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STUDY OF SOLUBILITY OF $CO(NH_2)_2$ - HOOC - COOH · $NH_2C_2H_4OH$ - H_2O SYSTEM

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ABSTRACT

In this work, the interaction of components in the $CO(NH_2)_2$ - HOOC - COOH ·$NH_2C_2H_4OH$ - H_2O system was studied by visual polythermic method in the temperature range from -11.2 to 61°C. A polythermal solubility diagram of the system was constructed and the crystallization sites of ice, urea, monoethanolammonium oxalate, and the new phase ureamonoethanolammonium oxalate were determined.

During the addition of monoethanolammonium oxalate to urea solutions of different concentrations, changes in rheological properties (pH, density, refractive index, viscosity) were recorded, and the results were found to be consistent with the polythermal solubility diagram. A new phase formed during the study of the $CO(NH_2)_2$ - HOOC-COOH · $NH_2C_2H_4OH$ - H_2O system, ureamonoethanolammonium oxalate, was isolated and analyzed by confirmed using appropriate analytical methods (IR, Thermal, X-ray phase).

Keywords: insecticide, physiologically active substance, solubility diagram, "composition-property", urea, monoethanolammonium oxalate, ureamonoethanolammonium oxalate, rheological property, X-ray phase analysis.

INTRODUCTION

Urea has been used in agriculture as an effective fertilizer for many years. Urea contains a large amount of nitrogen, is well soluble in water, and is one of the important substances that can be used for plant leaf nutrition [1, 2]. Urea is quickly absorbed on the surface of the leaf when it is applied through the plant leaf by spraying [3].

Ethanolamines perform some important functions in plants, such as growth and development, stimulation, and effective synergism [4, 5]. Under the influence of ethanolamine salts, ethylene is released in the plant and accumulates in the plant band, as a result of which the plant leaves fall prematurely, which provides the opportunity to harvest cotton with good quality.

In the previous studies, several scientific research were conducted based on inorganic and organic acids and their compounds, on obtaining physiologically active substances and using them in agricultural crops, and effective results were achieved. In particular, the interaction of acetic acid [6, 7], citric acid [8, 9], nitric acid [10, 11], and sulfuric acid [12, 13] with mono-, di- and triethanolamines and the system of oxalic acid with urea [14] have been studied at different temperatures and concentrations, and the resulting compounds were found to have physiological activity [15, 16].

Considering that the aqueous system of monoethanolammonium oxalate with urea has not been studied before, we were interested in studying the interaction of urea, oxalic acid, and monoethanolamine components in an aqueous solution.

EXPERIMENTAL

In the experiment, a TN-6 glass mercury thermometer with a detection limit of - 30 to 70°C and a TL-15 alcohol glass thermometer with a detection limit of - 100 to 20°C were used in the visual polythermal method [17]. For research purposes (pure for analysis) urea GOST 6671-77, "chemically pure" oxalic acid dihydrate (GOST 22180-76), and "chemically pure" monoethanolamine (TU 2423-159-00203335-2004) were used.

X-Ray phase (Rigaku Mineflix 600, Japan) was used. Thermo Scientific TA Instruments STD 650 (TA Instruments Trios V5.1.1.46572.USA) for thermal analysis and A Perkin Elmer Spectrum IR (Version 10.7.2) was used to obtain IR analysis.

A FE 20 precision pH meter supplied by the Mettler-Toledo International Inc. was used to measure the pH value, with a precision of ± 0.01. A PAL-BX/RI type Digital refractometer by the ATAGO COLTD, Japan, was used for determining the refractive index.

Measurement of the viscosity of solutions was determined on a capillary viscometer VPZh [18] with a capillary diameter of 1.16 - 1.84 mm. The viscosity of the solution was re-measured three times and the average were recorded. The relative densities of the solution were measured by the pycnometric method [19] on a 5 mL capillary pycnometer. By measuring the water three times and recording the mean. The density of the solution is measured in the same manner and the mean is recorded.

The pH value of the solutions was measured according to the method [20] on a FE20 Mettler Toledo pH meter. The pH meter was calibrated with standard buffer solutions (pH = 4.01).

The refractive indices of the solutions were measured using a digital refractometer (model PAL-BX/RI, Atago refractometer) at a temperature of 25°C. This digital refractometer complies with the EMC Directive 2004/108/EC, at 25°C with a precision of ± 0.0003 of the refractive index. Refractive index measurements were made in triplicate and the average values were recorded.

RESULTS AND DISCUSSION

By reacting $H_2C_2O_4$ and $NH_2C_2H_4OH$ in a 1:1 molar ratio, a compound consisting of HOOC - COOH · $NH_2C_2H_4OH$ was synthesized [21] and the interaction of the obtained compound with urea in an aqueous solution was studied by the visual polythermal method.

A polythermal solubility diagram of the system $CO(NH_2)_2$ - HOOC - COOH · $NH_2C_2H_4OH$ - H_2O was constructed between -11.2 and 61°C temperature using seven internal cuts and binary systems (Fig. 1).

Internal lines I - IV are directed from HOOC- COOH· $NH_2C_2H_4OH$ side to the $CO(NH_2)_2$ side, and lines V-VII are directed to the HOOC - COOH · $NH_2C_2H_4OH$ side from $CO(NH_2)_2$ side.

During the study of the system, the phase boundaries of ice, urea, monoethanolammonium oxalate, and ureamonoethanolammonium oxalate were identified in the diagram.

In the diagram, all phases combine at two ternary point. In this case, the first ternary point corresponds to the temperature of -16.0°C, the composition of the liquid phase is 16 % monoethanolammonium oxalate, 26 % urea and 58 % water, and this point is limited by the crystallization areas of urea, ureamonoethanolammonium oxalate and water. The next ternary point corresponds to 13.4 % monoethanolammonium oxalate, 14.6 % urea and 82 % water at a temperature of - 8°C and consists of monoethanolammonium oxalate, ureamonoethanolammonium oxalate and water according to the composition of the solid phase (Table 1).

The new phase formed in the diagram, ureamonoethanolammonium oxalate, was synthesized based on the solubility diagram, and its composition was determined using chemical and physical-chemical research methods.

In Fig. 2, the IR spectra of urea, monoethanolammonium oxalate, and urea monoethanolammonium oxalate were obtained, and the difference in the IR spectra of the starting materials and urea monoethanolammonium oxalate was observed in comparison with each other.

The results obtained from the DTA study of the ureamonoethanolammonium oxalate compound show that 4 exothermic effects were detected at temperatures of 160; 223.86; 244.98; 304.41°C and 4 endothermic effects at temperatures of 154.54; 175; 258.6; 279.32°C. The process started at a temperature of 19.66°C and ended at a temperature of 409.48°C, and complete mass reduction was observed. Fig. 3.

X-ray phase analysis was performed on a Dron-3.0 diffractometer with filtered copper radiation at a voltage of 40 kV, a current of 20 mA, and a counter disk speed

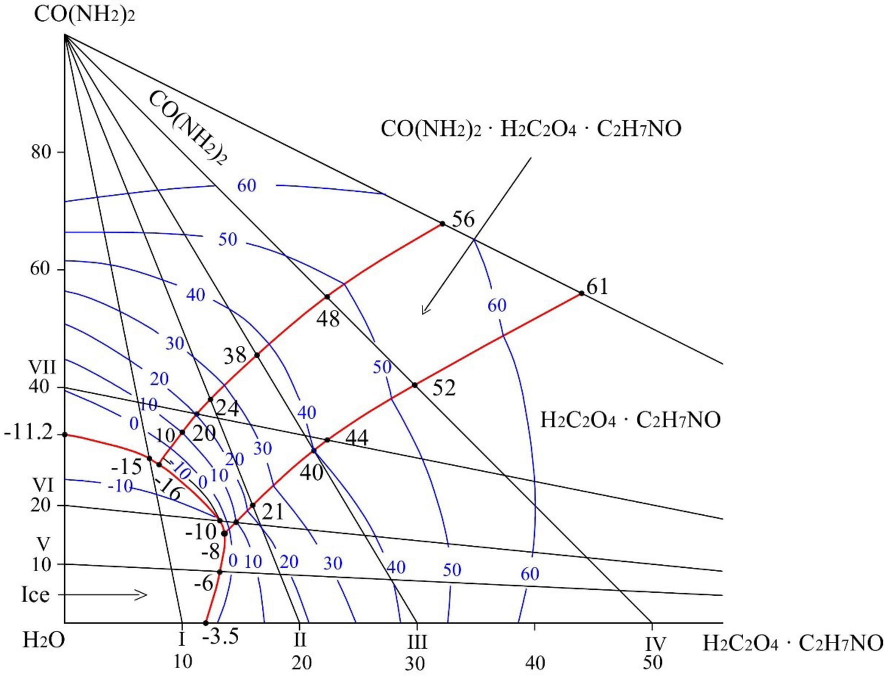


Fig. 1. Solubility diagram of the system $CO(NH_2)_2$ - HOOC - COOH · $NH_2C_2H_4OH$ - H_2O.

Table 1. Secondary and ternary points of the system HOOC - COOH ·$NH_2C_2H_4OH$ - $CO(NH_2)_2$.

Composition of the liquid phase, wt. %,			Cryst, T°C	Solid phase
HOOC-COOH ·$NH_2C_2H_4OH$	$CO(NH_2)_2$	H_2O		
32.4	67.6	0.00	56.0	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2C_2O_4 \cdot NH_2C_2H_4OH$
22.4	55.2	22.4	48.0	
16.4	45.6	38.0	38.0	
12.4	38.0	49.6	24.0	
11.4	35.6	53.0	20.0	
16.0	26.0	58.0	-16.0	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2C_2O_4 \cdot NH_2C_2H_4OH$ + Ice
7.40	26.8	65.8	-15.0	$CO(NH_2)_2$ + Ice
0.00	32.0	68.0	-11.2	
13.0	17.6	69.4	-10.0	$CO(NH_2)_2 \cdot H_2C_2O_4 \cdot NH_2C_2H_4OH$ + Ice
44.0	56.0	0.00	61.0	$CO(NH_2)_2 \cdot H_2C_2O_4 \cdot NH_2C_2H_4OH + H_2C_2O_4 \cdot NH_2C_2H_4OH$
29.6	40.8	29.6	52.0	
23.2	31.2	45.6	44.0	
21.4	29.2	49.4	40.0	
16.0	20,0	64.0	21.0	
13.4	14.6	82.0	-8.00	$H_2C_2O_4 \cdot NH_2C_2H_4OH + CO(NH_2)_2 \cdot H_2C_2O_4 \cdot NH_2C_2H_4OH$ + Ice
13.2	8.80	78.0	-6.00	HOOC - COOH · $NH_2C_2H_4OH$ + Ice
12.0	0.00	88.0	-3.50	

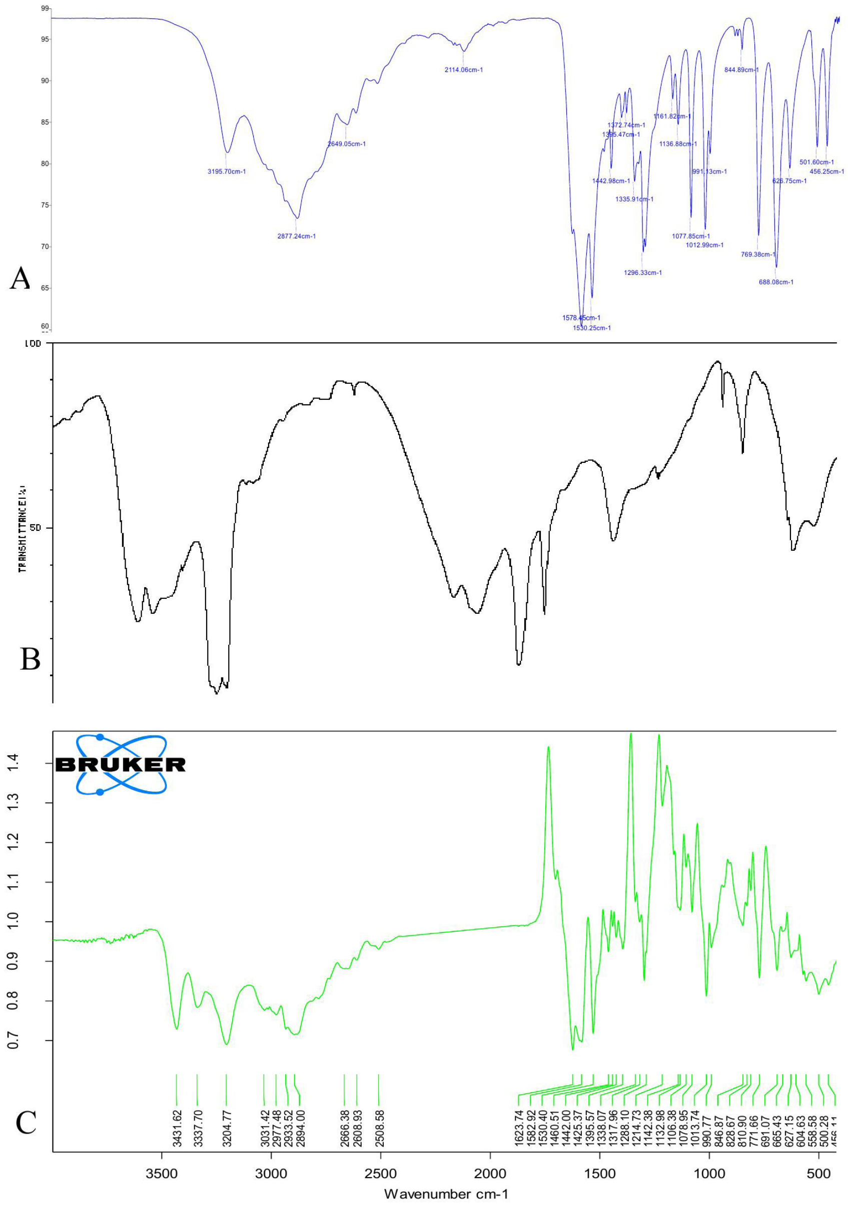


Fig. 2. IR spectra. A- monoethanolammonium oxalate; B-urea; C-ureamonoethanolammonium oxalate.

of 2 deg min^{-1}. The values of the interphase distances were found from the reference by the angle of reflection, and the intensity of the diffraction lines was studied between 5 and 60 on a hundred-point scale at the 2 theta angle (Fig. 4).

In order to physicochemically justify the interaction of components and draw relevant conclusions, the relative viscosity of urea solution with different concentrations was studied and the results were compared with the literature [22 - 25]. The findings are presented in a graphic form (Fig. 5). It was determined that the difference between the results of the experiment and the literature is related to the degree of purity of urea and random displacement of the viscometer.

In this manner, the density, pH, and refractive index of urea solution with different concentrations were determined, and the obtained results were compared with the results in the literature.

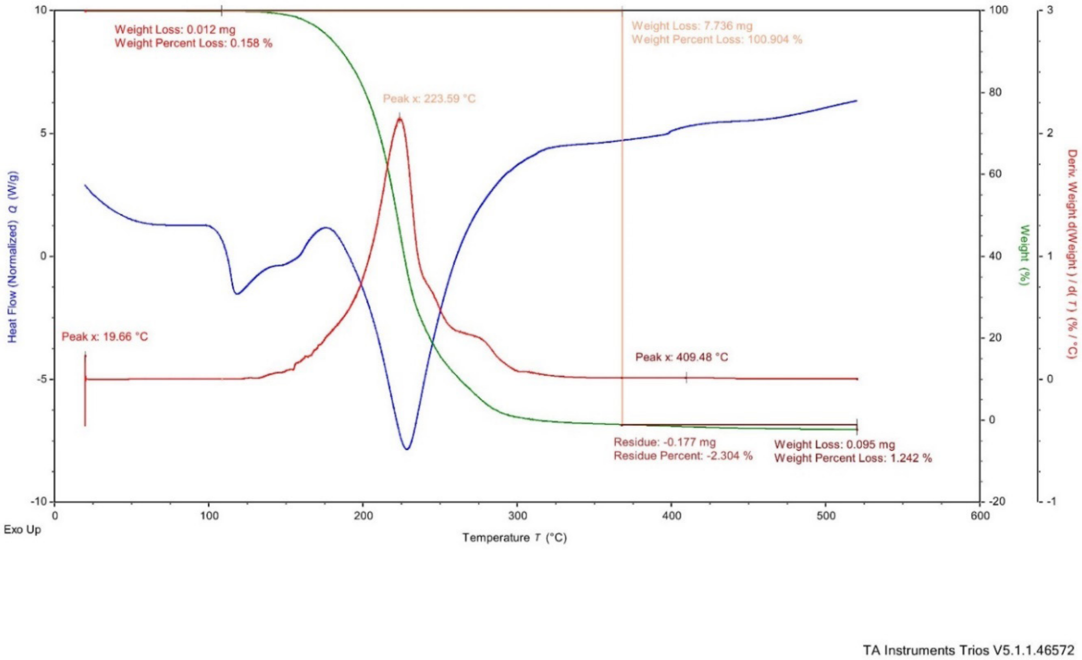


Fig. 3. DTA curve of ureamonoethanolammonium oxalate compound.

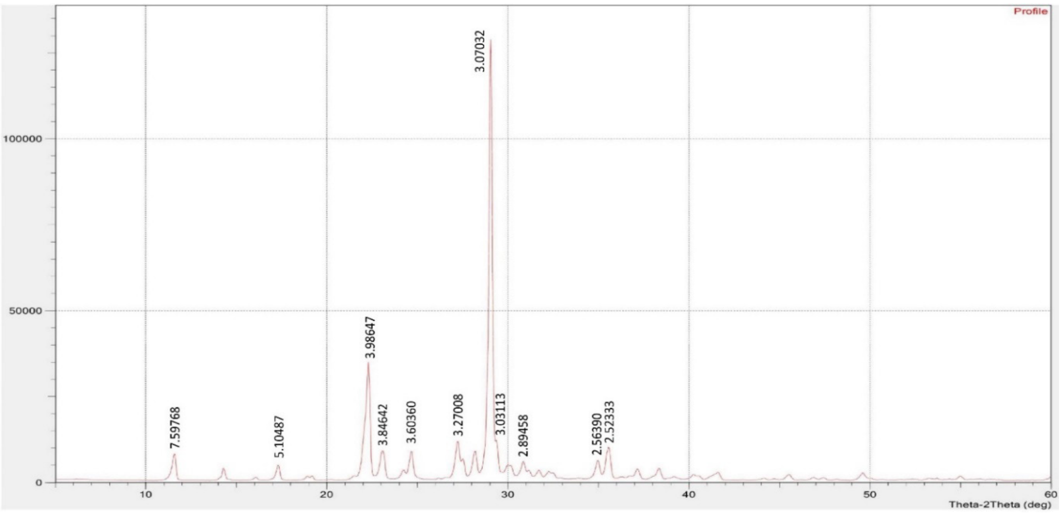


Fig.4. X-ray phase analysis of ureamonoethanolammonium oxalate.

In order to scientifically substantiate the rheological properties of the $CO(NH_2)_2$ - HOOC - COOH· $NH_2C_2H_4OH$ - H_2O system, refractive index, viscosity, density and pH parameters were determined by adding monoethanolammonium oxalate to solutions of different concentrations of urea. Below, the observed changes in rheological properties in the order of adding monoethanolammonium oxalate to 10, 20, 30, and 40 % urea solution at a temperature of 25°C (Fig. 6, 7, 8, 9).

It can be seen from the diagram that with an increase in the concentration of MEA-Ox, the value of the refractive index also increases in solutions with a concentration of 10, 20, 30 and 40 %. When MEA-Ox was added to the 40 % urea solution, a stable increase in the refractive index was observed and in the 30 % solution, it was observed that two phases were separated. The phase boundary was determined when the added MEA-Ox concentration reached 4.4 %. When MEA-

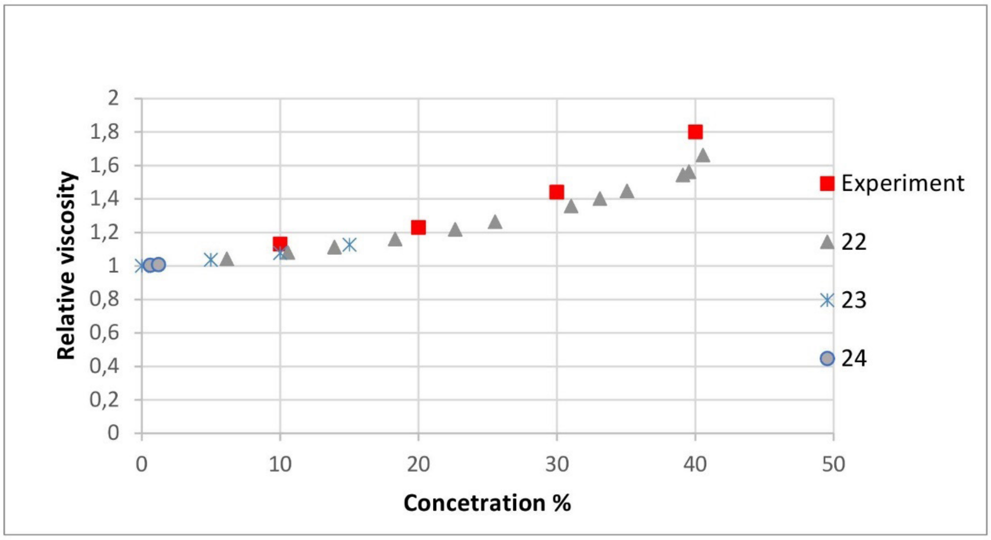
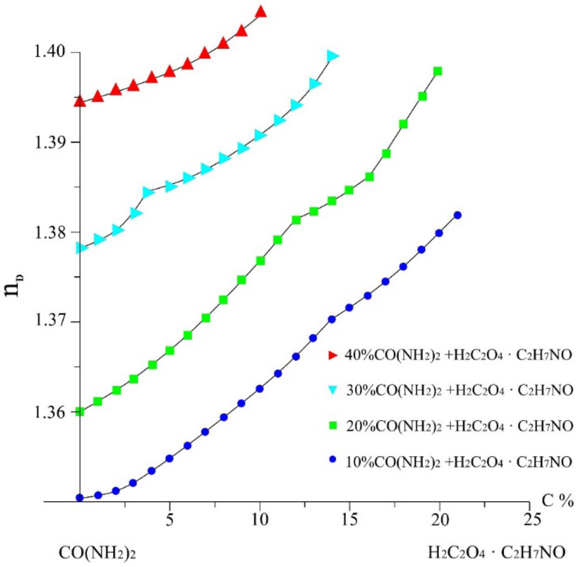


Fig. 5. Viscosity of urea solutions of different concentrations shown in the literature and the result obtained from the experiment.



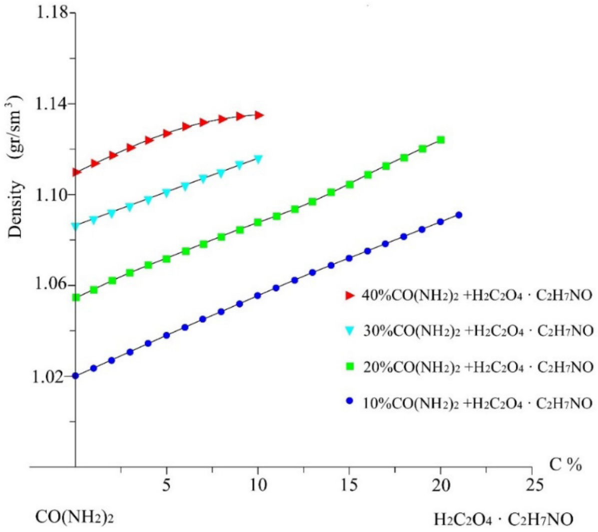


Fig. 6. Changes in refractive index when monoethanolammonium oxalate (MEA-Ox) is added to 10, 20, 30 and 40 % urea solution.

Fig. 7. Changes in density when MEA-Ox is added to 10, 20, 30, and 40% urea solution.

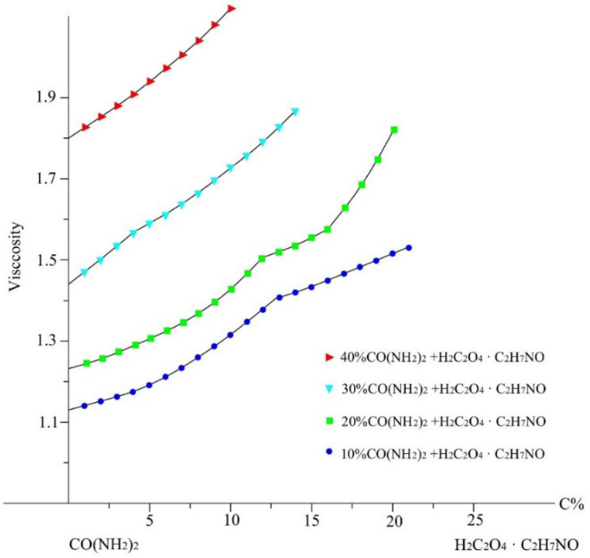


Fig. 8. Changes in relative viscosity MEA-Ox is added to 10, 20, 30, and 40 % urea solutions.

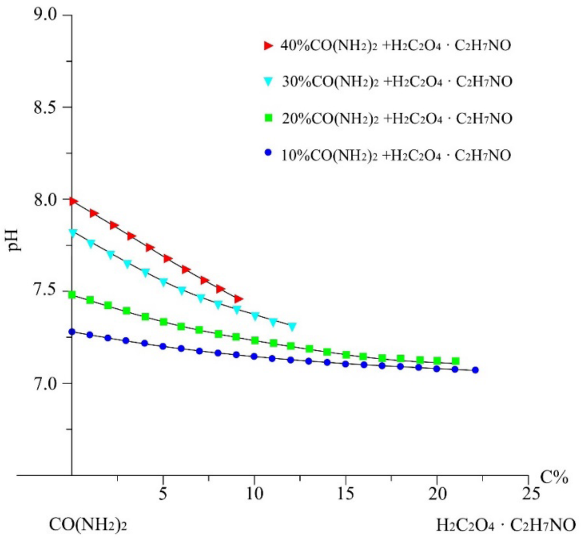


Fig. 9. Changes in pH when adding oxalate MEA-Ox to 10, 20, 30, and 40 % urea solution

Ox was added to a 20 % urea solution, separation into three phases was observed, when the added MEA-Ox concentration reached 12 %, the boundary of the first and second phases was determined, and when it reached 16 %, the boundary of the second and third phases was determined. Also, when oxalate monoethanolamine is added to a 10 % urea solution, separation into 2 phases is observed.

Fig. 7 shows that when monoethanolammonium oxalate (MEA-Ox) is added to urea solutions, the density of the solution increases uniformly.

Fig. 8 shows the increase in viscosity when MEA-Ox is added to 10, 20, 30, and 40 % urea solution. When 12 % MEA-Ox was added to a 10 % urea solution, separation into two different phases was observed. When the concentration of MEA-Ox added to 20 % urea solution is up to 12 %, between 12 % and 16 %, and when it exceeds 16 %, separation into new phases was observed.

When 4 % of MEA-Ox is added to a 30 % urea solution, separation into two different phases is observed, and when MEA-Ox is added to a 40 % urea solution, the viscosity increases uniformly.

Changes in the pH indicators of the solution were determined in the order of adding oxalate monoethanolammonium to 10, 20, 30, and 40 % urea solution (Fig. 9). As the concentration of monoethanolammonium oxalate increases, the pH indicators of all solutions decrease uniformly.

CONCLUSIONS

$CO(NH_2)_2$ - HOOC - COOH · $NH_2C_2H_4OH$ - H_2O polythermal solubility system was studied by the authors for the first time and a solubility diagram was constructed. The phase boundaries of the components were determined in the diagram and the composition of the new phase ureamonoethanolammonium oxalate was analyzed by chemical and physicochemical methods. Rheological properties were studied by adding monoethanolammonium oxalate to urea solution of different concentrations. Based on the change in viscosity, density, refractive index, and pH indicator of the solution, the content of 15 % monoethanolammonium oxalate added to 20 % urea was selected as optimal. In this case, density 1.1, pH = 7.15, viscosity 1.552, refractive index 1.3826. This composition allows to use it as a physiologically active and nutrient for plants.

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