_2O + Ca(NO_3)_2 \cdot 2H_2O + Mg(NO_3)_2 \cdot 6H_2O$
69.8	1.6	28.6	39.0	$Ca(NO_3)_2 \cdot 4H_2O + Ca(NO_3)_2 \cdot 3H_2O + Mg(NO_3)_2 \cdot 6H_2O$
46.2	3.4	50.4	-7.9	$Ca(NO_3)_2 \cdot 4H_2O + Mg(NO_3)_2 \cdot 9H_2O + Mg(NO_3)_2 \cdot 6H_2O$
41.9	4.0	54.1	-34.0	Ice+ $Ca(NO_3)_2 \cdot 4H_2O + Mg(NO_3)_2 \cdot 6H_2O$

From the data presented it is clear that in the system under study there is no formation of new chemical compounds based on the initial components. The system belongs to the simple eutonic type.

Analysis of the polythermal solubility diagram of the $Ca(NO_3)_2 –$ $Mg(NO_3)_2 - H_2O$ system shows that calcium nitrate, due to its good solubility, has a salting out effect on magnesium nitrate. With increasing concentration of system components, the crystallization field of magnesium nitrate expands.

From the solubility diagram of the studied system it follows that in order to obtain the optimal composition of a solution of calcium and magnesium nitrates, the concentration of calcium and magnesium nitrates should not be increased, otherwise $Mg(NO_3)_2 \cdot 6H_2O$ crystals will crystallize from the solution . This circumstance confirms that the 40% concentration of nitric acid, which was used to decompose dolomite, is optimal. At this concentration, it is possible to obtain a solution containing a sum of calcium and magnesium nitrates of 41.0÷42.0% with a crystallization temperature of -11.0°C.

The goal of further scientific research was to enrich the resulting solution of calcium and magnesium nitrates by introducing ammonium nitrate into its composition.

Therefore, to substantiate the process of obtaining the composition of a liquid fertilizer based on a solution of calcium, magnesium and ammonium nitrate nitrates, the dependence of changes in the physicochemical properties of solutions on the composition of the components in the system [41.53%$\sum Ca(NO_3)_2 + Mg(NO_3)_2 + 58.47\% H_2O$] - NH_4NO_3 .

In order to clarify the influence of the components on the physicochemical properties of solutions of the above system, the change in crystallization temperature, pH of the medium, density and viscosity of solutions depending on the composition was determined. Based on the data obtained, a “composition-properties” diagram of this system was constructed (Fig. 3).

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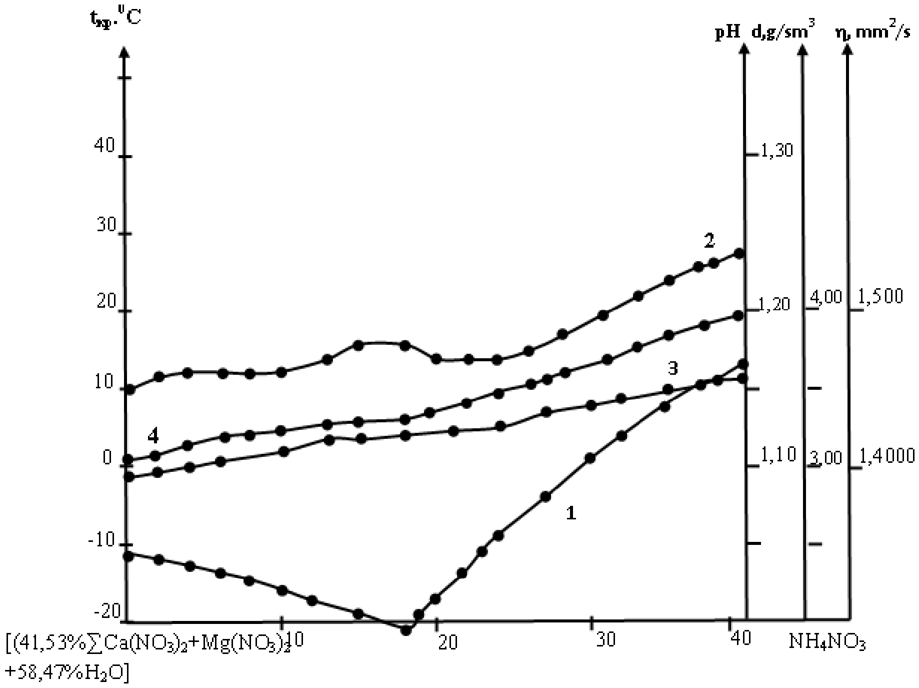

Fig.3. Dependence of changes in crystallization temperature (1), pH (2), density (3) and viscosity (4) of solutions on the composition in the system [41.53 %∑ $Ca(NO_3)_2 + Mg(NO_3)_2$ + 58.47 % H_2O] - NH_4NO_3

According to the data obtained, the composition-crystallization temperature diagram is characterized by the presence of two crystallization branches, with a clear break in the solubility curve (Fig. 3, curve 1). The first branch corresponds to crystallization [57.26% $Ca(NO_3)_2$ +42.74% $Mg(NO_3)_2$] and continues to 18% ammonium nitrate content at -21.0C°. With an increase in the concentration of ammonium nitrate to more than 18.0%, ammonium nitrate crystallizes in the system, which was confirmed by chemical and X-ray phase analysis methods.

Chemical analysis of the solid phase isolated from the suspected area gave the following results:

Found, mass. %: NH_4^+ = 22.05; NO_3^- = 76.9

Calculated for NH_4NO_3 wt.%: NH_4^+ = 22.5; NO_3^- = 77.5

A comparison of the diffraction lines and the corresponding interplanar spacing values of the X-ray diffraction pattern of the isolated solid phase showed that they are identical to the literature data for NH_4NO_3 [4,5] (Fig. 4).

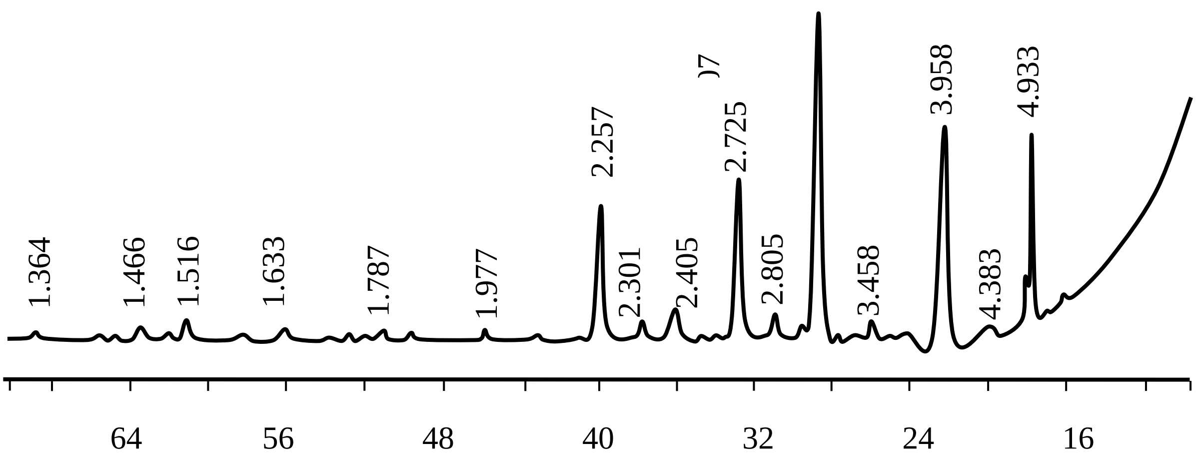

Fig. 4. X-ray diffraction pattern of the solid phase isolated from the system

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Analysis of the "composition-properties" diagram of the studied system shows that as ammonium nitrate is added to the initial solution of calcium and magnesium nitrates, the pH, density and viscosity values (Fig. 3, curves 2,3,4) of the newly formed solutions gradually increase, respectively: pH from 1.15 to 1.24; d from 1.3961 to 1.4580 g/cm ^{3}, η from 3.013 to 3.940 mm ^{2}/s.

According to the data obtained, to enrich a solution of calcium and magnesium nitrates with ammonium nitrate, it is necessary to dissolve it in a solution of calcium and magnesium nitrates at a mass ratio of 1.0:0.25. With this ratio of components, a solution is formed with satisfactory physicochemical properties: crystallization temperature -17.0°C , density 1.4240 g/cm ^{3}, viscosity 3.370 mm ^{2}/s and pH 1.17.

$_{2}$O into the resulting solution and further enrich the composition with nitrogen, the mutual influence of the components in the system { 80%[41.53∑ Ca(NO_3) $_2$ + Mg (NO_3)$_2$ + 58.47% H_2O]+20% NH_4NO_3 } - KNO_3 by determining changes in the crystallization temperature, density, viscosity and pH of the solution medium depending on the composition (Fig. 5).

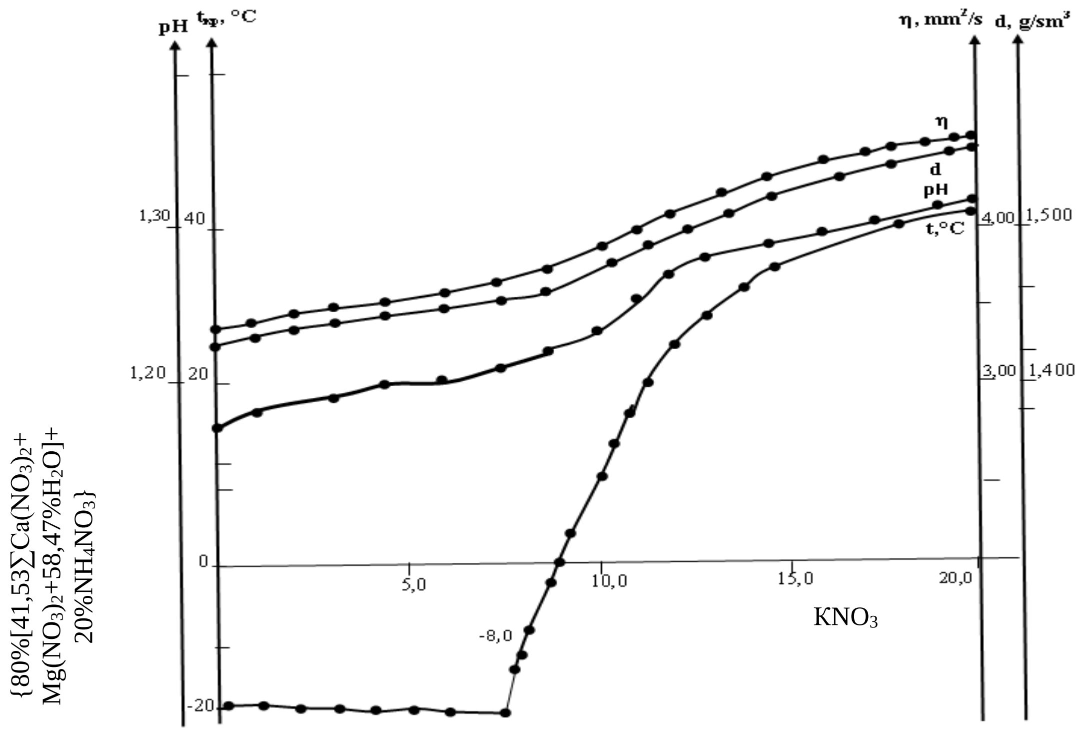

Fig.5. Dependence of changes in crystallization temperature (1), pH (2), density (3) and viscosity (4) of solutions on the composition in the system
{ 80%[41, 53 ∑Ca(NO_3)$_2$+Mg(NO_3)$_2$+58, 47 %H_2O]+20%NH_4NO_3} –
K NO_3

Based on the data obtained, it was established that in order to obtain a liquid fertilizer containing potassium, it is necessary to dissolve potassium nitrate in an amount of 8.0% in a solution of calcium, magnesium and ammonium nitrates. The resulting solution has the following physicochemical properties: crystallization temperature -8.0°C, density 1.4520 g/cm3, viscosity 3.660 mm2 / s, pH=1.21. An increase in the concentration of KNO_3 more than 8.0% leads to an increase in the crystallization temperature of the resulting solution. As a result of the salting out effect of calcium and magnesium nitrates on potassium nitrate, crystals precipitate into the solid phase potassium nitrate.

Chemical analysis of the solid phase isolated from the KNO_3 crystallization branch , gave the following results: found (mass %): K^+ = 38.3; NO_3^- =61.2. The melting point of the isolated solid phase is 333°C, that is, it corresponds to potassium nitrate [6].

Since, the product of nitric acid decomposition of dolomite, i.e. a solution of calcium and magnesium nitrates, as well as a solution obtained after its enrichment with ammonium and potassium nitrates are acidic;

therefore, the process of neutralization of a solution obtained on the basis of calcium, magnesium, ammonium and potassium nitrates using monoethanolamine was studied and its physico- chemical properties (Table 2).

Table-2

Dependence of changes in the physicochemical properties of solutions on the composition in the system {72.0% [41.53%∑ $Ca(NO_3)_2$ + $Mg(NO_3)_2$ +58.47% H_2O] + 20% NH_4NO_3 + 8.0% KNO_3 } - $NH_2C_2H_4OH$

No.	Content of components, %		tcr , °C	d , g/cm 3	ŋ, mm 2 /s	pH
	{72.0% [41.53%∑$Ca(NO_3)_2$ + $Mg(NO_3)_2$ + 58.47%H_2O]+ 20%NH_4NO_3 +8.0% KNO_3 }	$NH_2C_2H_4OH$				
1	100	-	-8 , 0	1.4550	3.65	1.22
2	99.78	0.22	-10.0	1.4580	3.68	1.24
3	99.45	0.55	-1 2 .0	1.4542	3.69	1.60
4	90.04	0.96	-10 .0	1.4536	3.70	2.03
5	98.33	1.67	-7.2	1.4520	3.72	2.97
6	97.7	2.30	-7.0	1.4508	3.78	4.10
7	96.97	3.03	-6.0	1.4484	4.08	6.13
8	96.75	3.25	-6.0	1.4478	4.28	7.0
9	96.46	3.54	-6.0	1.4468	4.41	7.23
10	96.24	3.76	-6.0	1.4459	4.46	7.30

The solution obtained after neutralization with monoethanolamine has a crystallization temperature of -6.0°C, a density of 1.4478 g/cm ^{3} and a viscosity of 4.2800 mm ^{2} /s, pH = 7 and contains (wt. %): N = 13.14 , Ca =3.99, Mg =1.97,

K_2O =3.64.

This solution can be recommended as a complex liquid fertilizer containing simultaneously such nutrients as N , Ca , Mg and K_2O.

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