# STABILITY OF UREA SOLUTIONS IN PRESENCE OF BUFFERING ADDITIVES

Mladen E. Lilov

*University of Chemical Technology and Metallurgy*
*8 Kliment Ohridski blvd., Sofia 1756, Bulgaria*
*E-mail: mladen_lilov@abv.bg*

*Received 25 November 2020*
*Accepted 15 March 2021*

## ABSTRACT

*The stability of urea water solutions, containing 20 % nitrogen in presence of phosphates: [$NH_4H_2PO_4$+ $(NH_4)_2HPO_4$], [$KH_2PO_4$+$K_2HPO_4$] and citric buffering additives: potassium citrate, citric acid and glycine has been studied. The study was carried out at temperature 298.15 K for a period of 150 days by periodic measurement of the electrical conductivity and pH of solutions. It was found that the most suitable composition for liquid fertilizer among the urea water solutions with additives of citrate buffers is the urea solution with additive of citric acid as well as mixture of citric acid and glycine. A possibility was shown to study the behavior of urea solutions through periodical measurement of two very easy to register and very precise parameters - pH and conductivity during the prolonged storage and the possibility for stabilizing of these solutions.*
Keywords: *urea solution decomposition, stabilized urea solution, stabilizing additives, pH, conductivity.*

## INTRODUCTION

The main problem in using of urea solutions for foliage of plants is that, during the storage for a long time, the urea decomposes partially into ammonium cyanate, which, on its part, into ammonium carbonate. This results in the gradually increasing of solution pH and formation of non-dissociated ammonia ($NH_3$) [1]. The presence of ammonia is the reason for the appearance of leaf „scorching", „burning" after spraying with such solution and, in some case, to scorch them [2, 7]. The accumulation of ammonia results also in increasing of pH value of the solution, which hinder the jointly applying of some secondary nourishing elements and microelements because of their deposition at these conditions.

In order to solve the problem of the urea solution non-stability, it is necessary to find suitable additives, which can to slow down or suppress these undesired processes and to prepare solutions, stable for a prolonged storage.

A lot of experiments have been carried out to solve this problem. In most cases, the authors sought to establish the mechanism of urea decomposition by performing kinetic analysis. These studies were carried out with relatively dilute solutions of urea (0.1 N) at high temperatures, between 60°C and 100°C. No data on the behavior of the urea in concentrated solution under the conditions concerning liquid fertilizers, namely the long-term storage at ambient temperature.

The urea decomposition to isocyanic acid and ammonia in presence of ethyleneglycol has been studied [3]. A method for stabilizing solutions, containing urea, and designed for foliar application by addition of chlorides or nitrates of calcium, magnesium and zinc (single or in combination) has been patented [4]. A method was described [5] to produce neutral, clear and stable solutions through acid catalyzed reaction of urea and acetaldehyde or mixtures of propionaldehyde and acetaldehyde. The products of this process are suitable as nitrogen-containing solutions for foliar application, which are not phytotoxic.

The urea is widely used in cosmetic and pharmaceutical products [6], but its non-stability gives rise to some difficulties. In spite of very small degree of urea decomposition, the undesired effects as ammonia odor and increasing of pH value are very important. The stability of urea solutions has been studied [8] as a function of temperature (25°C, 40°C and 60°C), pH (3.11 - 9.67), the initial urea concentration (2.5, 5 и 10 %) and the presence of lactate, phosphate and citrate buffer, all of them with pH 6.0. The urea concentration was defined through periods of 3, 7 and 14 days. The lowest degree of decomposition was received at pH 6.4 - 7.4. The urea stability decreases with increasing of the temperature at all studied pH values.

It was proved, that the urea can be maintained in stable condition [9] by adding into solution of small quality of lactone. Among all studied lactones, gama-butirolactone has shown the best results. Lin et al. [10] have studied the change of cyanate concentration in 8M urea solutions, buffered with 0.1 M sodium citrates, phosphates and borates, during 14 days at room temperature. The best results were received with sodium citrates at pH 5 and 6. At the presence of the citrate buffer at pH 6 the cyanate concentration has been kept less than 0.5 mM.

The effect of ammonium-containing buffers for inhibit the protein/peptide carbamilation in urea solutions was studied by Sun et al. [11]. The ammonium hydrogen carbonate and the other two ammonium-containing buffers – ammonium acetate and trietilammonium hydrogen carbonate, have shown the best inhibiting efficiency compared to the phosphate buffer and Tris-HCl buffer.

In our previous work [12] we studied the stability of the aqueous urea solutions (20 % N) in presence of additives of inorganic acids $HNO_3$, $H_2SO_4$ and $H_3PO_4$, and their ammonium salts $NH_4NO_3$, $(NH_4)_2SO_4$ and $NH_4H_2PO_4$. It was established, that from the three studied acids, only the phosphoric acid can be used as a stabilizing additive. The solution 20 % N + 0.39 % $H_3PO_4$ can be preserved during 5 - 6 months without exceed the critical value of pH = 7.5. The three studied ammonium salts $NH_4NO_3$, $(NH_4)_2SO_4$ and $NH_4H_2PO_4$ even in minimal amounts (3 % w/w) are very suitable for the urea solution stabilizing. The solutions are with stable pH value and insignificant change of the conductivity during the time.

## EXPERIMENTAL

### Materials

Urea (technical grade) with composition: 46 % N, free $NH_3$ = 0.02 %, biuret = 0.75 %; citric acid ($C_6H_8O_7$) (Merck); $C_6H_5K_3O_7.H_2O$ (Merck); glycine ($C_2H_5NO_2$) (Merck); $NH_4H_2PO_4$ (Merck); $(NH_4)_2HPO_4$ (Merck); $KH_2PO_4$(Merck); $K_2HPO_4$ (Merck) are used.

### Methods

Urea and additives were dissolved in distilled water to prepare solutions, containing 20 % N. 100 mL samples of the solutions were transferred into 100 mL plastic bottles which were sealed and maintained at a constant temperature at 298.15 ± 0.5 K for 150 days. The bottles were removed at regular time intervals (days), and the pH and specific conductivity were measured. The solution density was determined at 298.15 K with a 25-mL pycnometer and Mettler Toledo balance with an accuracy of 0.0001 g. Conductivity was measured with a BOECO model conductivity meter. pH was measured with a calibrated pH meter Mettler Toledo, model FE 20. Determination of urea content was done using the standard procedure described in ISO/DIS 22241-2, Annex B. The ammount of free ammonia (alkalinity) in the urea was measured according to the standard procedure described in ISO/DIS 22241-2, Annex D. Determination of the biuret content was doneusing standard procedure described in ISO/DIS 22241-2, Annex E.

## RESULTS AND DISCUSSION

### Urea solution with additives of citrate buffers

During this study the effect of the citrate buffer additives: citric acid, potassium citrate and (citric acid + glycine) was determined. For the purpose the following solutions were prepared:

20 % N+ 3 % , $\rho$ = 1.1320 g $cm^{-3}$

20 % N+ 3 % potassium citrate, $\rho$ = 1.1335 g $cm^{-3}$

20 % N+ 3 % (2 % citric acid + 1 % glycine), $\rho$ = 1.1313 g $cm^{-3}$.

Data about the changes in pH and in conductivity of the urea water solutions in presence of citrate buffers is presented in Table 1 and on Figs. 1 and 2. The change in pH values of the three studied solutions during the time, presented in Fig. 1 are totally identical. In almost the whole period pH increase linearly with a small decreasing at t = 10 days. In the end of the studied period the highest is the pH value of the solution with potassium citrate as additive (pH = 5.28) and the lowest – with additive of citric acid (pH = 4.15). With respect to the pH the three solutions a restable for a storage period minimum 5 month sand they can be used as leaf fertilizers.

Table 1. Effect of time on pH and conductivity of urea solutions in presence of additives of citrate buffers.

| Day | Urea +citric acid | | Urea +potassium citrate | | Urea +citric acid+glycine | |
|---|---|---|---|---|---|---|
| | pH | σ, mS cm$^{-1}$ | pH | σ, mS cm$^{-1}$ | pH | σ, mS cm$^{-1}$ |
| 0 | 2.89 | 1.60 | 3.91 | 4.47 | 3.25 | 1.62 |
| 10 | 2.86 | 1.76 | 3.91 | 4.71 | 3.24 | 1.79 |
| 20 | 3.07 | 2.09 | 4.17 | 5.25 | 3.50 | 2.13 |
| 30 | 3.19 | 2.41 | 4.28 | 5.78 | 3.61 | 2.46 |
| 40 | 3.28 | 2.74 | 4.38 | 6.30 | 3.71 | 2.80 |
| 50 | 3.37 | 3.07 | 4.47 | 6.81 | 3.80 | 3.14 |
| 70 | 3.52 | 3.73 | 4.65 | 7.75 | 3.99 | 3.81 |
| 90 | 3.68 | 4.38 | 4.82 | 8.61 | 4.19 | 4.47 |
| 110 | 3.84 | 5.04 | 4.98 | 9.40 | 4.38 | 5.14 |
| 130 | 3.99 | 5.69 | 5.13 | 10.07 | 4.57 | 5.80 |
| 150 | 4.15 | 6.34 | 5.28 | 10.64 | 4.76 | 6.46 |
| | ΔpH=1.26 | Δσ=4.74 | ΔpH=1.37 | Δσ=6.17 | ΔpH=1.51 | Δσ=4.84 |

The curves, presented in Fig. 2, show the increasing of electrical conductivity with the time. The particularity here is that the lines corresponding to the additions of citric acid and to the mixture (citric acid + glycine) coincide and are with lower values of conductivity compared to the additive of potassium citrate. According to the presented data the most suitable composition of liquid fertilizer among the studied here is urea solution with additive of citric acid and of (citric acid + glycine).

**Urea solutions (20 % N) with additives of phosphate buffers**

In this study the effect of additives of phosphate buffers: ($NH_4H_2PO_4$ + $(NH_4)_2HPO_4$), ($KH_2PO_4$+$K_2HPO_4$) and ($NH_4H_2PO_4$+citric acid) was determined. For the purpose the following solutions were prepared:

Urea + 3 % ($NH_4H_2PO_4$ + $(NH_4)_2HPO_4$) (2 % $NH_4H_2PO_4$ + 1 % $(NH_4)_2HPO_4$), ρ = 1.1359 g cm$^{-3}$

Urea + 3 % ($KH_2PO_4$ + $K_2HPO_4$) (1.5 % $KH_2PO_4$ + 1.5 % $K_2HPO_4$), ρ = 1.1389 g cm$^{-3}$

Urea + 3 % ($NH_4H_2PO_4$ + citric acid) (1 % $NH_4H_2PO_4$ + 2 % citric acid), ρ = 1.2330 g cm$^{-3}$

The alterations in pH and conductivity of the water urea solutions in presence of additives of phosphate buffers are presented in Table 2 and on Figs. 3 and 4.

As can be seen on Fig. 3, pH of the urea solutions with additives of ammonium and potassium phosphates increase very slow during the whole studied period. More different is the alteration of pH of urea solution with additive of ($NH_4H_2PO_4$ + citric acid). Here, the

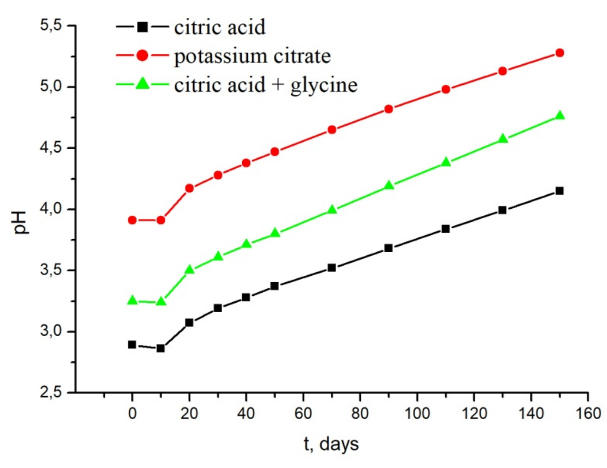


Fig. 1. Alteration of pH values of urea solutions with additives of citrate buffers with time at T = 298.15 K.

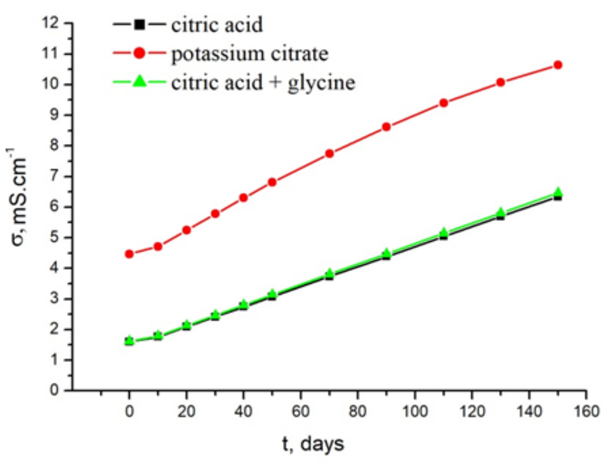


Fig. 2. Alteration of the electrical conductivity of the urea solutions with additives of citrate buffers with time at T = 298.15 K.

Table 2. Effect of time on pH and conductivity of urea solutions in presence of additives of phosphate buffers.

| Day | Urea + $NH_4H_2PO_4$ + $(NH_4)_2HPO_4$ | | Urea + $KH_2PO_4$ + $K_2HPO_4$ | | Urea + $NH_4H_2PO_4$ + citric acid | |
|---|---|---|---|---|---|---|
| | pH | σ, mS $cm^{-1}$ | pH | σ, mS $cm^{-1}$ | pH | σ, mS $cm^{-1}$ |
| 0 | 6.73 | 13.26 | 7.03 | 11.88 | 3.45 | 5.02 |
| 10 | 6.66 | 13.53 | 6.98 | 12.22 | 3.28 | 5.29 |
| 20 | 6.69 | 13.72 | 7.04 | 12.50 | 3.39 | 5.45 |
| 30 | 6.72 | 14.52 | 7.10 | 13.40 | 3.49 | 6.05 |
| 40 | 6.71 | 14.80 | 7.16 | 13.88 | 3.57 | 6.38 |
| 50 | 6.73 | 15.02 | 7.21 | 14.25 | 3.65 | 6.72 |
| 70 | 6.78 | 15.30 | 7.30 | 14.76 | 3.81 | 7.37 |
| 90 | 6.81 | 15.57 | 7.35 | 15.22 | 4.02 | 8.00 |
| 110 | 6.85 | 15.85 | 7.39 | 15.61 | 4.23 | 8.68 |
| 130 | 6.91 | 16.09 | 7.45 | 15.98 | 4.48 | 9.33 |
| 150 | 7.03 | 16.36 | 7.59 | 16.36 | 4.75 | 10.01 |
| | ΔpH = 0.30 | Δσ = 3.10 | ΔpH = 0.56 | Δσ = 4.48 | ΔpH = 1.30 | Δσ = 4.99 |

increase of this parameter with the time is stronger, but the final value pH = 4.8 is the lowest among the three studied additives.

Studying the alteration of electrical conductivity with the time, presented in Fig. 4, it can be seen that here again the additive of ($NH_4H_2PO_4$ + citric acid) is the most effective compared to the additives of ammonium and potassium phosphates and the differences between

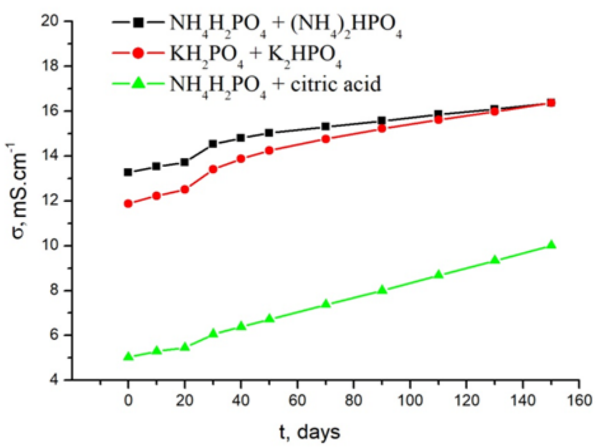


Fig. 3. Alteration of pH values of urea solutions with additives of phosphate with time at T = 298.15 K.

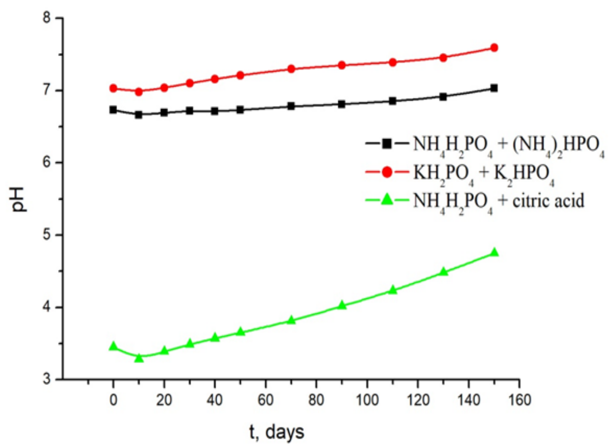


Fig. 4. Alteration of the electrical conductivity of the urea solutions with additives of phosphate buffers with time at T = 298.15 K.

them is quite big.

In our previous work [12] we studied the behavior of urea water solution (20 % N) without additives trough pH measurements and the conductivity for a period of 150 days. It was established, that during the time the solution pH at the beginning decreases from 9.22 to 8.60, goes through a minimum at 20-th day and after that lighly increases and goes to a constant value of 9.15.

Regarding the conductivity in the beginning of the process a sharp increase of this parameter is seen about 4 times for the first 20 days (от 242 to 783 μS $cm^{-1}$). This is due to the fast accumulation of ammonium cyanate in the solution during this period. With the time the concentration of ammonium cyanate goes through maximum and after that decreases. The reason for this phenomenon is that after the 60-th day an appreciable part of the ammonium cyanate in the solution hydrolyses in to $NH_4HCO_3$ and $(NH_4)_2CO_3$.

Comparing data, received in regard to the stability of the studied urea solutions without and with buffers it was established, that in the presence of buffering additives the increase of pH and the conductivity during the studied period of 150 days was considerably slowed down. This is a sure indication about hindering of the undesired processes of urea decomposition in water solutions, which obstruct their using as leaf fertilizers.

## CONCLUSIONS

On the base of the study carried out with respect to the stability of the urea water solutions (20 % N) in presence of phosphate $[NH_4H_2PO_4 + (NH_4)_2HPO_4]$, $[KH_2PO_4 + K_2HPO_4]$ and citrate buffer additives (potassium citrate, citric acid and glycine), was established:

The most suitable composition for liquid fertilizer among the urea water solutions with additives of citrate buffers is the urea solution with additive of citric acid as well as mixture of citric acid and glycine.

Studying the effect of additives of phosphate buffers it was established, that the additive of ($NH_4H_2PO_4$ + citric acid) is the most effective compared to the additives of ammonium and potassium phosphates, with a quite big difference between them.

A possibility was shown to study the behavior of urea solutions through periodical measurement of two very easy to register and very precise parameters - pH and conductivity during the prolonged storage and the possibility for stabilizing of these solutions. The obtained original results related to pH and electrical conductivity of stabilized foliar liquid fertilizers can be used to control and manage the technological process of their preparation and storage.

## REFERENCES

1. J.M. Bremner, Problems in the use of urea as a nitrogen fertilizer, Soil Use and Management, 6, 2, 1990, 70-71.
2. J. M. Bremner, Recent research on problems in the use of urea as a nitrogen fertilizer Nitrogen economy in tropical soils, 1995, 321-329.
3. A. Samuilov, A.R. Valeev, F.B. Balabanova, D.Ya. Samuilov, A.I. Konovalov, Quantum-chemical study on thermal transformations of urea in ethyleneglycol, Russian Journal of Organic Chemistry, 2013, 49, 1, 28-33.
4. WO1990011262A1, Stabilized urea based fertilizers for foliar applications, 1990.
5. US4591375A, Urea-acetaldehyde and urea-acetaldehyde-propionaldehyde solutions, 1986.
6. US 6,303,656 B1, Composition comprising urea and its uses in the field of cosmetics and/or dermatology, 2001.
7. J. Chris Stiegler , Michael D. Richardson, Douglas E. Karcher, Trenton L. Roberts, Richard J. Norman, Field-Based Measurement of Ammonia Volatilization Following Foliar Applications of Urea to Putting Green Turf, Crop Science, 51, 4, 2011, 1767-1773.
8. N. Panyachariwat, H. Steckel, Stability of urea in solution and pharmaceutical preparations, J. Cosmet. Sci., 65, 2014, 187-195.
9. US4672078A, Urea stabilized with a lactone in various pharmaceutical and cosmetic preparations, 1985.
10. M.-F. Lin, C. Williams, M.V. Murray, G. Conn, P.A. Ropp, Ion chromatographic quantification of cyanate in urea solutions: estimation of the efficiency of cyanate scavengers for use in recombinant protein manufacturing, J. Chromatogr. B, 803, 2004, 353-362.
11. S. Sun, J.-Y. Zhou, W. Yang, H. Zhang, Inhibition of protein carbamilation in urea solution using ammonium-containing buffers, Anal. Biochem., 446, 2014, 76-81.
12. Ml. Lilov, Pl. Kirilov, Stability of urea solutions in the presence of mineral acids and their ammonium salts, J. Chem. Technol. Metall., 54, 2, 2019, 319-325.