Journal of Chemical Technology and Metallurgy, 58, 2, 2023, 310-317

STUDY OF SOLUBILITY OF CH_3COOH - $CO(NH_2)_2$ - H_2O SYSTEM

Zhamshid Shermatovich Bobozhonov, Abdulaziz Abdumanop Ugli Sidikov,
Zhamshid Sultonovich Shukurov

The Institute of General and Inorganic Chemistry
Academy of Sciences of the Republic of Uzbekistan
Mirzo Ulugbek 77A, 100071 Tashkent, Uzbekistan
E-mail: jamshid_chem@mail.ru

Received 08 April 2022
Accepted 15 Otober 2022

ABSTRACT

The solubility of the components in the $CH_3COOH – CO(NH_2)_2 – H_2O$ system was studied by the visual-polythermal method in the temperature range from -28.0°C to 20.0°C. The phase diagram delimits the crystallization fields of ice, CH_3COOH, $CH_3COOH{\cdot}CO(NH_2)_2$ and $CO(NH_2)_2$. A solubility diagram has been constructed, a new urea acetate compound has been isolated and identified by chemical, X-ray phase and thermogravimetric methods of analysis.

Keywords: acetic acid, urea, urea acetate, physiologically active substance, visual polytherm, X-ray phase analysis.

INTRODUCTION

Interest in the study of solubility in the CH_3COOH – $CO(NH_2)_2$ – H_2O system is due to the practical importance of the initial components for agriculture. It is known that dicarboxylic acids and aliphatic amides, amines, aminoalcohols [1 - 5], as well as their derivatives, have biological activity [6, 7]. In addition, physiologically active compounds with herbicidal properties were obtained in the presence of sodium salt of monochloroacetic acid [8].

Previously, the solubilities of systems of acetic acids with monoethanolamine [9], diethanolamine, and triethanolamines [10] were studied and their physiological properties were confirmed in agrochemical tests [11 - 13]. The solubility and thermodynamic properties of aqueous systems containing urea are known from a number of studies [14 - 17].

It is known that the use of urea leads to an increase in the oil content in the seeds of a plant. Besides urea activates the action of the desiccant, as it binds heavy metals that are part of the chlorophyll molecule and thereby inactivates it. Suppression of chlorophyll formation at growth points suspends growth processes in plants, inhibits the activity of catalysis, and enhances the enzymatic activity of peroxidase [18, 19]. After treat of plants with urea, tissue respiration is sharply weakened. In addition, the use of components containing acetic acids and urea in the composition of the defoliant leads to an improvement in their defoliating properties [20 - 23]. The defoliation event is considered important for obtaining abundant and high-quality cotton harvests in agriculture [24, 25].

EXPERIMENTAL

Acetic acid grade "pfa" (GOST 61-75) 98 % was used and chemically pure urea salt grade "chemically pure" (GOST 6691-77).

To confirm the formation of the compound $CH_3COOH{\cdot}CO(NH_2)_2$ in the system, X-ray phase (Rigaku Miniflex 600, Japan) method was used [26] as well as thermal analysis (Linseis thermal analysis PT1610) [27].

The visual-polythermal method was used in the study. The crystallization temperatures of the solutions were determined using a glass mercury thermometer TN-6 with a measuring range from -30 to 60°C and an alcohol glass thermometer TL-15 with a measuring range from -100 to 20°C [28]. The pycnometric method (GOST 31992.1-2012) also was used to determine the density of solutions [29]. The content of urea was determined from amine nitrogen by the spectrophotometric method (GOST 20851); elemental analysis for carbon, nitrogen, and hydrogen was carried out according to (Zeiss EVO MA10) [30]. The viscosity of solutions was measured using a VTL viscometer, the pH of solutions was measured on a FE20 METTLERTOLEDO pH meter, and the refractive index on a digital refractometer (model PAL-BX/RI, ATAGO refractometer).

RESULTS AND DISCUSSION

The solubility and properties of the components of the acetic acid-urea-water system in a wide range of temperatures and concentrations were studied for the purpose of physico-chemical substantiation of obtaining physiologically active, nutritious, and also reducing the cruel action of chlorates compounds based on carboxylic acids and urea. The CH_3COOH - $CO(NH_2)_2$ - H_2O system was studied using ten internal incisions (Fig. 1). From these, incisions I-V were studied from the side of $CO(NH_2)_2$-H_2O to the peak of CH_3COOH, and incisions VI-X from the side of CH_3COOH-H_2O to the peak of $CO(NH_2)_2$. Based on binary systems and internal incisions, a polythermal solubility diagram for the CH_3COOH - $CO(NH_2)_2$ - H_2O system was constructed in the temperature range from -28.0 to 20.0°C. On the phase diagram of the condition of the system, the fields of crystallization of ice, acetic acid, urea acetate and urea are delimited. These fields converge at two triple points of the system.

The equilibrium composition of solutions at the double and triple points of the system and the corresponding crystallization temperatures were determined (Table 1). The first triple point corresponds to 60.2 % acetic acid, 2.6 % urea and 37.2 % water with a crystallization temperature of -28.0°C. In this case, the solid phase will consist of acetic acid, ice and urea acetate. The composition of the second tertiary point corresponds to 32.4 % acetic acid, 14.8 % urea and 52.8 % water, the crystallization temperature is -19.0°C, and the composition of the solid phase consists of urea, urea acetate and ice.

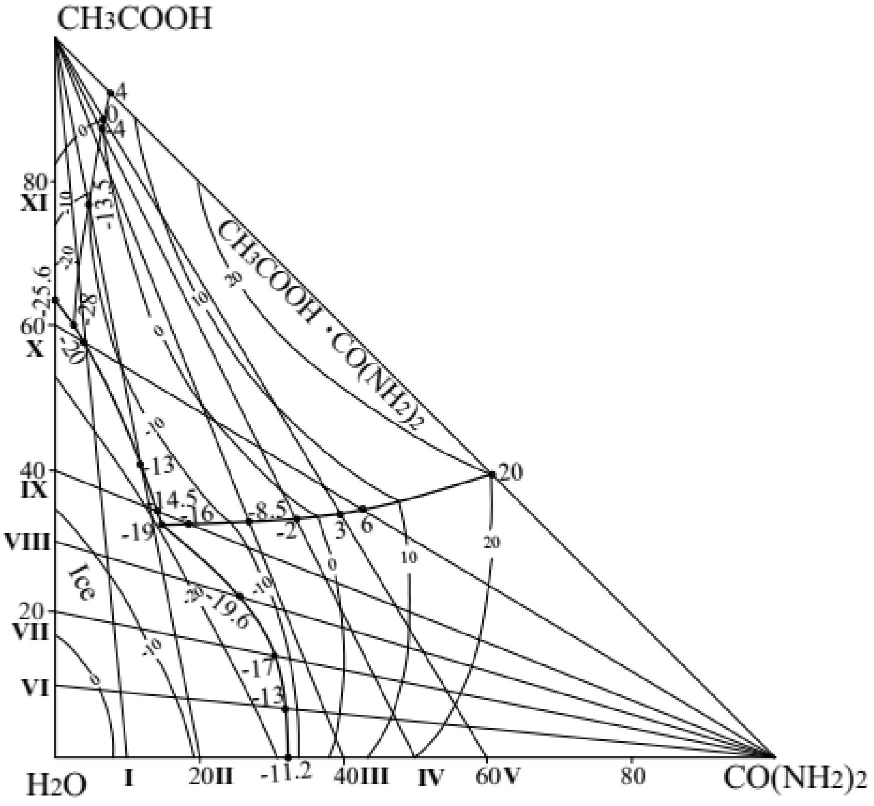

Fig. 1. Polythermal diagram of the solubility of the CH_3COOH - $CO(NH_2)_2$ - H_2O system.

On the phase diagram of the system, solubility isotherms are plotted every 10°C. The obtained results show that a new phase, the compound $CH_3COOH·CO(NH_2)_2$, has formed in the system. To identify a new compound in the system, physicochemical analyzes, such as X-ray phase, IR spectroscopic and thermal were carried out.

Changes of viscosity, density, pH, and light refractive index in systems with different ratios of components in [40 % CH_3COOH + 60 % H_2O] – $CO(NH_2)_2$, [50 % CH_3COOH + 50 % H_2O] – $CO(NH_2)_2$ and [60 % CH_3COOH + 40 % H_2O] – $CO(NH_2)_2$ were studied. Based on the obtained results, the “composition-properties” diagrams of the systems were constructed (Figs. 2 - 5).

Fig. 2 shows a diagram of the dependence of the pH of the medium on the concentration of urea in three 40 %, 50 % and 60 % aqueous solutions of acetic acid. From these three dependency curves, it can be seen that they have two turns each.

In the case of a 60 % aqueous solution of acetic acid (curve 1), two turns can be seen. The first turn is observed at 4 % (pH-medium 2.68), and the second at 42.2 % (pH-medium 4.92) concentrations of urea. Comparison of this curve with 2- and 3-curves (50 and 40 % aqueous solutions of acetic acid) shows that these turns are observed in relatively wide concentration and

Table 1. Double and triple points of system $Ca(ClO_3)_2·2CO(NH_2)_2$- $CH_2ClCOONa$ - H_2O.

Composition of the liquid phase (%)			The crystallization temperature, ºC	Solid phase
CH_3COOH	$CO(NH_2)_2$	H_2O		
63.8	-	36.2	-25.6	CH_3COOH + Ice
60.2	2.6	37.2	-28.0	$CH_3COOH + CH_3COOH·CO(NH_2)_2$ + Ice
57.6	4.0	38.4	-20.0	$CH_3COOH·CO(NH_2)_2$ + Ice
45.2	10.1	44.7	-15.0	
40.8	30.0	29.2	-13.0	
34.0	14.4	51.6	-14.5	
32.4	14.8	52.8	-19.0	$CH_3COOH + CH_3COOH·CO(NH_2)_2$ + Ice
22.2	26.0	51.8	-19.6	$CO(NH_2)_2$ + Ice
13.6	30.5	55.9	-17.0	
68	32.2	61.0	-13.0	
-	32.2	67.8	-11.2	
92.2	7.8	-	4.0	$CH_3COOH + CH_3COOH·CO(NH_2)_2$
88.8	6.9	4.3	0	
87.2	6.4	6.4	-2.0	
84.8	6.0	9.2	-4.0	
76.4	4.5	19.1	-13.5	
32.4	18.4	49.2	-16.0	$CH_3COOH·CO(NH_2)_2 + CO(NH_2)_2$
32.8	26.9	40.3	-8.5	
33.2	33.4	33.4	-2.0	
34.0	39.5	26.5	3.0	
34.6	42.2	23.2	6.0	
37.0	53.2	9.8	14.5	
39.4	60.6	-	20.0	

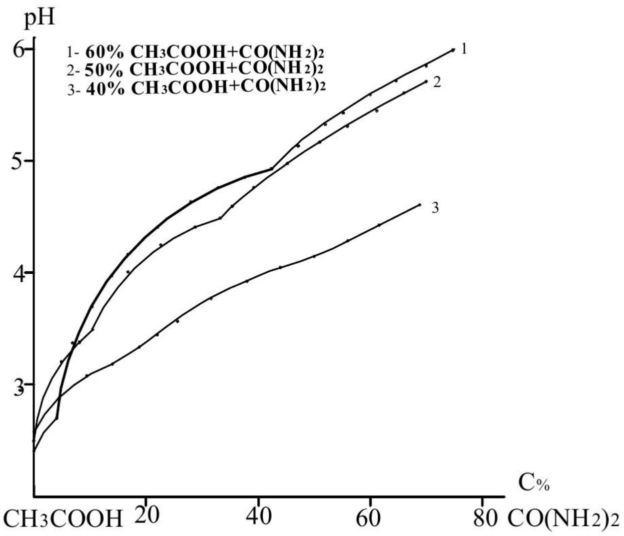

Fig. 2. Dependence of the pH of the medium on the concentration of urea in 40 %; 50 % and 60 % solutions of acetic acid.

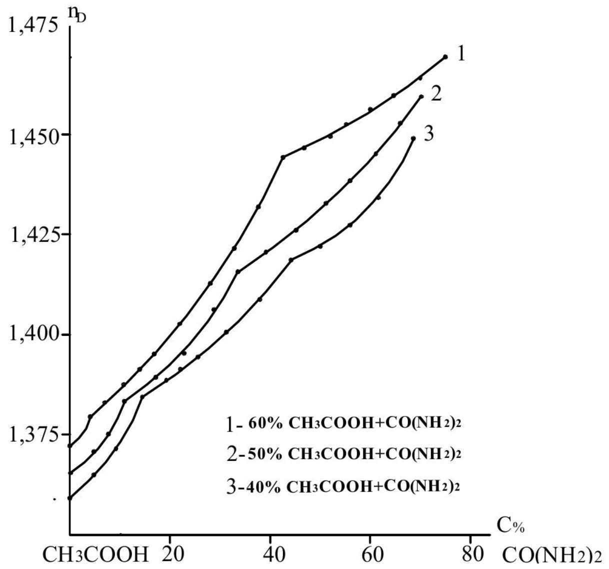

Fig. 3. Dependence of the refractive index on the concentration of urea in 40 %; 50 % and 60 % solutions of acetic acid.

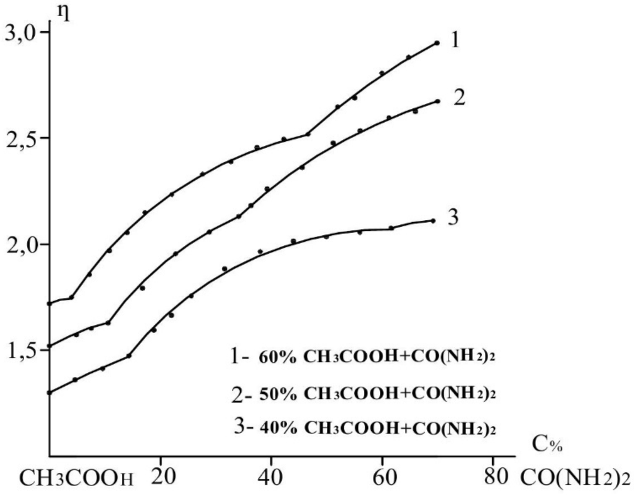

Fig. 4. Dependences of the viscosity of solutions on the concentration of urea in 40 %; 50 % and 60 % solutions of acetic acid.

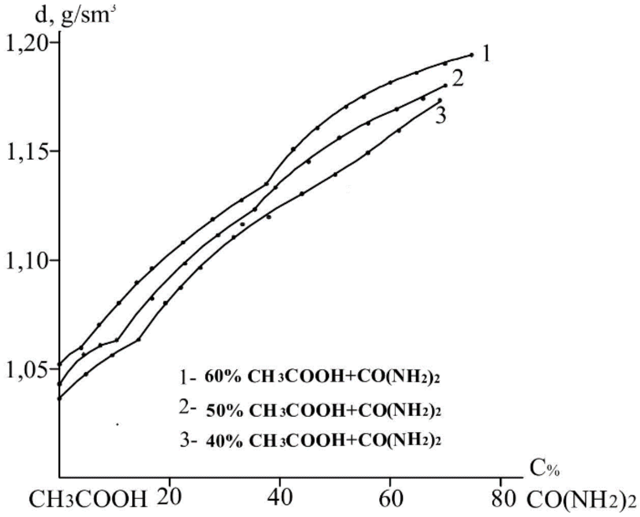

Fig. 5. Dependence of the density of the solution on the concentration of urea in 40 %; 50 % and 60 % solutions of acetic acid.

pH ranges. This shows that the use of a 60 % acetic acid solution for the production of urea acetate is the best option. During studying the dependence of the refractive index of light on the concentration in the system [40 % CH_3COOH + 60 % H_2O] – $CO(NH_2)_2$, [50 % CH_3COOH + 50 % H_2O] – $CO(NH_2)_2$ and [60 % CH_3COOH + 40 % H_2O] – $CO(NH_2)_2$ it was found that with an increase in the concentration of urea, the refractive index rises (Fig. 3). At the same urea content the values for the refractive index of light in the systems with higher acetic acid concentration are higher. It also can be noticed in the curves on Fig. 3 two turns which position is at similar urea concentration compared to the dependences established on the corresponding pH dependences.

Fig. 4 shows the graph "composition-viscosity" of 40, 50, 60 % aqueous solutions of acetic acid, depending on the concentration of urea. The curves of the dependence of the system [60 % CH_3COOH + 40 % H_2O] – $CO(NH_2)_2$ have 2 turns at different concentrations, which correspond to a viscosity value of 1.746 $mm^2\ s^{-1}$ at the first turns and 2.508 $mm^2\ s^{-1}$ at the second. Two small turns can also be seen on the viscosity curve of the [50 % CH_3COOH + 50 % H_2O] – $CO(NH_2)_2$ system, but turns were observed in a shorter concentration range than in the system of a 60 % aqueous solution of acetic acid. The first turn point had a viscosity of 1.612 $mm^2\ s^{-1}$ at 10.45 % urea concentration, and the second turn point had a viscosity of 2.198 $mm^2\ s^{-1}$ at a concentration of 33.2 %. Analysis of the viscosity diagram of the system [40 % CH_3COOH + 60 % H_2O] – $CO(NH_2)_2$ showed one small turn in the viscosity curve, which corresponded to 1.483 $mm^2\ s^{-1}$ at a urea concentration of 14.8 %.

Fig. 5 shows graphs of the dependence of the density of 40, 50, 60 % aqueous solutions of acetic acid on the concentration of carbamide, on which the density increases with increasing concentration. It can be seen that the density increases in the system [60 % CH_3COOH + 40 % H_2O] – $CO(NH_2)_2$ is from 1.052 to 1.195 g cm^{-3} and in the system [50 % CH_3COOH + 50 % H_2O] – $CO(NH_2)_2$ from 1.043 to 1.180 g cm^{-3}.

As can be seen from Fig. 5, there are two turns in the dependence of density on concentration. The first turn is observed in the area of transition from the area of water to the area of urea acetate, and the second turn from the area of urea acetate to the area of urea.

The studied composition-property diagrams serve as a scientific basis for the development of technology for the production of physiologically active substances based on acetate carbamide. That is, as a result of the conducted studies, optimal compositions were selected with indicators pH-3.82, n_D-1.428, η-3.10, d-1.130 g/cm^3. The interaction of the resulting urea acetate with ethanolamines will be studied in further studies.

Chemical analysis of the synthesized compound gave the following results: found, mass. %:
N_{amide} = 22.99; C = 29.56; H = 6.73; O = 40.72
For $CH_3COOH{\cdot}CO(NH_2)_2$ calculated, mass. %:
N_{amide} = 23.33; C = 30.0; H = 6.67; O = 40.0

The individuality of the obtained compound was confirmed using modern methods of physico-chemical analysis. As shown by X-ray phase analysis, the obtained compound of the composition $CH_3COOH{\cdot}CO(NH_2)_2$ in the ratio 1:1 is characterized by its own values of interplanar distances, which confirms their individuality, Fig.6.

A derivatographic study has established that four endothermic effects at 114, 195, 260 and 405°C and

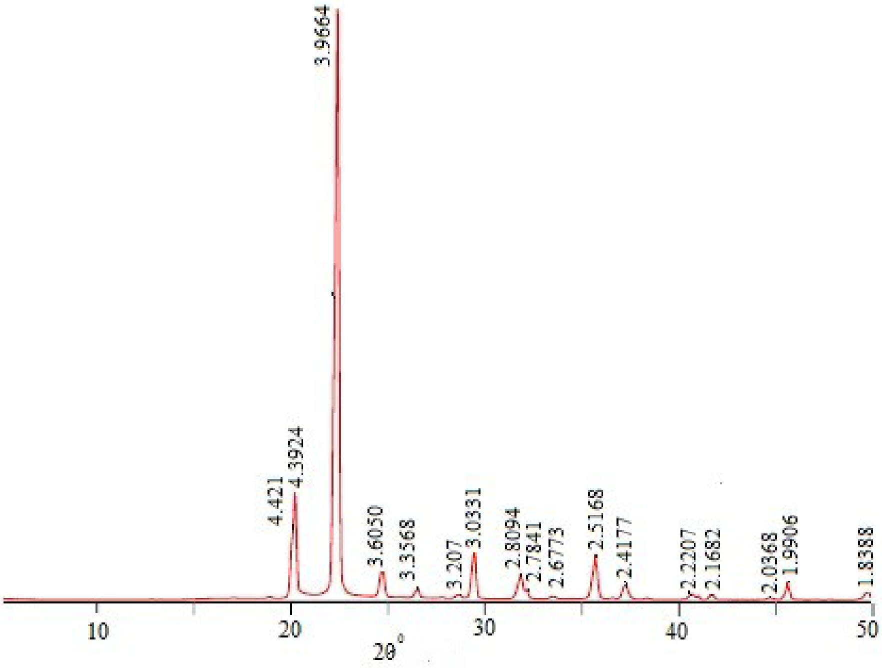

Fig. 6. X-ray pattern of $CH_3COOH{\cdot}CO(NH_2)_2$.

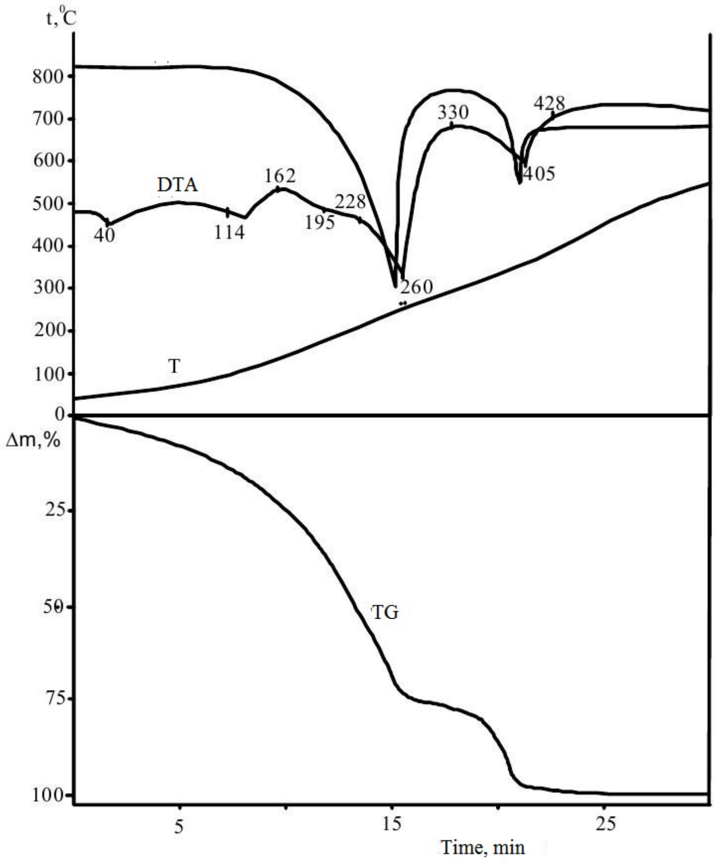

Fig. 7. Derivatogram of the compound $CH_3COOH·CO(NH_2)_2$.

four exothermic effects at 162, 228, 330 and 428°C were observed on the heating curve of the resulting $CO(NH_2)_2·CH_3COOH$ compound. The first, endothermic effect at 114°C corresponds to the melting of the compound (Fig. 7). The subsequent effects concern the subsequent stages of the compounds decomposition and the liberation of combustion products during the thermolysis.

CONCLUSIONS

Based on data for the changes in the solubility of components in the CH_3COOH - $CO(NH_2)_2$ - H_2O system and the physico-chemical properties of solutions (density, viscosity, refractive index, pH), the optimal conditions for obtaining a new compound urea acetate have been developed. The resulting urea acetate was analyzed by physico-chemical methods. In the future studies will be investigated the solubility and interaction of urea acetate with ethanolamines.

REFERENCES

1. A.Yu. Tsyplenkova, O.V. Kol'tsova, N.N. Lobanov, M.A. Yershov, V.G. Skvortsov, Physico-chemical systems of dicarboxylic acids, amino alcohol and water at 25°C, Butl. Comm. 36, 2013, 146-200, https://roi: jbc-01/13-36-11-146, (in Russian).
2. A.Yu. Tsyplenkova, O.V. Kol'tsova, Yu.Yu. Pylchikova, V.G. Skvortsov, Reserch of malonic acid and monoethanolamine interaction, Bull. of the I.Ya. Yakovlev ChSPU. 2, 78, 2013, 192, (in Russian)
3. A.Yu. Tsyplenkova, V.G. Skvortsov, O.V. Koltsova, Yu.Yu. Pylchikova, M.A. Ershov, Research of succinic acid and monoethanolamine interaction, Bull. of the I.Ya. Yakovlev ChSPU. 2, 74, 2012, 179, (in Russian)
4. S. Tukhtaev, F.R. Tolipov, Zh.S. Shukurov, A.S. Togasharov, Polyterm in solubility sistem of nitrate carbamide - monoethanolamine – water, Univ.:

Techn. Sc.: el. Sc. j. 8, 65, 2019. http://7universum.com/ru/tech/archive/item/7731, (in Russian)

5. T.I. Iskandarov, M.M. Maxamatkhanov, M.X. Muxitdinova, Carbomoylthioglycolic acid anilides showing defoliating activity on cotton, Patent IAP 03896 Res. Uz. - Declared. 27.09.2005; published. 30.04.2009 Official bulletin. 4, 2009, (in Russian)
6. G.S. Muromtsev, D.I. Chkanikov, O.N. Kulaeva, Fundamentals of chemical regulation of plant growth and productivity, Moscow, Agro-industrial publishing, 2001 (in Russian)
7. C. Broekgaarden, L. Caarls, I.A. Vos, C. Pieterse, S. van Wees, Ethylene: Traffic Controller on Hormonal Crossroadsto Defense, Pl. Physiol. 169, 2015, 2371. https://doi./10.1104/pp15.01020
8. K.A. Turayev, A.S., Togasharov, S. Tukhtaev, An effective defoliant based on calcium chlorate and sodium salt of monochloroacetic acid, J. Chem. Technol. Metall., 57, 5, 2022, 977-983.
9. E.S. Khusanov, Zh.S. Shukurov, A.S. Togasharov, B.B. Akhmedov, S. Tukhtaev, Study of the solubility of components in the $H_3PO_4 \cdot CO(NH_2)_2$- $NH_2C_2H_4OH$-H_2O system, Comp. mat. Uz. scientific those. Prod. Jour. 4, 2021, 3, (in Russian)
10. A.A. Sidikov, A.S. Toghasharov, J.S. Shukurov, S. Tukhtaev, Solubility and Rheological Properties of the System $NaClO_3 \cdot CO(NH_2)_2$–$H_2SO_4 \cdot N(C_2H_4OH)_3$–$H_2O$, Russ. J. Inorg. Chem. 66, 2021, 1554–1560. https://doi.org/10.1134/S003602362110017X
11. S.O. Rajaeian, A.A. Ehsanpour, Physiological responses of tobacco plants (*Nicotiana rustica*) pretreated with ethanolamine to salt stress, Russ. J. Plant Physiol., 62, 2015 246–252. https://doi.org/10.1134/S1021443715020156
12. Z.S. Shukurov, E.S. Khusanov, M.S. Mukhitdinova, A.S. Togasharov, Component Solubilities in the Acetic Acid–Monoethanolamine–Water System, Russ. J. Inorg. Chem. 66, 2021, 902–908. https://doi.org/10.1134/S0036023621060176
13. R.A. Ozubekova, Solubility in aqueous systems including sodium tricarbamidochlorate and 2-chloroethylphosphonates of mono-, di- and triethanolamines, Collection of scientific papers of graduate students of the Osh city, Osh, Kyrgyzstan, 2000, (in Russian)
14. D.A. Kosova, A.L. Voskov, N.A. Kovalenko, I.A. Uspenskaya, A Watere-Urea-Ammonium Sulfamate system: Experimental investigation and thermodynamic modelling, Fl. Ph. Equil. 425, 2016, 312-323. http://dx.doi.org/10.1016/j.fluid.2016.06.021
15. E. Loeser, M. DelaCruz, V. Madappalli, Solubility of Urea in Acetonitrile-Water Mixtures and Liquid-Liquid Phase Separation of Urea-Saturated Acetonitrile-Water Mixtures, J. Chem. Eng. 56, 2011. 2909–2913. dx.doi.org/10.1021/je200122b
16. K.A. House, J.E. House, Thermodynamics of dissolution of urea in water, alcohols, and their mixtures, J. Mol. Liq., 242, 2017, 428-432, https://doi.org/10.1016/j.molliq.2017.07.020.
17. V.P. Danilov, E.A. Frolova, D.F. Kondakov, Phase Equilibria in the Sections of the $Ca(NO_3)_2$–$CO(NH_2)_2$–H_2O System and Deicing Properties of Nitrate–Urea Mixtures, Theor. Found. Chem. Eng. 55, 2021, 990–995. https://doi.org/10.1134/S0040579521050031
18. I.I. Lieberstein, G.I. Lungu, Composition for sunflower desiccation № (21) 2911092/30-15 (in Russian) Patent A.S. 880386 USSR. - Declared. 25.02.1980; published. 15.11.1981, Bulletin. 42, 1981, (in Russian)
19. J.H. Zhang, S.J. Guo, P.Y. Guo, X. Wang, The interacting effect of urea and fenoxaprop-P-ethyl on photosynthesis and chlorophyll fluorescence in Perilla frutescens, Photosynthetica, 52, 3, 2014, 456. https://doi.org/10.1007/s11099-014-0050-9
20. K. Sulaimankulov, Urea compounds with inorganic salts, Frunze, Ilim, 1971. (in Russian)
21. Z.S. Shukurov, S.S. Ishankhodzhaev, M.K. Askarova, S. Tukhtaev, Study of the solubility of components in the $NaClO_3 \cdot 2CO(NH_2)_2$-$NH_2C_2H_4OH \cdot CH_3COOH$-$H_2O$ system, Russ. J. Inorg. Chem. 56, 2011, 463–466. https://doi.org/10.1134/S0036023611010207
22. J.Sh. Bobojonov, J.S. Shukurov, A.S. Togasharov, M.X. Axmedjanova, N.A. Dadamukhamedova, Solubility of components in the system $NaClO_3 \cdot CO(NH_2)_2$ - $C_{10}N_2H_{22}O_9$ - H_2O, Uzb. Chem. jour. 2, 2020, 10-16, (in Russian)
23. Z.S. Bobozhonov, Z.S. Shukurov, A.S. Togasharov, M.Kh. Akhmadzhonova, Study of Solubility of $Ca(ClO_3)_2$–[90% C_2H_5OH + 10% $C_{10}H_{11}ClN_4$]–H_2O System, Russ. J. Inorg. Chem. 66, 2021, 1031–1035. https://doi.org/10.1134/S0036023621070032
24. E. Karademir, C. Karademir, S. Basbag, Determinationthe effect of defoliation timing on cotton yield and quality, J. Centr. E. Agr., 3. 8, 2007, 357-362.

25. S.D. Wright, R.B. Hutmacher, A. Shrestha, G. Banuelos, S. Rios, K. Hutmacher, D.S. Munk, M.P. Keeley, Impact of Early Defoliation on California Pima Cotton Boll Opening, Lint Yield, and Quality, J. Cr. Impr. 29, 5, 2015, 528-541, DOI: 10.1080/15427528.2015.1056399
26. V.A. Liopo, V.V. War, X-ray diffractometry. Grodno, GrSTU, 2003 (in Russian)
27. L.G. Berg, N.G. Burmistrova, M.I. Ozerova, Practical guide to thermography. Kazan, Kazan University Publishing Houses, 1976, (in Russian).
28. A.S. Trunin, D.G. Petrova, Visual-polythermal method, Kuibyshev, KPU, 1977, (in Russian).
29. A.B. Zdanovsky, Gallurgy, Leningrad, Chemistry, 1972, (in Russian).
30. V.A. Klimova, Basic micromethods for the analysis of organic compounds. Moscow, Chemistry, 1975, (in Russian).