ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 6, Issue 8 , August 2019

The solubility of the components in the system carbamide - dibasic monoethanolammonium citrate - water

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ABSTRACT: To justify the process of obtaining a new liquid fertilizer of complex action based on them, the solubility in aqueous systems was studied, including: urea - dibasic monoethanolammonium citrate - water. Data on the solubility of the components in the urea - dibasic citric acid monoethanolammonium - water system are not available in the literature. To characterize the behavior of the starting components in polythermal conditions, this system was studied from -38.6 to 60°C. The system $CO(NH_2)_2$ - $2NH_2C_2H_4OH \cdot H_3C_6H_5O_7$ - H_2O was studied by six internal sections: of these, I-III from the side $CO(NH_2)_2$ - H_2O to the pole $2NH_2C_2H_4OH \cdot H_3C_6H_5O_7$, and IV-VI from the $2NH_2C_2H_4OH \cdot H_3C_6H_5O_7$ - H_2O to the top of $CO(NH_2)_2$.

KEY WORDS: Urea Ammonium Nitrate (UAN), liquid nitrogen fertilizer (LNF), physiologically active substances (PAS), citric acid, monoethanolamine (MEA), urea (carbamide), water, solubility, visual polythermal method.

I.INTRODUCTION

The global introduction of chemicals for farming has led to the formation of a powerful international industry for their production, as well as a wide network of logistics and distribution [1]. According to the International Association of Fertilizer Manufacturers, compared with the 60s of the last century, the global consumption of mineral fertilizers by 2015 increased by almost 6 times [2]. Currently, the market is one of the most monopolized [3]. The largest producers on it are five countries: China, USA, India, Russia and Canada. На эти государства приходится около 60% от всего объёма производимой агрохимической продукции [4, 5].

A high degree of concentration of the production of mineral fertilizers is confirmed by the fact that 15 countries account for almost 80% of the global ammonia output; 85% of phosphorus ore production is concentrated in 10 states; More than 85% of the global volume of potassium chloride is produced in 6 countries [6, 7]. At the same time, the demand for nitrogen fertilizers increases by 1.4%, phosphorus fertilizers - by 2.2%, potash fertilizers - by 2.6% [8-10].

Currently, more than 180 million tons of NPK are used annually in world agricultural production. According to FAO estimates, the global fertilizer production in 2013 amounted to 183.4 million tons, the annual growth of nitrogen fertilizer production is 10% [11]. Along with solid nitrogen fertilizers, their liquid forms are used all over the world. The range of liquid nitrogen fertilizers used in agricultural production includes liquid ammonia (anhydrous) (82.3% N), aqueous ammonia (16-24% N), urea-ammonium nitrate (UAN) (total content of N ammonia, amide and nitrate N, from 28 to 34%) [12, 13].

In Uzbekistan, the production of mineral fertilizers is one of the most developed segments of the chemical industry. However, the measures implemented are clearly not enough for a radical improvement of the technical condition of production, a significant reduction in the cost of production and increase its competitiveness in the foreign market. It is completely obvious that the long-term effectiveness of the chemical industry should consist in the transition to new technologies that make it possible to transform the existing raw materials base into highly liquid products.

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
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Among them, solutions of UAN (12.5 million tons) and liquid NH_3 (~ 6.5 million tons) dominate. It is in the countries of North America (USA, Canada) that their share in the assortment of fertilizers is very high (~ 35%), including 50% in the group of nitrogen. In Western Europe, the proportion of liquid forms is noticeably smaller than in North America, and amounts to 10-15%. In Denmark, a high level of liquid ammonia; in France and Austria, UAN is actively used [14, 15]. UAN (urea-ammonium nitrate) is a liquid fertilizer that is a mixture of a solution of urea and ammonium nitrate. UAN is a light colored liquid having a density of 1.26 - 1.34 g/cm^3 and containing 28-32% nitrogen. It consists of a solution of ammonium nitrate - 38-43% and urea - 31-42%. When combining urea and ammonium nitrate, the solubility of the mixture increases. UAN is used for main application and foliar top dressing. The combined use of fertilizers and plant protection products can significantly reduce the cost of introducing chemicals. Great opportunities in this direction are presented by the use of UAN. When using UAN tank mixtures with additives, an increase in action can be observed and it is possible to reduce the doses of the latter without reducing their agrochemical effectiveness. Therefore, of great interest is the study of the combined use of UAN with other plant protection products: fungicides, growth regulators, insecticides [17]. Currently, much attention is paid to the integrated use of liquid fertilizers. From the literature review it follows that the integrated use of liquid fertilizers with plant growth stimulants play a crucial role in the development of plants and to obtain effective yields. The system of applying liquid fertilizers with intensive technologies for cultivating crops is calculated to obtain high yields [18].

II. SIGNIFICANCE OF THE SYSTEM

The main focus of the article is on how the visual-polythermic methods can be used to predict the formation factors of new compounds in a wide temperature range. A study of the literature review is presented in section III, the methodology is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and conclusion.

III. LITERATURE SURVEY

As was excellent in the literary review, the introduction of physiologically active substances into the composition of fertilizers accelerates the growth and development process, as well as increases the yield and quality of crops.

In this regard, in order to characterize the behavior of urea and the constituent components of physiologically active substances, with their joint presence, as well as to justify the process of obtaining a new liquid fertilizer with a complex effect based on them, the solubility in aqueous systems was studied.

Data on the solubility of the components in the urea - dibasic citric acid monoethanolammonium - water system are not available in the literature. To characterize the behavior of the starting components in polythermal conditions, this system was studied from -38.6 to 60°C. The binary systems that make up this system are well covered in the literature [19] and are consistent with our results.

IV. METHODOLOGY

The study of heterogeneous phase equilibria using the visual - polythermal method [20].

According to the visual-polythermal method, the temperature of the appearance of the first crystals was observed with uniform cooling or disappearance of the last crystals with slow heating and continuous stirring of the solutions. Solubility was determined in a test tube, closed with a stopper, with a stirrer and a thermometer with a division value of 0.1°C. For uniform cooling, the test tube was placed in an external test tube - a clutch located in the cooling mixture. Heating is also carried out through the coupling, cooling is carried out in Dewar vessels with liquid nitrogen or dry ice.

The composition and crystallization temperature of nodal invariant points and the nature of the change in the saturation line of two coexisting solid phases were determined by constructing the projection of the polythermal solubility curves on the corresponding lateral water sides of the system. The composition points corresponding to the solubility isotherms were found by interpolating data on polythermal sections.

The construction of polythermal solubility diagrams of the studied systems was carried out by us in a right triangle. The concentration of solutions is expressed in mass percent [21].

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
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V. EXPERIMENTAL RESULTS

The system $CO(NH_2)_2$ - $2NH_2C_2H_4OH \cdot H_3C_6H_5O_7$ - H_2O was studied by six internal sections: of them I-III from the side $CO(NH_2)_2$ - H_2O to the pole $2NH_2C_2H_4OH \cdot H_3C_6H_5O_7$, and IV-VI from the side $2NH_2H_2C_2 \cdot H_3C_6H_5O_7$ - H_2O to the top of $CO(NH_2)_2$ (Fig: 1).

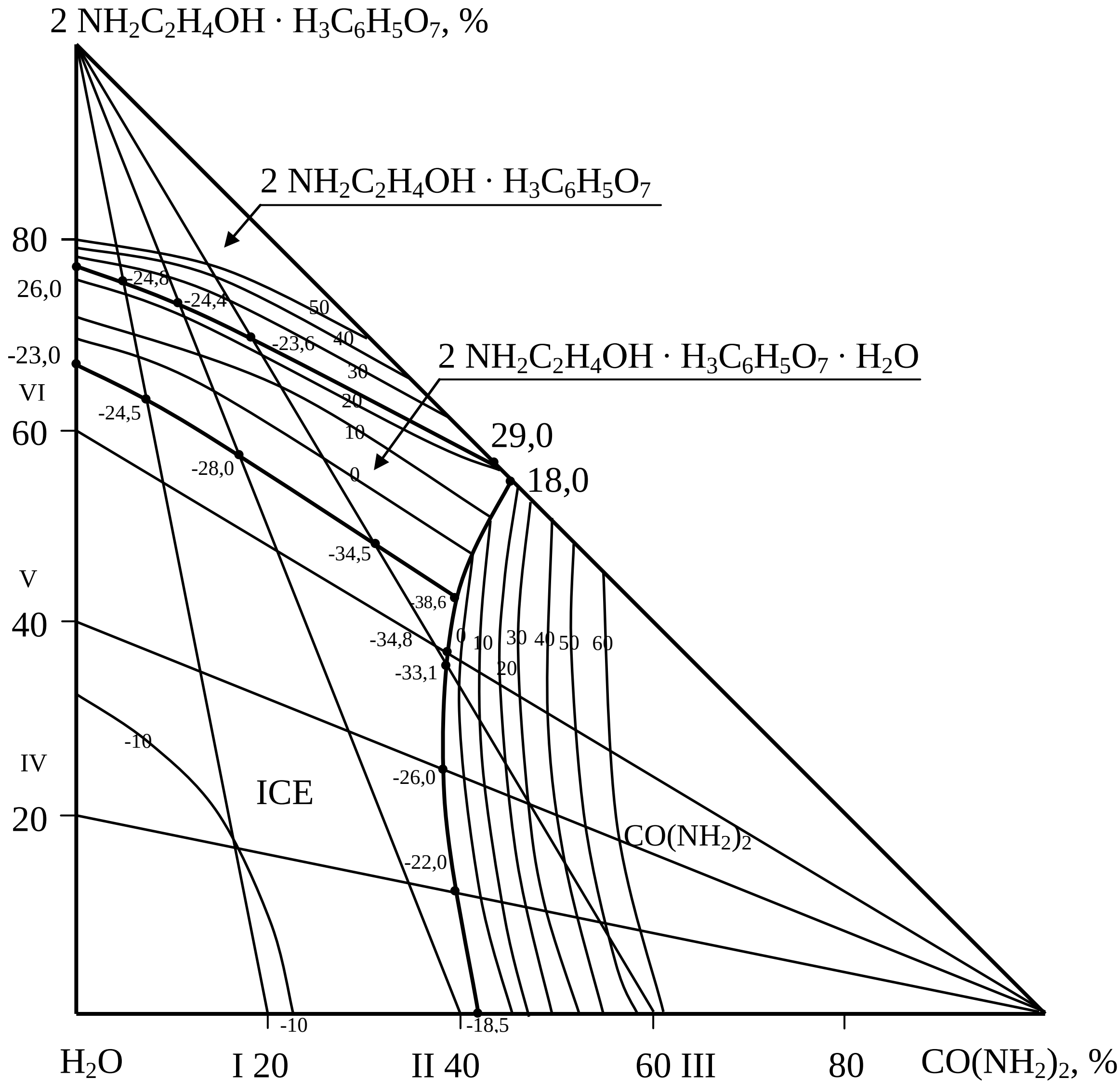

Fig 2: System solubility diagram: $CO(NH_2)_2 – 2NH_2C_2H_4OH \cdot H_3C_6H_5O_7 – H_2O$.

Based on the solubility polytherms of binary systems and internal sections, a polythermal solubility diagram of the $CO(NH_2)_2$ - $2NH_2C_2H_4OH \cdot H_3C_6H_5O_7$ - H_2O system from the total freezing temperature (-38.6°C) to 60°C, on which ice crystallization fields are distinguished, was constructed , urea, monohydrate and anhydrous bisubstituted citric acid monoethanolammonium. One triple and five double nodal points of the system were established that correspond to the joint crystallization of three and two different solid phases (Table 1). In the polythermal solubility diagram, isotherms

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
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are plotted inside the crystallization fields every 10°C. Projections of polythermal curves on the urea - water and dibasic monotanolammonium - water sides were constructed.

Table 1. Double and triple points of the system: $CO(NH_2)_2$ - $2NH_2C_2H_4OH \cdot H_3C_6H_5O_7$ - H_2O

The composition of the liquid phase, %			T_{cr}, °C	Solid phase
$CO(NH_2)_2$	$2NH_2C_2H_4OH \cdot H_3C_6H_5O_7$	H_2O		
41,9	-	58,1	-18,5	Лед + $CO(NH_2)_2$
39,2	12,1	48,7	-22,0	Also
38,1	24,9	37,0	-26,0	" "
38,4	35,9	25,7	-33,1	" "
38,7	43,2	18,1	-34,3	" "
39,4	42,5	18,1	-38,6	$CO(NH_2)_2$ + Лед + $2NH_2C_2H_4OH \cdot H_3C_6H_5O_7 \cdot H_2O$
-	67,0	33,0	-23,0	Лед + $2NH_2C_2H_4OH \cdot H_3C_6H_5O_7 \cdot H_2O$
7,6	63,0	29,4	-24,5	Also
17,2	57,2	25,6	-28,0	" "
31,6	37,9	30,6	-34,5	" "
-	77,0	23,0	26,0	$2NH_2C_2H_4OH \cdot H_3C_6H_5O_7 \cdot H_2O$ + $2NH_2C_2H_4OH \cdot H_3C_6H_5O_7$
5,0	75,4	19,6	24,8	Also
10,7	63,2	26,1	24,4	" "
18,4	59,1	22,5	23,6	" "
43,8	56,2	-	20,0	" "
45,0	55,0	-	18,0	$CO(NH_2)_2$ + $2NH_2C_2H_4OH \cdot H_3C_6H_5O_7 \cdot H_2O$

VI. CONCLUSION AND FUTURE WORK

In the studied temperature and concentration range, the system components retain their individuality, and, consequently, the necessary physiological activity.

A feature of the solubility polytherm of the studied system is that when a dibasic monoethanolammonium of citric acid is introduced into a system saturated with urea, the crystallization temperature of solutions corresponding to crystallization decreases.

An analysis of the polythermal solubility diagram shows that in the $CO(NH_2)_2$ - $2NH_2C_2H_4OH \cdot H_3C_6H_5O_7$ - H_2O system, the salting out effect of dibasic monoethanolammonium of citric acid on urea is observed.

REFERENCES

[1] Lyzhin Dmitry Nikolaevich. Current trends in the global market of mineral fertilizers and plant protection products: competitive positions of Russia // Problems of the national strategy. – № 3 (36). – 2016. – P. 123-124.
[2] World fertilizer trends and outlook to 2018 // Food and agriculture organization of the united nations. – Rome. - 2015. - P.78.
[3] Kondratyev V. B. World Chemical Industry // Historical Perspective Fund. 04.05.2011. URL: http://www.perspektivy.info/print.php?ID=88615.
[4] Kalinkova I. The task of creating an innovative competitive chemical industry in Russia with a proper degree of economic security // Expert North-West. 25.08.2014. URL: http://www.expertnw.ru/news/2014-07-25/zadacha-sozdat-v-rossii-innovatsion-nuyu-konkurentosposobnuyu-khimicheskuyu-otrasl-s-dolzhnoy-stepenyu-ekonomicheskoy-bezopasnosti.
[5] Putin took on fertilizer producers // Agro2b.ru - the Internet portal for the food business. 08.11.2015. URL: http://agro2b.ru/ru/news/24507-Putin-vzyalsyaproizvoditelej-udobrenij.html.
[6] Zinchenko V. A. Chemical protection of plants: means, technology and environmental safety. - M .: Kolos, 2005. - P. 11.
[7] Description of the world production of mineral fertilizers // New Chemical Technologies. Analytical portal of the chemical industry. 10.11.2015. URL: http://www.newchemistry.ru/ letterphp?n_id=2247.
[8] Mogilevsky E. Mineral fertilizers in numbers // Belarusian Agriculture. 03.12.2015.URL: http://agriculture.by/news/ mirovye-rynki/mirovoj-rynok-mineralnyh-udobrenij-v-2015-godu-dostignet-280-mln.t.
[9] World Pesticide Market by 2019 // Business Agrarian Internet Resource. 25.07.2014. URL: http://www.agrotimes.net/rastenievodstvo /mirovoj-rinok-pesticidov-k2019-g--sostavit-75-9-mlrd.

ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 6, Issue 8 , August 2019

[10] EPA rules will strengthen pesticide safety on farms // Dailymail: 28.09.2015. URL:http://www.dailymail.co.uk/wires/ap/article-3252463/EPA-rules-strengthen-pesticide-safety-farms.html.
[11] The location of the chemical complex // Encyclopedia of the economist: website. URL: http://www.grandars.ru.
[12] Chernyshev A. Supply ahead of demand. Mineral fertilizer production - challenges of the domestic and foreign market. - P. 39.
[13] Zhukova A. Chemical dependence // Russian Business Newspaper: Industrial Review. -№1011. 08/18/2015. – P. 9. URL: http://www.rg.ru/2015/08/18/zavisimost.
[14] P Statistical Review of World Energy // British Petroleum Statistical Reviews. -June. -2015. -P.20. URL: http://www.bp.com.
[15] A. A. Zavalin, E. N. Efremov, A. A. Alferov, L. N. Samoilov, L. S. Chernova, G. G. Blagoveshchenskaya. Advantages and problems of using liquid nitrogen fertilizers in agriculture // Agrochemistry. - 2014. - №5. - P. 20. http://naukarus.com.
[16] E. Dudkina, agronomist-technologist-Corporation (Agro-Union). Urea Ammonium Nitrate (UAN). - 2013. – P. 20- 22.
[17] Mineev V. G. Journal of Agrochemistry, Science. – 2006. - P. 526.
[18] V.V. Budaev, D.Y. Yakimov. Biologically active complexes from crop wastes and wild plants // Polzunovsky Bulletin. -№3. -2007. –P. 15-24.
[19] Togasharov A.S. Technology for the production of defoliants based on magnesium, sodium chlorates and gin waste. Dis. Cand. Chem. sciences. – Tashkent. - 2011. – P. 37.
[20] Garkushin I.K., Kondratyuk I.M., Egortsev G.E., Istomova M.A. Theoretical and experimental methods for studying multicomponent systems. Tutorial. - Samara: Samara State Technical University. - 2012. – P. 125. ISBN 978-5-7964-1554-2.
[21] Arthur Pelton. Phase Diagrams and Thermodynamic Modeling of Solutions. –Elsevier: 1st Edition, 2018, -P. 100.