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SCIENTIFIC PAPER

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SOLID-LIQUID EQUILIBRIUM IN LIQUID COMPOUND FERTILIZERS

Article Highlights

- After KCl and $\text{NH}_4\text{H}_2\text{PO}_4$ conversion in the liquid phase, K^+ , NH_4^+ , Cl^- and PO_4^{3-} concentrations were determined
- The solid-liquid equilibrium in the liquid phase after conversion was determined
- N content in the liquid phase increased and crystallization temperature decreased with adding of $\text{NH}_4\text{NO}_3(\text{s})$
- Basic properties of liquid compound fertilizers were determined
- The liquid phase after conversion can be used as a liquid compound fertilizer during the summer

Abstract

Liquid compound fertilizers (LCF) are aqueous salt solutions which nourish the soil. They contain nitrogen, phosphorus, potassium, sometimes calcium, magnesium and micronutrients. An LCF solution has practically no insoluble residue and contains the elements in a fully digestible form and is a high-speed, highly effective fertilizer. It is important to assess the equilibrium in the solid-liquid system when creating liquid compound fertilizers, since their basic properties, concentration and crystallization temperature, depend on it. The aim of the study was to determine properties of a liquid multicomponent (K^+ , NH_4^+ , Cl^- and PO_4^{3-}) system. This liquid multicomponent system, which was obtained as a by-product in the conversion of KCl and $\text{NH}_4\text{H}_2\text{PO}_4$, can be used as a liquid fertilizer. This work investigates liquid fertilizers' chemical composition and their physicochemical properties, such as crystallization temperature, pH, density, viscosity and corrosivity. In order to increase nitrogen concentration, ammonium nitrate was added. Composition of the solid phase obtained by crystallization was identified by methods of chemical and instrumental analysis (radiography, infrared molecular absorption spectroscopy and optical microscopy). The results show that all properties of liquid fertilizers are best when the concentration of NH_4NO_3 in liquid solutions equals 8%.

Keywords: solubility, equilibrium, solid, liquid, conversion, fertilizers.

Agriculture is a sector of the economy that plays a crucial role in the world as a producer of food and as an employer of millions of people. Agriculture has been growing steadily since the end of the 18th century when intensification of agricultural production became possible due to the use of high yielding vari-

eties, irrigation and mechanization as well as to soil feeding with mineral fertilizers and crop protection with the use of pesticides. Consumption of these agrochemicals has drastically increased in the last fifty years, which resulted not only in the growth of agricultural production, but also in the pollution of the natural environment [1].

The major types of fluid fertilizers are suspension fertilizers and solution fertilizers. Solution or liquid compound (LCF) fertilizers are dissolved completely in water. Suspension fertilizers are partially dissolved in water, but some of the nutrients, particularly potash, are suspended in water in the same way mud is suspended in water [2].

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Liquid compound fertilizers are popular because of the ease of handling and use. As they can be sprayed by a pump they are usually easier to handle and can be applied to soil without any manual labor, which significantly reduces the costs. LCFs are not toxic, non-flammable and non-explosive. Some pesticides can be injected into the fluid, saving trips across the field. Fertilizers custom blended to specifications are available. Properly applied, liquid fertilizers are no more or less efficient than dry fertilizers. Most liquid fertilizers contain the same basic ingredients as dry fertilizers. The only difference is that liquid fertilizers are dissolved in water, and dry fertilizers are not. The efficiency of liquid fertilizers is determined by the way they are applied [3].

Thus, LCF can be applied not only in spring but also in late summer (under a winter crop) and in the autumn (under the following year's spring crop). Plants can absorb liquid fertilizers through both their roots and through leaf pores. Foliar feeding can supply nutrients when they are lacking or unavailable in the soil, or when roots are stressed. It is especially effective on fast-growing plants like vegetables, giving an extra boost during the growing season. Therefore, knowledge of chemical and physical properties of fertilizers in aqueous solutions is becoming increasingly important [4-6].

Viscosity, density, pH, corrosivity and crystallization temperature are important characteristics of liquid fertilizer solutions. Viscosities and densities of liquid mixtures are required in many engineering applications involving mass and heat transfer processes. Accurate viscosity and density data are needed for the design of most liquid flow equipment. It is very important to measure the density of the solution in order to calculate the dosage of fertilizers. Solid fertilizers are sold and invoiced by weight. Therefore, all commercial quantities are quoted in kilograms or in metric tons. Liquid fertilizers, however, are metered/applied by density (in liters per area unit). Therefore, it is important to know the density of each liquid fertilizer source [7].

When selecting both liquid fertilizers and equipment employed for its application, its pH must be taken into consideration. Solutions used in fertigation through drip, micro-jet and micro-sprinklers (made wholly of plastic materials and no metallic components) may have a low pH, which aids in impeding the clogging of emitters with calcium and magnesium carbonates that settle out whenever the irrigation water has a high pH and a high carbonate content. Even if the irrigation water is maintained in pH range of 5.5-6.5, the pH of the fertilizer solution does not have a

long-term effect on the soil's pH, due to the soil's buffering capacity. In order to avoid corrosion of fertigation equipment with metallic components (such as sprinklers, pivots, etc.) or of liquid fertilizer sprayers and injectors, only fertilizer solutions with a pH above 6 should be used. Corrosivity is a characteristic that expresses the degree to which the fertilizer solution attacks various metals. Corrosivity solutions are classified as:

- a) very corrosive solutions (with a pH below 3.5); they corrode all metals, including stainless steel;
- b) weakly corrosive solutions (with a pH in the range from 3.5 to 6.0); they corrode iron and steel but do not attack stainless steel;
- c) non-corrosive solutions (with a pH above 6.0); they do not corrode metals such as iron, steel, stainless-steel, aluminum, bronze, etc.

The composition of a fertilizer solution determines its corrosivity. As a general rule, a strongly acidic solution with a pH below 3.5 is considered to be very corrosive. Solutions with a pH above 3.5 are generally weakly corrosive or non-corrosive. Most fertilizer solutions containing phosphorous are corrosive, except for those specially prepared at the client's request as non-acidic. Acidic fertilizer solutions containing chlorides are considered to be very corrosive; these solutions are prepared with potassium chloride.

However, the most important characteristic of liquid fertilizers is their crystallization temperature, which can be determined by the equilibria between liquid and solid phase in the system [8].

The equilibria between the solid phase and the liquid phase are the thermodynamics of all crystallization processes from the melt and the solution and thus of fundamental importance for the design of industrial crystallization processes. The informative value of SLE data of a particular substance, and thus of phase diagrams as their graphical representation, is miscellaneous. Beside the general questions, for example whether a given separation task is feasible by crystallization techniques, much more detailed questions such as the maximum (hypothetical) yield, the purity achievable, and the occurrence of more solid phases (*e.g.*, polymorphs) can be answered. Finally, a crystallization procedure facilitating the separation of the target compound can be derived, which in combination with kinetic data allows for systematic process design [9].

Different phase equilibrium studies are often a part of various research works in chemical engineering. The phase diagrams of the $\text{CH}_3\text{CH}_2\text{OH} + \text{Cs}_2\text{SO}_4 + \text{H}_2\text{O}$ system were determined at 10, 30, and 50 °C and samples of the solid phase analyzed by thermo-

gravimetric analysis showed that it was an anhydrous salt [10]. A systematic scheme for the experimental determination of isobaric solid-liquid equilibrium phase diagrams at atmospheric pressure is presented. To illustrate the execution of this scheme, the isobaric SLE phase diagrams of two organic systems were measured [11]. Liquid-liquid and solid-liquid equilibrium data are presented for the PEG 4000 + Na₂SO₄ + water system at 298.15 K. Six equilibrium regions were found. Densities and refractive indices were determined for the solutions in equilibrium. Samples of the solid phase analyzed by X-ray diffraction showed it consisted of anhydrous Na₂SO₄ [12].

EXPERIMENTAL

Apparatus and reagents

Chemically pure substances of potassium chloride (KCl, 99–100.5%, Sigma-Aldrich), ammonium dihydrophosphate (NH₄H₂PO₄, 99.0%, Fluka Analytical), ammonium nitrate (NH₄NO₃, 98.0%, Sigma-Aldrich) and distilled water were used in this work.

The conversion reaction between potassium chloride and ammonium dihydrophosphate at different temperatures was analyzed by determination of balance between liquid and solid phases. The conversion reaction was carried out with the use of a temperature-controlled glass reactor (Figure 1). The temperature of the reaction zone was controlled with a universal measuring instrument, Almemo 2450-1L. Initial aqueous solutions (saturated solutions) of these salts were prepared by dissolving starting materials, namely potassium chloride and ammonium dihydrophosphate, in mole ratio 0.8:0.2. In each experiment, a total amount of salt was 5.5 mol and 200 cm³ of distilled water was used.

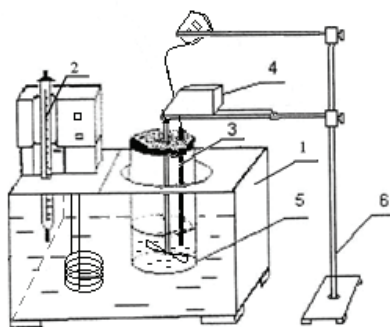


Figure 1. Temperature-controlled glass reactor: 1 - circulation thermostat; 2 - contact thermometer; 3 - thermocouple; 4 - electric mixer; 5 - glass reactor; 6 - stand.

The chemical composition of the crystalline solid phase was analyzed by methods of chemical ana-

lysis: concentration of ammonium nitrogen (NH₄⁺) by the Kjeldahl method (Vapodest 45s) [13]; concentration of phosphorus (P₂O₅) by photocolometric method (T70/T80 UV-Vis); concentration of chlorine (Cl⁻) by potentiometric method, with the use of silver nitrate (TitroLine alpha plus) [14]; concentration of potassium (K₂O) by marginal solutions method using the flame photometer PFP-7 [15].

Diffraction analysis of roentgen rays was performed with a DRON-6 X-ray diffractometer with CuK_α radiation where a nickel filter was used. The movement step of the detector was 0.02°, the duration of intensity measurement in the step 0.5 s, the voltage 30 kV, the current 20 mA, the rotation angle 2θ, from 3 to 70°. The substances were identified by PDF-2 software.

FTIR analysis was performed with a Perkin Elmer FTIR system spectrometer. A tablet pressed in tablet form was used for the analysis (1 mg of substance mixed with 200 mg KBr). The analysis was implemented in the main range of the IR spectrum from 400 to 4000 cm⁻¹ [16].

The optical microphotographs were taken on a Leica DM500 optical-biological microscope. One gram of the crystalline solid phase was placed on a glass plate, onto which drops of water were dripped.

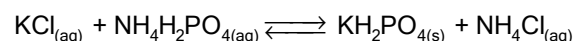
Density is an important characteristic of LCF. It represents the weight of the fertilizer solution in g/cm³. 1 g/cm³ = 1 metric ton/m³. The two most common means to determine the density of a fertilizer solution are:

- the hydrometer: an easy to use instrument, it is immersed in the fertilizer solution and the density is read directly on its scale in units of g/cm³;
- by laboratory analysis with three replicates: the average weight of 10 cm³ of the fertilizer solution determined on an exact scale.

Densities in the present study were measured by using method b in the same conditions for each liquid solution. Other properties (viscosity, pH, corrosivity) of the liquid solutions were measured by standard physicochemical methods [17], using a capillary Ostwald viscometer tube VPZ-2 (capillary section size 1.31 mm) and a HANNA instruments pH 211 pH meter with a HI1131B glass electrode.

Experimental procedure

The solid phase has been obtained carrying out a conversion reaction between potassium chloride and ammonium dihydrophosphate:



at temperatures of 20, 40, 60 and 80 °C. The reaction was carried out for 8 h at different temperatures in both saturated salt solutions (according to their solubility at 20 °C) and the refractive index values were investigated (Figure 2). It was judged that equilibrium was reached after 5 h, as after that the refractive index of the liquid fraction reached final value and ceased changing. The solid phase (crystalline potassium dihydrophosphate) was obtained by filtering the mixture through a vacuum glass filter and drying it in a drying oven. The liquid phase, consisted of K^+ , NH_4^+ , Cl^- and PO_4^{3-} , was separated from reaction products. After separation of crystalline potassium dihydrophosphate, it was appropriate to investigate how the liquid phase may be used as LCF. The chemical composition of the liquid phase, determined by chemical methods, is presented in Table 1. To increase nitrogen concentration in liquid solutions, ammonium nitrate, urea and sodium hydroxide were used. The crystallization temperature was determined by cryscopy-polythermal method. Solubility in the temperature range from 5 to 25 °C was investigated, as the solutions were cooled until crystallization occurred and then heated very slowly with continuous stirring, until the last crystal dissolved. A series of solutions of different concentrations of $NH_4NO_3(s)$, $CO(NH_2)_2(s)$ and $NH_4OH(aq)$ were cooled, and a certain number of crystals formed in each solution as a result. With adding

of $NH_4OH(aq)$ to the solution, the temperature of crystallization increased and the solutions were cloudy and not stable, even at room temperature. Therefore, $CO(NH_2)_2$ was used and better results were obtained. The influence of $CO(NH_2)_2$ on all properties (pH, density, viscosity and crystallization temperature) of liquid solutions was presented in the International conference of Lithuanian Society of Chemistry [18]. This work was continued with NH_4NO_3 in order to get even better results.

RESULTS AND DISCUSSION

As shown in Table 1, after the separation of $KH_2PO_4(s)$, the concentration of nitrogen in the liquid is very low, remains somewhat the same (varies from 1.19 to 1.45%) and increases with an increase in conversion temperature. The concentration of other elements does not depend on conversion temperature and varies: P_2O_5 - from 1.96 to 2.93%; K_2O - 14.15 to 16.02% and Cl - from 13.42 to 15.71%. The data shows that concentration of potassium and chlorine is the highest. Variation of plant nutrients in the liquid phase depends on the composition of the crystallized solid phase under those conditions. The results indicate that the composition of the solid phase is not greatly influenced by temperature. The equilibrium between solid and liquid phases and their composi-

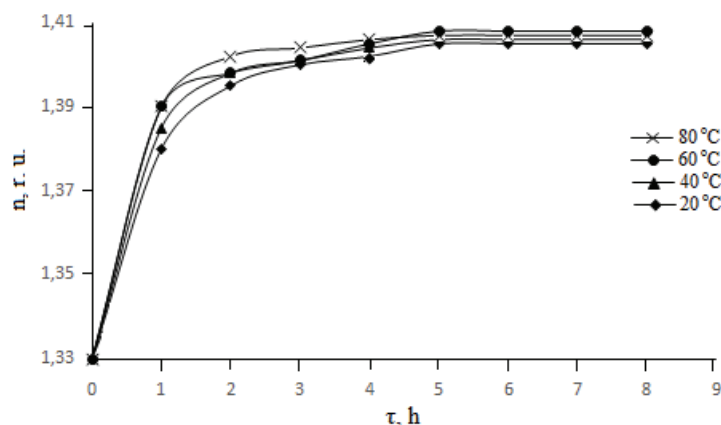


Figure 2. Dependence of the refractive index on the reaction time at 0.8:0.2 molar ratio of starting materials at different temperatures.

Table 1. Chemical composition of the liquid phase, obtained during conversion

t/ °C	Nutrient concentrations in the liquid phase ^a , %					
	N	P	P ₂ O ₅ ^b	K	K ₂ O ^c	Cl
20	1.19	1.11	2.55	13.29	16.02	13.52
40	1.26	1.28	2.93	12.84	15.46	13.42
60	1.39	1.14	2.61	12.41	14.96	15.71
80	1.45	0.83	1.91	11.75	14.15	13.63

^aUp to 100% other elements present in the liquid phase (O, H); ^bP recalculated into P₂O₅ according to the fertilizer regulations; ^cK recalculated into K₂O according to the fertilizer regulations

tions after conversion reaction depends on the ratio of the initial materials, conversion temperature and solubility of salts. The solid phase can be composed of potassium dihydrogen phosphate, potassium hydrogen phosphate, potassium chloride, ammonium chloride, ammonium phosphate or mixtures of these salts. With increased temperature, the solid phase composition varied as follows: concentration of phosphorus (21.66-20.19%) and potassium (33.40-27.14%) increased, while concentration of nitrogen (0.58-1.89%) and chlorine decreased, when the mole ratio of potassium chloride to ammonium dihydrophosphate was 0.8:0.2. A part of data obtained from the study of solid phase concentration was published in our articles [19,20].

For solutions to be used as LCF, it is necessary to determine their crystallization temperature. Because the concentration of nitrogen was very low, and this element is very important for plants, a nitrogen component, ammonium nitrate, was added. The crystallization polytherm of the liquid solutions, obtained during conversion reactions at temperatures of 20, 40, 60

and 80 °C with different concentrations of ammonium nitrate, was investigated (Figure 3). In the liquid system, interaction takes place between K^+ , NH_4^+ , Cl^- and PO_4^{3-} and with decreasing temperature a different solid phase crystallizes. As it is shown in Figure 3, all polytherms are in standard form and different salts crystallize in different parts of the curves. They have only one eutectic (breaking) point, which meets the lowest temperature of crystallization and the biggest concentration of NH_4NO_3 in these systems.

The temperature of crystallization is lowest (4 °C) at 7% of NH_4NO_3 concentration, as shown in Figure 3a. Accordingly, crystallization temperature is 6 °C and the concentration of NH_4NO_3 is 8% in Figure 3b, 5 °C and 8.3% in Figure 3c and 5 °C and 7% in Figure 3d. In each part of the polytherm, before and after the eutectic point, a different solid phase crystallized, whose chemical composition was investigated. The solid phase with 2 and 14% ammonium nitrate obtained during crystallization was analyzed using chemical and instrumental methods of analysis (Table 2).

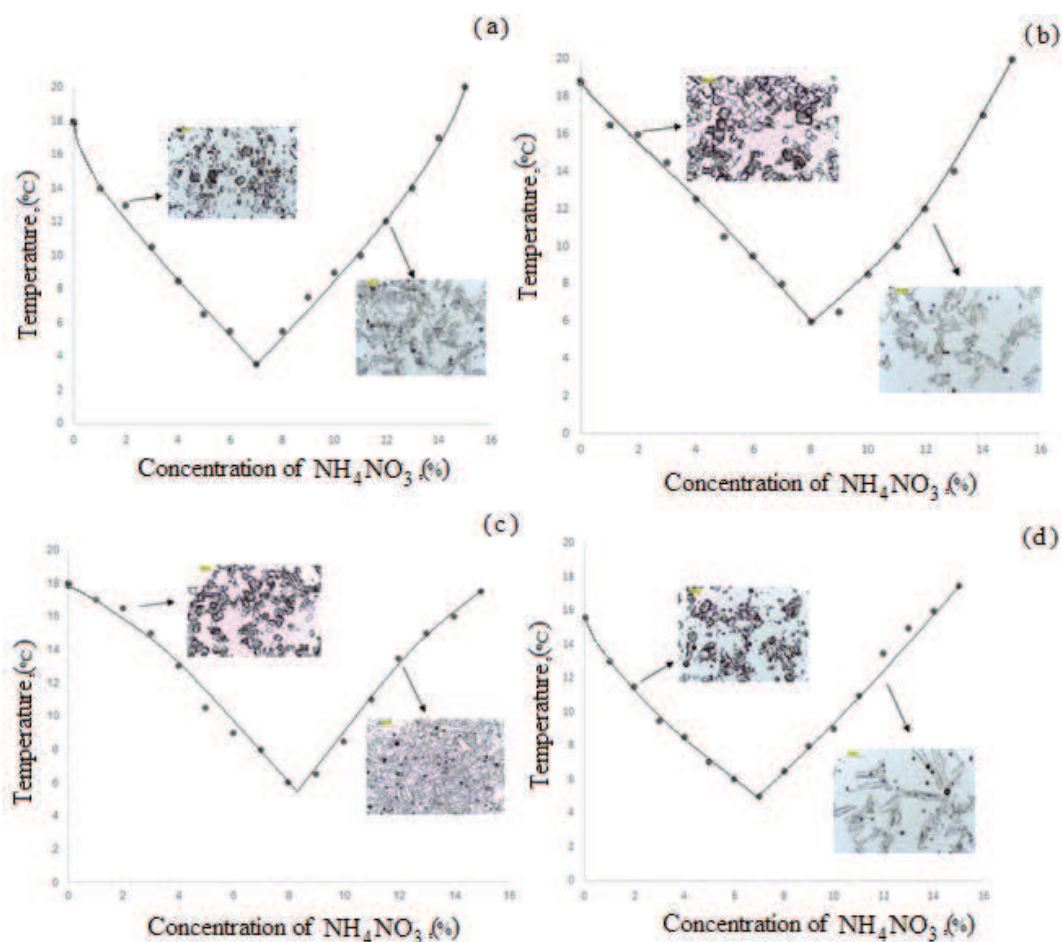


Figure 3. The crystallization polytherm of the liquid solutions, obtained during conversion reaction at temperatures of: a) 20, b) 40, c) 60 and d) 80 °C. Optical microscopic image of powder solid phase.

Table 2. Chemical composition of the solid phase with 2 and 14% ammonium nitrate obtained at crystallization

<i>t</i> / °C	Composition of the solid phase, %		
	N	K	Cl
Before breaking point (with 2 % NH ₄ NO ₃)			
20	1.08	45.20	40.67
40	1.34	49.68	45.05
60	1.38	43.87	43.86
80	1.71	41.67	45.06
After breaking point (with 14 % NH ₄ NO ₃)			
20	11.14	32.17	0.71
40	11.47	35.67	0.58
60	12.18	37.32	0.59
80	12.68	42.32	1.17

The results indicate that the composition of the solid phase is not dependent on conversion temperature, but dependent on ammonium nitrate concentration. The data in Table 2 shows that the chemical composition (especially K and Cl) of the obtained solid phase with 2% NH₄NO₃ is very different from the solid phase with 14% NH₄NO₃. It can be consequently stated that the solid phase with 2% ammonium nitrate is very close to the composition of potassium chloride. The solid phase with 14% NH₄NO₃ is the closest to the composition of potassium nitrate. Optical microscopic images have confirmed different chemical compositions of the solid phase (Figure 3). As we can see in Figure 3, the crystals before the eutectic point contain KCl and in all cases the crystals after breaking point contain KNO₃.

On the basis of the data acquired by X-ray analysis (Figure 4, I), it is safe to claim that all compositions of the solid phase are closest to ammonium

nitrate, not dependent on conversion temperature. X-ray images presented below show most of the peaks that are characteristic of ammonium (interplanar spacings - d : 0.5309, 0.3383, 0.3055, 0.2639 and 0.2369 nm).

In accordance with the data in literature [21], in our opinion, the X-ray diffraction pattern of a fertilizer show that with addition of ammonium nitrate at 14% in Figure 4, II, all compositions of the solid phase can be attributed to the potassium nitrate. The X-ray images below show most of the peaks that are characteristic to potassium nitrate (interplanar spacings - d : 0.5309, 0.3383, 0.3055, 0.2639 and 0.2369 nm).

Image (Figure 4, I) shows that one peak of low intensity (0.3149 nm) has been identified that can be related to potassium chloride. Identification of this reacting material supports the results of the chemical analysis showing a certain amount of Cl⁻ found in the solid phase. In the case of different temperatures (Figure 4, I, II), identical compounds have been identified in the X-ray pictures, with varying peak intensities.

IR spectra (Figure 5) have been created in order to analyze the crystallized solid phases in more detail. IR spectra in Figure 5 (I) show absorption bands in the 3134.10 - 3141.58 cm⁻¹ part, and these bands can be related to valence vibrations of the NH₄⁺ functional group [22]. These groups confirm the presence of inorganic salts (*e.g.*, NH₄NO₃) in the crystallized solid phase.

In accordance with data in literature [23], in our opinion, the vibrations in the spectrum part 1661.58-1665.99 cm⁻¹ can be attributed to the NO₃⁻ group. Considering the studies presented in the same scientific paper, it can be stated that the peaks of abs-

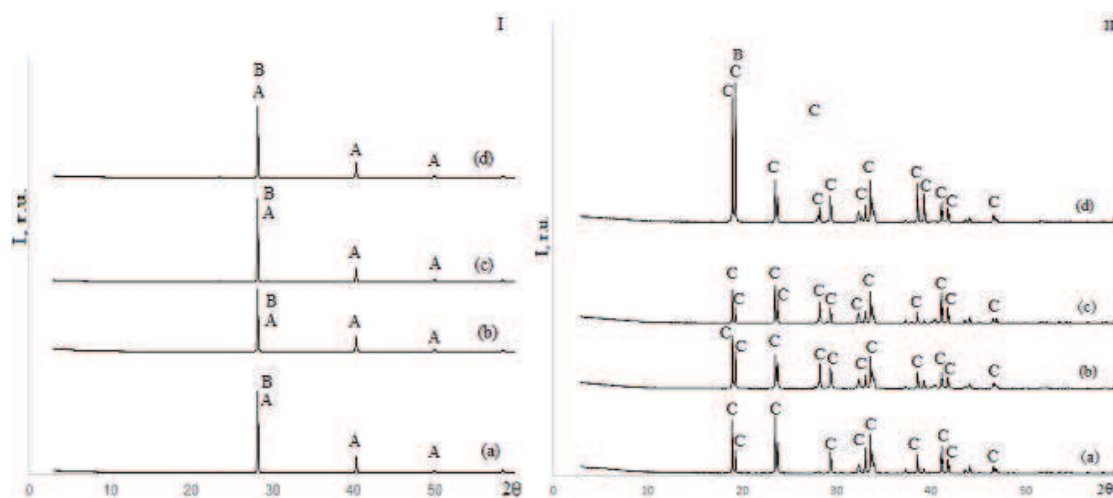


Figure 4. The XRD analysis curves of the solid-crystalline phase, crystallized from liquid solutions: I - with 2% NH₄NO₃; II - with 14% NH₄NO₃, obtained during conversion reaction at temperatures (°C): a) 20; b) 40; c) 60 and d) 80. A - NH₄NO₃; B - KCl; C - KNO₃.

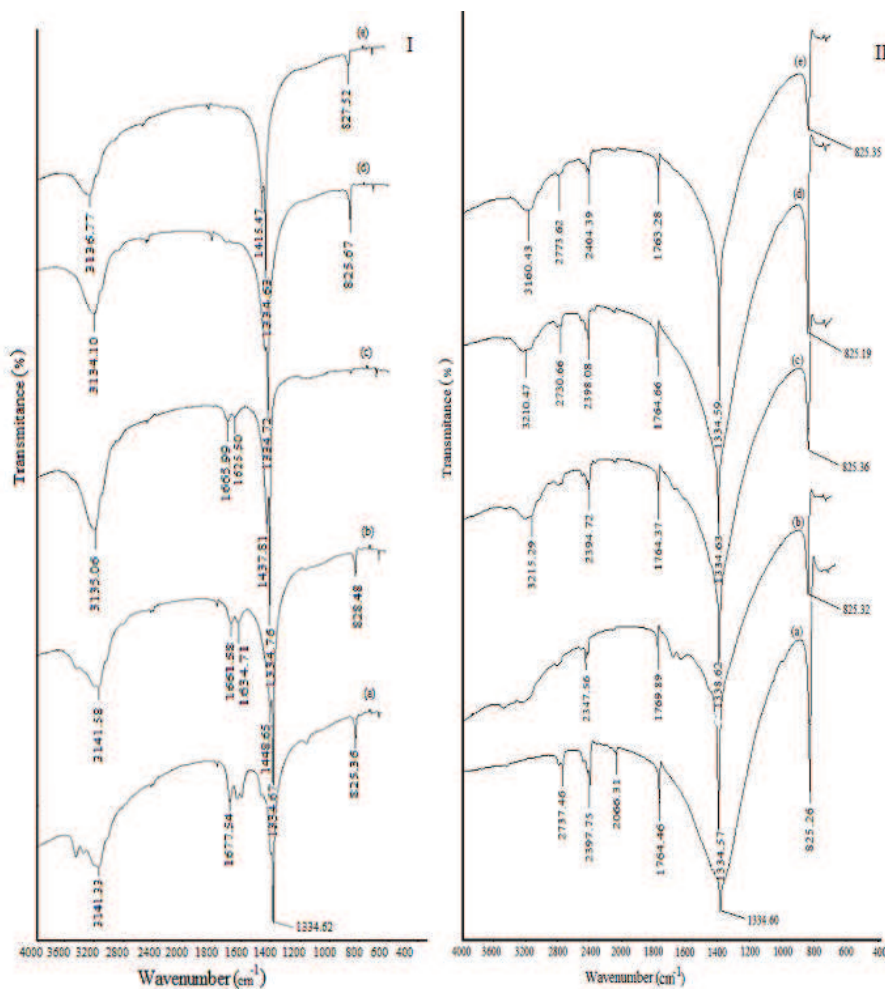


Figure 5. IR spectrums of the solid-crystalline phase, crystallized from liquid solutions: I - with 2% NH_4NO_3 ; II - with 14% NH_4NO_3 , obtained during conversion reaction at temperatures ($^{\circ}\text{C}$): a) 20; b) 40, c) 60 and d) 80. I(a) - pure NH_4NO_3 ; II(a) - pure KNO_3 .

orption bands in the $1415.47\text{--}1437.81\text{ cm}^{-1}$ and $1334.62\text{--}1334.76\text{ cm}^{-1}$ parts are specific to valence vibrations of the NH_4^+ and NO_3^- functional groups.

Absorption bands in the $825.36\text{--}828.48\text{ cm}^{-1}$ part of all spectra can be attributed to valence vibrations of the NO_3^- functional group [23]. It can be seen that in all cases the spikes of the absorption bands do not change their position. These vibrations infer the presence of inorganic salt (NH_4NO_3) in the obtained solid phases.

IR spectra in Figure 5 (II) show absorption bands in the $3210.47\text{--}3215.59\text{ cm}^{-1}$ part, and these bands can be related to valence vibrations of the N-H functional group [22].

In addition, peaks of absorption bands beside the $2347.56\text{--}2404.39\text{ cm}^{-1}$ part of spectrum can be attributed to valence vibrations of NH_3^+ and this agrees with the published data [24]. In accordance with data in the previously mentioned publications, the spectrum parts $1334.57\text{--}1338.62\text{ cm}^{-1}$ and $825.19\text{--}825.35\text{ cm}^{-1}$ can be attributed to the NO_3^- groups.

These groups confirm the presence of inorganic saline (e.g., KNO_3) in the crystallized solid phase.

Viscosity and density values are very important in selecting equipment for LCF production and use (Figure 6). Therefore, the viscosity and density of liquid solutions obtained during the conversion reaction at different temperatures, with added NH_4NO_3 , was determined. It can be stated that with increased concentration of NH_4NO_3 , the viscosity and density also increased.

The pH of liquid compound solutions, obtained during the conversion reaction at different temperatures with NH_4NO_3 was also determined (Table 3). It can be stated that with increased concentration of NH_4NO_3 , pH is changing independently of conversion temperature and varies in values from 3.34 to 4.31. Such solutions are classified as weakly corrosive solutions and can corrode iron and steel but do not corrode stainless steel.

The most important characteristic of liquid fertilizers is their chemical composition, which can be

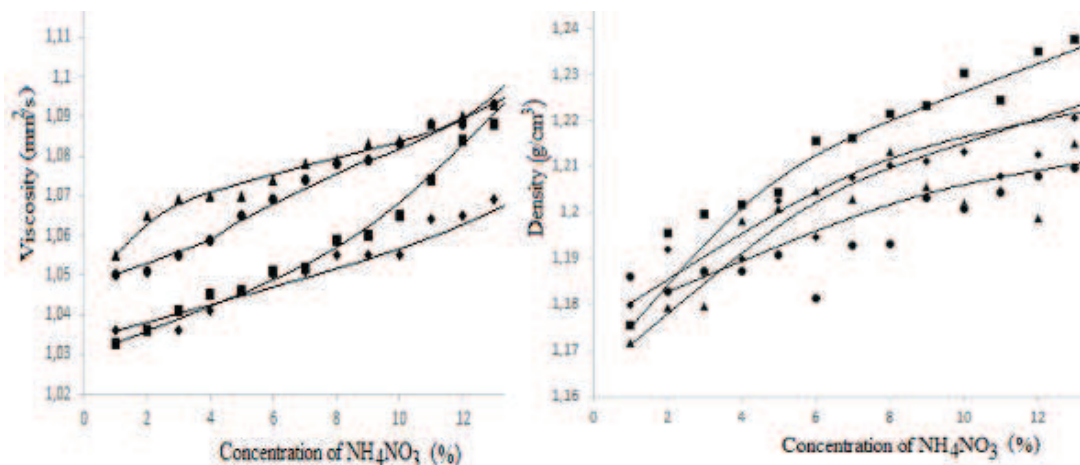


Figure 6. Viscosity (a) and density (b) of liquid solutions, obtained during conversion reaction at different temperatures (°C): ♦ 20; ■ 40, ▲ 60; ● 80 with adding NH_4NO_3 .

determined with an isotherm at temperatures of 0 or 10 °C (depending on the weather conditions of production and use). Other investigated physicochemical properties of the liquid phase with added NH_4NO_3 such as pH, viscosity and density, do not differ much than when the liquid phase was without NH_4NO_3 . Therefore, according to the available data in the investigated system, the LCF composition with the lowest crystallization temperature (5 °C), which corresponds to 8% NH_4NO_3 , was selected (Figure 3c).

Table 3. pH of liquid solutions, obtained during conversion reaction at different temperatures with NH_4NO_3

Concentration of NH_4NO_3 , %	Temperature of conversion, °C			
	20	40	60	80
1	4.02	3.80	3.77	4.15
2	4.08	3.65	3.43	4.04
3	4.08	3.82	3.43	3.93
4	3.98	4.01	3.50	4.12
5	3.91	3.76	3.44	3.94
6	3.90	3.75	3.72	3.89
7	4.02	3.92	3.46	3.87
8	3.96	3.93	3.94	3.88
9	3.90	3.75	3.79	3.86
10	3.85	3.73	3.48	3.84
11	3.86	3.68	3.43	3.81
12	4.25	3.68	3.38	4.31
13	3.85	3.67	3.37	3.82
14	3.69	3.79	3.35	3.97
15	3.79	3.69	3.34	4.07

Assessment of all properties (chemical composition, temperature of crystallization, pH, density and viscosity) led to the conclusion that the solution which remains after conversion at temperature of 60 °C and

includes 8% of NH_4NO_3 is the most appropriate liquid solution to be used for the production of LCF. Corrosivity studies were performed using this liquid and using carbon and stainless steels (Figure 7). The measurements were obtained measuring mass change.

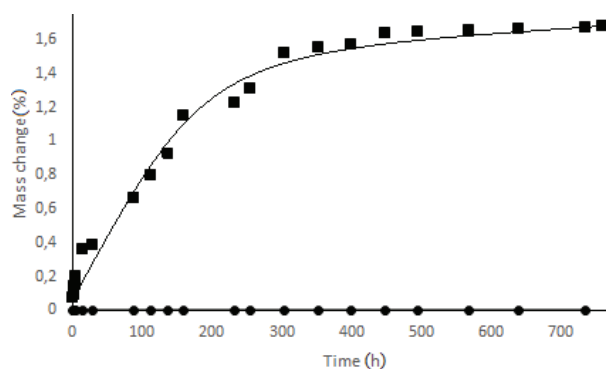


Figure 7. The corrosivity of the steels in the liquid solutions, obtained during conversion reaction at 60 °C temperature with 8% NH_4NO_3 : ■ - carbon steel (ST3); ● - stainless steel (35S22099).

It was determined that the carbon steel corroded and stainless steel did not and that confirmed the data in the literature [8] about the influence of LCF's pH on steel. The highest corrosion rate on carbon steel was during the first 300 h and then the corrosion rate stabilized. Maximum mass change in 760 h in carbon steel was 1.7%.

CONCLUSIONS

Chemical analysis methods determined that after KCl and $\text{NH}_4\text{H}_2\text{PO}_4$ conversion, there were K^+ , NH_4^+ , Cl^- and PO_4^{3-} in the liquid phase. The crystallization temperature was determined and the crysco-polythermal method established that in all

cases after conversion the crystallization temperature of the solutions was above 0 °C. When $\text{NH}_4\text{NO}_{3(s)}$ was added, the crystallization temperature was the lowest, but still positive. The crystallization temperature (8.3 °C) corresponds to a higher concentration (8%) of NH_4NO_3 . Such solutions can be used to produce liquid fertilizers to be used during the summer for cereal crops. Basic properties (pH, density, viscosity and corrosivity) of liquid fertilizer were determined. They were all very similar in all cases and varied in the following way: pH - from 3.34 to 4.31; density - from 1.17 to 1.24 g/cm³ and viscosity - 1.03 to 1.107 mm²/s. It was determined that liquid fertilizer is corrosive to carbon steel and not corrosive to stainless steel.

REFERENCES

- [1] K. Lubkowski, Pol. J. of Chem. Tech. **18** (2016) 72-80
- [2] L. Oldham, Extension Service, Fluid Fertilizers, <https://extension.msstate.edu/sites/default/files/publications/publications/p1466.pdf> (accessed 18 January 2016)
- [3] P. Baranov, Liquid Fertilizers, <http://encyclopedia2.thefreedictionary.com/Liquid+Fertilizers> (accessed 10 May 2016)
- [4] R. Staff, Everything You Need To Know About Organic Fertilizer, <http://www.rodalorganiclife.com/garden/everything-you-need-know-about-organic-fertilizer> (accessed 6 September 2015)
- [5] Z. El hattab, L. Zerrouk, A. Jourani, M. Kaddami, Fluid Phase Equilibria. **354** (2013) 47-53
- [6] W. Beckmann, Crystallization, Wiley-VCH, Weinheim, 2013, p. 35
- [7] H.M. El-Sayed, Viscosities and Densities of Some Multi-Component Regular Liquid Solutions at Different Temperature Levels, PhD Thesis, 2010, p. 8
- [8] F.G. Lorca, Properties of Solid and Liquid Fertilizers, Fertigation In Olive Plantation, <http://www.gatfertilizers.com/properties-of-solid-and-liquid-fertilizers> (accessed 2 May, 2016)
- [9] J.W. Mullin, Crystallization, Butterworth, Heinemann, 2001, p. 600
- [10] M. Hu, Q. Zhai, Z. Liu, S. Xia, J. Chem. Eng. **48** (2003) 1561-1564
- [11] K.S. Kwok, H.C. Chan, Ch.K. Chan, Ind. Eng. Chem. Res. **44** (2005) 3788-3798
- [12] M.E. Taboada, O.A. Rocha, T.A. Graber, J. Chem. Eng. **46** (2001) 308-311
- [13] Standards Association of Lithuania. Lithuanian standard: Fertilizers-Determination of ammoniacal nitrogen, 2009, EN15475-2009.
- [14] N.T. Crosby, N. Patel, The Fertilizers (Sampling and Analysis) regulations // Agriculture. Statutory Instruments, Laboratory of the Government Chemist, London, 1991, p. 7
- [15] Standards Association of Lithuania. Lithuanian standard: Fertilizers - Determination of the water-soluble potassium content, 2009, EN15477-2009
- [16] R. Šiaučiūnas, K. Baltakys, A. Baltušnikas, Instrumental analysis of the silicate materials, Vitae Litera, Kaunas, 2007, p. 56
- [17] M. Kimura, Testing methods for fertilizers. Basic Concepts and Industrial Applications, www.famic.go.jp/ffis/fert/obj/TestingMethodsForFertilizers2013 (accessed 12 January 2016)
- [18] K. Jančaitienė, R. Šlinkšienė, Properties of liquid-multi-component systems, International conference of Lithuanian society of chemistry, Vilnius, Lithuania, 2016, p. 65
- [19] K. Jančaitienė, R. Šlinkšienė, Pol. J. of Chem. Tech. **18** (2016) 1-9
- [20] K. Jančaitienė, R. Šlinkšienė, Chem. **25** (2014) 89-95
- [21] M. Hafez, I. S. Yahia, S. Taha, Acta Phys. Pol., A **127** (2015) 734-740
- [22] N. Nakamoto. Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, New York, 1991, p. 521
- [23] H.B. Wu, M.N. Chan, Ch.K. Chan, Aero Science Tech. **41** (2007) 581-588
- [24] D.M. Dooslin, G. Jayam, M. Johnson, P. Selvarajan, Int. J. Inn. Res. Ad. Eng. **2** (2015) 123-131.

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NAUČNI RAD

RAVNOTEŽA ČVRSTO-TEČNO U TEČNIM ĐUBRIVIMA

Tečna đubriva su vodeni rastvori soli kojim se hrani zemljište, koja sadrže azot, fosfor, kalijum i ponekad kalcijum, magnezijum i mikronutritiente. Ovaj rastvor praktično nema nerastvornih ostataka, sadrži elemente u potpuno iskoristljivim oblicima i predstavlja veoma brzo i visoko efikasno đubrivo. Za formiranje tečnih đubriva važno je proceniti ravnotežu u sistemu čvrsto-tečno, jer njihova osnovna svojstva - koncentracija i temperatura kristalizacije - zavise od nje. Cilj ovog rada je bio da se odrede svojstva tečnog viškomponentnog sistema (K^+ , NH_4^+ , Cl^- , PO_4^{3-}). Ovaj tečni viškomponentni sistem, koji je dobijen kao nusproizvod u konverziji KCl i $NH_4H_2PO_4$, može se koristiti kao tečno đubrivo. U radu su istraženi za hemijski sastav i fizičko-hemijska svojstva tečnih đubriva, kao što su temperatura kristalizacije, pH, gustina, viskozitet i korozivnost. U cilju povećanja koncentracije azota dodat je i amonijum nitrat. Sastav čvrste faze dobijene kristalizacijom identifikovan je metodama hemijske i instrumentalne analize (radiografija, infracrvena molekularna apsorpciona spektroskopija i optička mikroskopija). Rezultati pokazuju da su sva svojstva tečnih đubriva najbolja kada je koncentracija NH_4NO_3 u tečnim rastvorima 8%.

Ključne reči: rastvorljivost, ravnoteža, čvrsto, tečno, konverzija, đubriva.