

Synthesis and study of the agrochemical properties of urea salts with nitric and orthophosphoric acid

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Abstract. The paper presents the results of the synthesis, IR spectroscopic and agrochemical study of the products of adduct formation (internal salts) of urea with nitric and orthophosphoric acids. It has been established that the synthesized substances are hygroscopic, readily soluble in water. IR spectral data indicate that, depending on the “acid : urea” ratio in the final products CO, NH₂, urea groups and acid molecules are involved in the formation of various compositions: [H₂O⋯(NH₂)₂C(OH)⁺⋯ONO₂] and [O₂N-O⋯⁺H₃N(H₂N)C(OH)⁺⋯O-NO₂], [-NH₃⁺⋯-O-P(O)(OH)₂] and [-C(OH)⁺⋯-O-P(O)(OH)₂] salt bridges. The solubility of poorly soluble salts, which are included in a series of metal ion compounds accumulating in the soil under the action of urea mononitrate, has been studied. According to the results of an agrochemical study of the effect of synthesized urea salts on the digestibility of P₂O₅ by Tr-B and citric acid in the soil, an increase in these parameters under the action of urea dinitrate and diorthophosphate was found to be within 8.26–11.52 and 8.28–9.52%, relative to control 1.07 and 0.787%, respectively. **Key words:** molecular complex, nitric acid, phosphoric acid, urea, hydrogen bond, IR spectroscopy, digestibility, agrochemistry, Trilon-B, citric acid.

1 Introduction

With prolonged use of arable land in agriculture due to the irrational use of mineral fertilizers, the total content of nutrients (P₂O₅, CaO, MgO ...) in the soil exceeds the norm, and their efficiency becomes very low, so their digestibility decreases to a minimum. Along with this, in case of violation of agrotechnical measures, crop rotation, and so on, year after year in the soil, the accumulation of slightly soluble compounds of heavy metal ions of different categories of toxicity occurs, which are not sufficiently decomposed with moderate acidity or reduced activity of humic components. As a result, despite the sufficient (and sometimes supernormal) consumption of mineral fertilizers, the productivity and fertility of arable lands remain low, the results obtained are economically unprofitable

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and the manufactured products do not meet environmental quality standards, and the geomechanical and hydroreclamation characteristics of the soil are brought to the brink of critical [1-4].

Based on the totality of all the above, there is, most likely for a long time, the need to create conditions and take measures to improve the efficiency of applied or already excessively applied (accumulated due to low digestibility of nutrients) fertilizer in the land. One of these methods is the cultivation of the land with a sufficient amount of organic fertilizers, however, the possibilities for this are limited due to their inadequacy on the scale of our republic.

Therefore, for these purposes, it is necessary to introduce into the soil substances consisting of components of organic and inorganic origin, which give the soil additional necessary acidity and provide the plants with the necessary nutrients (N_2 , P_2O_5). Although this may be the subject of criticism from specialists in “additional pumping” of the earth with chemicals, this approach should be taken as one of the ways to solve the existing problem [1,2]. Taking into account all of the above, the main functions of such substances should be: stimulating an increase in the solubility of excessively accumulated mineral fertilizer and the digestibility of its nutrient components in the soil; contribute to the dissolution or decomposition and entrainment (washout) from the soil of accumulated poorly soluble compounds of toxic heavy metal ions; slowing down the processes of denitrification, i.e. preventing the removal of ammonium nitrogen from the soil under the influence of climatic factors [2-4].

In our opinion, urea salts with nitric and phosphoric acids, more specifically, urea nitrates and orthophosphates of various compositions (in 1:1, 1:2 and 1:3 molar ratios) can exhibit similar properties. For this purpose, we have synthesized and studied some agrochemical properties of nitric and orthophosphoric acid salts of urea in relation to the soils of the Bukhara region, the results of which are presented in this communication.

2 Synthesis of nitrate and orthophosphate salts of urea

Salts of mononitrate (MNU), dinitrate (DNU) and trinitrate (TNU) of urea were synthesized by mixing aqueous solutions (30 g urea, 40.0, 80 ml and 120 ml of 56%, $\rho = 1.40 \text{ g/cm}^3$) in ratios 1:1, 1:2 and 1:3 $CO(NH_2)_2:HNO_3$ and evaporation of the resulting solutions at 80 °C isolated white polycrystalline substances, highly soluble in water.

Urea orthophosphates of composition 1:1 and 1:2 were synthesized by dissolving 18 g (0.3 mol) of urea in 100.2 and 200.4 ml of 25.6% ($\rho = 1.150 \text{ g/cm}^3$) solutions of orthophosphoric acid at room temperature. Evaporation of the resulting transparent solutions at 110-120°C isolated white solid, highly hygroscopic substances.

All synthesized substances are molecular compounds (internal salts) or addition complexes in terms of composition and type of their formation from the starting materials.

Diffractiongrams were taken on an XRD-6100 diffractometer (Shimadzu, Japan) in the solid state, IR spectra were taken in tablets with KBr on an IRTracer-100 spectrometer (Shimadzu, Japan). Photometric measurements were carried out using a UV-1280 spectrophotometer (Shimadzu, Japan) at $\lambda=560 \text{ nm}$; melting points were determined on a Stuart SMP10 instrument.

3 IR spectroscopic study of the synthesized nitric and phosphate salts of urea

3.1 Study of nitrate salts of urea

The formation and individuality of urea mono-, di- and trinitrate are proven and identified by determining the melting point (t_{mp}^0): 135 °C (MNU), 148 °C (DNU), 144 °C (TNU), which differ from each other and from the original urea, as evidenced by comparison diffractogram (Fig.1. a, b) and IR spectra (Fig.2. a-c).

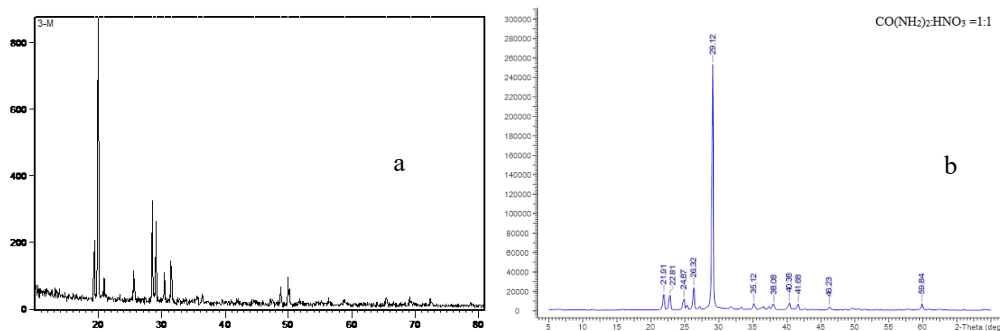


Fig. 1. Diffractograms: a) urea, b) mononitrourea.

Let us note the most distinctive feature in the IR spectra of MNU and DNU (Fig. 2 a-c), in comparison with the spectrum of the original urea, in addition to the main characteristic absorption bands $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$, $\nu(\text{CN})$, $\nu(\text{NO})$, $\delta(\text{HNH})$, $\delta(\text{ONO})$ corresponding frequencies is the appearance of new absorption bands in the frequency range 2800-2100 cm^{-1} . In the MNU spectrum, these bands include 7 weakly intense bands with a maximum at 2400.04 cm^{-1} . The totality of these detected bands is due to the presence of the $[\text{H}_2\text{O}\cdot(\text{NH}_2)_2\text{C}(\text{OH})^+\cdots\text{ONO}_2]$ fragment in the MNU composition. Judging by their frequencies and the change in the nature of the manifestation of the $\nu(\text{C}=\text{O})$ band of urea, it was concluded that protonated amino and carbonyl groups are present in the DNU fragment with the formation of a hydrogen bond and salt bridges of the type: $[\text{H}_2\text{O}\cdots(\text{NH}_2)_2\text{C}(\text{OH})^+\cdots\text{ONO}_2]$ и $[\text{O}_2\text{N}\cdot\text{O}^-\cdots\text{H}_3\text{N}(\text{H}_2\text{N})\text{C}(\text{OH})^+\cdots\text{O}\cdot\text{NO}_2]$, which is the result of an increase in ratio $\text{CO}(\text{NH}_2)_2:\text{HNO}_3$ up to 1:2 in favor of the acid reagent [5].

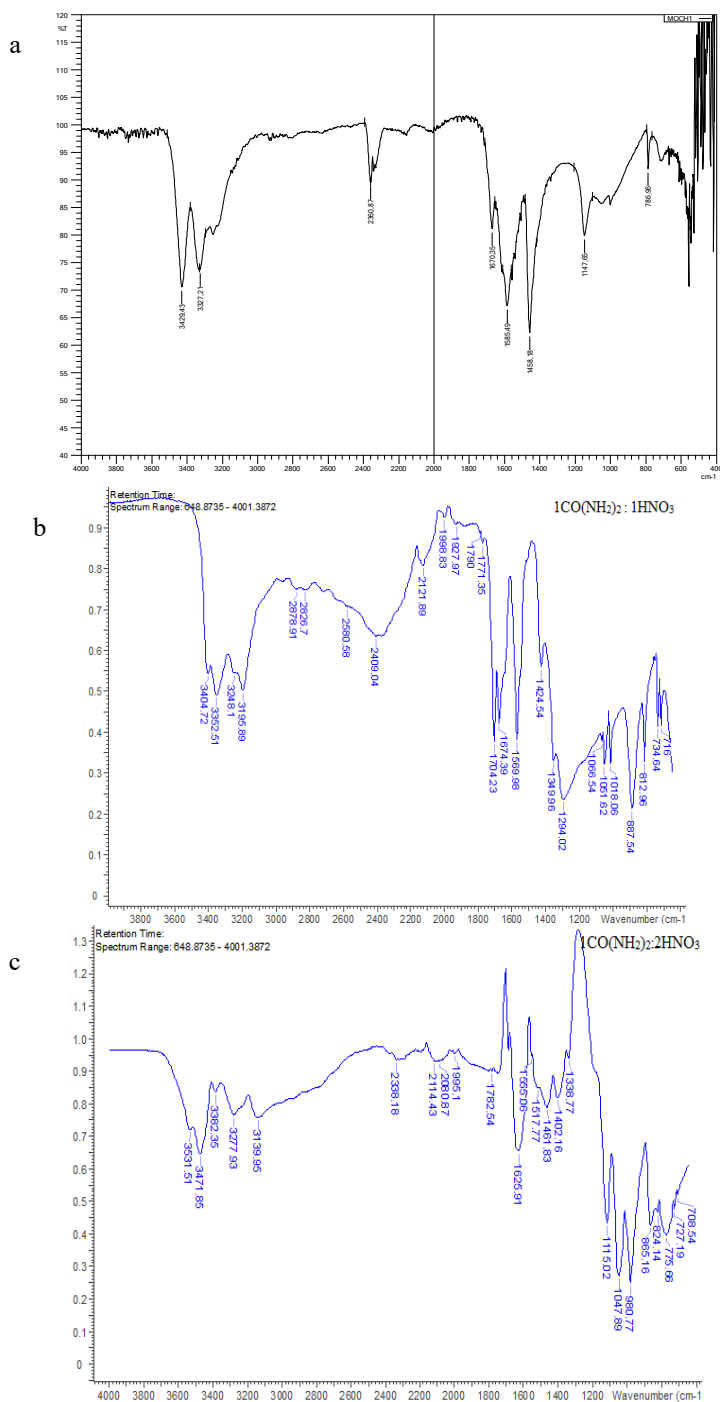


Fig.2. IR spectra: a) urea, b) mononitrourea, c) dinitrourea.

3.2 The study of urea phosphate salts

Urea orthophosphates with the composition $\text{CO}(\text{NH}_2)_2:\text{H}_3\text{PO}_4=1:1$ and $1:2$ were synthesized. The compositions and structures of the obtained samples of urea phosphates were studied by XRD and IR methods. This is evidenced by a comparison of the IR spectra of urea and the obtained salts, in which with the main characteristic absorption bands of C=O and NH_2 groups of urea (Fig. 1a), in the spectra of the obtained salts (Fig. 3 a, b) a number of new weakly and moderately intense bands appear with a maximum at 2345.64 cm^{-1} . This row of bands at 2815.51 ; 2620 , 2375.47 ; 2345.64 cm^{-1} are due to the occurrence $[-\text{NH}_3^+\cdots\text{O}-\text{P}(\text{O})(\text{OH})_2]$ and $[-\text{C}(\text{OH})^+\cdots\text{O}-\text{P}(\text{O})(\text{OH})_2]$, salt bridges between urea and phosphoric acid molecules. Note that, depending on the molar ratio of $\text{CO}(\text{NH}_2)_2 : \text{H}_3\text{PO}_4$, phosphate urea salts of composition $1:1.1:2$ are formed and their IR spectra differ in the manifestation of absorption bands in the frequency range of $1000\text{--}500 \text{ cm}^{-1}$, where valence and deformation vibrations of P-O and O-P-O bonds (Fig. 3-a,b) [5].

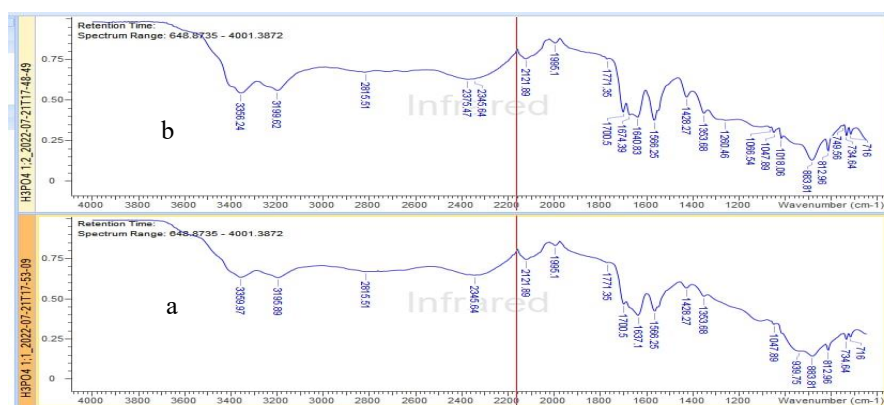


Fig. 3. IR spectra: Orthophosphate salts of urea: a) $\text{CO}(\text{NH}_2)_2:\text{H}_3\text{PO}_4 = 1:1$, b) $\text{CO}(\text{NH}_2)_2:\text{H}_3\text{PO}_4 = 1:2$.

4 Study of the solubility of poorly soluble salts under the action of urea nitrate

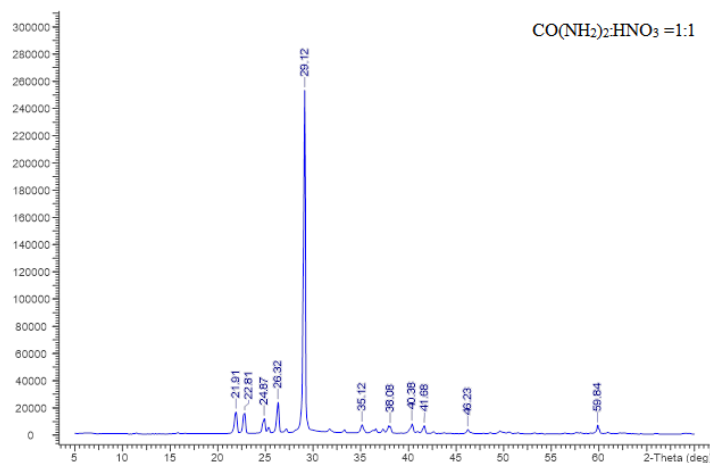
This part of the report presents the results of studying the solubility of various poorly soluble compounds under the action of urea mononitrate (MNU). Judging by the composition, it can be seen that when the salt of urea nitrate is dissolved in water, an acidic environment ($\text{H}^+ + \text{NO}_3^-$) is created, which contributes to the dissolution or decomposition of acid-sensitive, poorly soluble salts of metal ions. On the other hand, there are three donor (O, N, N) atoms in the composition of the dissolved urea molecule, due to which it enters into a donor-acceptor interaction with metal ions to form complex compounds, thereby acting as a ligand ensures the irreversibility of the process of dissolution of compounds of metal ions. This leads to the opinion that by introducing nitric acid salts of urea into the soil, it is possible to create a chemically active acidic and complexing environment, in which many accumulated poorly soluble compounds undergo change and dissolution to varying degrees. As a result, it becomes possible to reduce the content of poorly soluble compounds and turn them into a useful form of existence in the soil [2-4]. With this in mind, we carried out a preliminary exploratory study of the dissolution of a number of compounds of metal ions under the action of urea mononitrate, the results of which are shown in Table 1.

Table 1. The results of the study of the dissolution of some compounds of metal ions under action of urea mononitrate (MNU).

No.	Compound	Weight, g	Solubility		The content of the main chemical elements in solution (g / l)			
			By weight, g	%	Ca	P	Fe	Cu
1	CaHPO ₄	3.0	1.526	50.86	0.434	0.348	-	-
2	Fe ₂ O ₃	3.0	0.290	9.7	-	-	0.202	-
3	CaSO ₄	3.0	0.078	2.6	0.230	-	-	-
4	(Cu(OH)) ₂ CO ₃	3.0	1.902	63.4	-	-	-	1.102

The solubility of selected compounds was studied at T:W=1:3 (3 g compound: 9 ml of MNU solution, C=1 mol/l) at 25°C. According to the results of the experiment, it was found that the studied compounds, depending on the composition and chemical nature, dissolve differently under the action of MNU. Sufficiently greater solubility is characterized by copper hydroxocarbonate, which can be considered one of the forms of existence of copper ions in the soil and, according to the anionic component, is prone to acid decomposition. The next compound with noticeable solubility is disubstituted calcium phosphate. The choice of this substance is purposeful, and the result obtained can be perceived as the most valuable in terms of the fact that this compound is one of the forms of existence of the phosphate fertilizer introduced into the soil [1-4]. Comparison of diffractograms (Fig. 4 a, b) indicates that

Iron (III) oxide turned out to be relatively slightly soluble, although this compound is not the main form of the existence of iron compounds as a trace element in the soil, the solubility of this compound has been studied as one of the most stable form of iron in the soil. Under the action of urea mononitrate, calcium sulfate, that is, the gypsum component of the soil, turned out to be slightly soluble (stubborn). From this it follows that in order to dissolve the gypsum components of the soil, either a more concentrated solution of urea nitrate is needed, or another reagent that contributes to a greater dissolution of calcium sulfate.



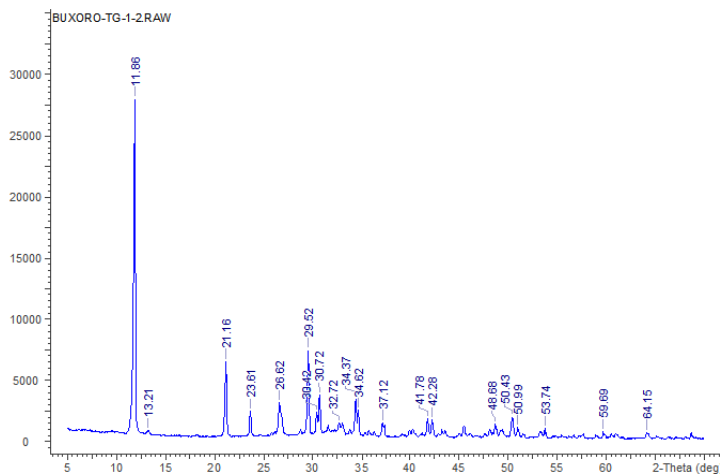


Fig. 4. Diffractograms: a) $\text{CO}(\text{NH}_2)_2 \text{HNO}_3$, b) $\text{CaHPO}_4 + \text{CO}(\text{NH}_2)_2 \text{HNO}_3$.

5 Study of the digestibility of P_2O_5 under the action of nitric and phosphate salts of urea

In order to study the effect of nitrate and phosphoric acid salts of urea on the digestibility of P_2O_5 , as the main nutrient component of phosphorus fertilizers in the soil, laboratory experiments of a preliminary exploratory nature were carried out. A soil sample was chosen for the experiment Vobkent district, Bukhara region. The experiments were carried out according to the method [7], the results of which are given in Table 2. It can be seen from these experiments that the soil sample treated with distilled water, which was used as a control, is characterized the lowest digestibility of P_2O_5 1.07% for Trilon-B and 0.787% for 2% citric acid.

After treatment with solutions of nitrate and phosphate salts of urea, the indicators for both types of P_2O_5 digestibility of the studied soil sample are not consistent. From the data of Table 1 it can be seen that among nitrate salts, the greatest influence on the increase in the assimilation of P_2O_5 by Tr-B by 8 times, compared with the control soil sample, is exerted by a solution of urea dinitrate, and the remaining compositions are 1:1 and 1:3 slightly have this property. The low value in the case of urea mononitrate can be explained by a twofold lower content of nitric acid, and for urea trinitrate such a conclusion cannot be made, i.e., in the discovered fact, another yet unknown factor has an influence [2,6].

Table 2. The results of studying the digestibility of P_2O_5 under the action nitric and phosphate salts of urea.

The digestibility of P_2O_5	Studied samples					
	Soil + H_2Odis	Soil +MNU	Soil+DNU	Soil+ TNU	Soil +MPU	Soil +DPU
P_2O_5 TR-B, %	1.07	1.20	8.26	2.70	1.37	11.25
P_2O_5 citric acid, %	0.787	1.061	8.28	0.959	0.990	9.52

Phosphoric acid salts of urea show the same character of activation of P_2O_5 digestibility by Tr-B. It should be noted that when using urea phosphate salts, we assumed that these compounds can have a higher effect on increasing the digestibility of P_2O_5 [6.8]. However, as it can be seen from the data in Table 2, this assumption had a rather weak effect on the expected results in improving the digestibility of P_2O_5 as a whole. Of the studied salts, urea

diorthophosphate increases the digestibility of P_2O_5 according to Tr-B to 11.56%, i.e. only 3.3% more than the analogous salt of urea with nitric acid, but 11 times more than the control soil sample. Another variety of urea phosphate salt (composition 1:1) had a weak stimulating effect on the absorption of P_2O_5 by Tr-B. Both nitrate and phosphoric acid salts of urea show similar influences and tendencies on the increase in the assimilation of P_2O_5 by citric acid of the studied soil sample (Table 2).

6 Conclusion

Nitric and phosphoric acid salts of urea of various compositions, well soluble in water, have been synthesized. It has been experimentally established that aqueous solutions of nitrate salts of urea are capable of dissolving various poorly soluble compounds of metal ions, which are included in the series of heavy metal ions accumulating in the soil. According to the results of preliminary exploratory laboratory studies, it was revealed that the solutions of synthesized salts to varying degrees affect the digestibility of P_2O_5 for Tr-B and citric acid in the soil, while urea dinitrate and diorthophosphate show the highest efficiency in the range of 8.26 - 11.52 and 8.28 - 9.52%, relative to the control soil sample, which has values of 1.07 and 0.787%, respectively.

Acknowledgments

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