The Austrian Journal of Technical and Natural Sciences, No 9–10
ISSN 2310-5607

PREMIER Publishing
ppublishing.org

DOI:10.29013/AJT-23-9.10-21-26

SOLUBILITY OF COMPONENTS IN THE $NH_4H_2PO_4$-$NH_2C_2H_4OH$-H_2O SYSTEM

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Cite: *Mardanov S., Khamdamova Sh. (2023). Solubility of Components in the $NH_4H_2PO_4$-$NH_2C_2H_4OH$-H2O System. Austrian Journal of Technical and Natural Sciences 2023, No 9-10.* https://doi.org/10.29013/AJT-23-9.10-21-26

Abstract

The solubility of components in the $NH_4H_2PO_4$-$NH_2C_2H_4OH$-H_2O system was studied from the temperature of complete freezing (–53.0 °C) to 68.0 °C. A polythermal solubility diagram has been constructed, on which the regions of crystallization of ice, monoammonium phosphate, $NH_4H_2PO_4 \cdot NH_2C_2H_4OH$, $2NH_4H_2PO_4 \cdot 3NH_2C_2H_4OH$ compounds, two-, one-, and anhydrous monoethanolamine are demarcated.

Keywords: *solubility, temperature, polytherm, diagram, crystallization, ice, mono ammonium phosphate, monoethanolamine*

Introduction

Currently, to increase the productivity of agricultural crops, the use of chemical regulators of plant growth and development is expanding simultaneously with increasing doses of mineral fertilizers. World practice has accumulated experience in growing plants with desired properties using individual chemicals with stimulating activity (Nesbit, J. C., 1860).

It has been established that ethanolamine has high biological activity. Its active participation in redox processes, in enhancing the synthesis of organophosphorus compounds, stimulating protein metabolism and enhancing the activity of enzymatic systems has been revealed.

When explaining the growth activity of ethanolamines, it should be taken into account that in the presence of carbon dioxide and oxygen, ethanolamines can form glycerol, glycol, oxalic, formic, naphthenic and acetic acids, which belong to the group of growth substances (Леопольд, А., 1968; Сухова С. И., Симочатова Е. П., Бесков С. Д., 1967; Гусейнов, Д. М., 1966; Нурахметов, Н. Н., & Беремжанов, Б. А., 1978).

Increased interest in the interaction of ethanolamines with fertilizer components, as well as chlorate-containing defoliants, is due to the fact that when used together, the effectiveness of the synthesized drugs increases. Consequently, physicochemical studies of the interaction of ethanolamines with macro-

and microcomponents of fertilizers are of significant theoretical and practical interest.

Methodology

This system at 25 °C was previously studied using isothermal methods (Набиев, М.Н., Исабаев, З., & Саибова, М.Т., 1976). We studied the solubility of the components in the $NH_4H_2PO_4$-$NH_2C_2H_4OH$-H_2O system using the visual-polythermal method (Трунин, А.С., & Петрова, Д.Г., 1978) from the temperature of complete freezing (–53.0 °C) to 68.0 °C. For quantitative chemical analysis of liquid and solid phases, elemental analysis for carbon, nitrogen, and hydrogen was used (Климова, В.А., 1975); the P_2O_5 content was determined using a spectrophotometer using the colourimetric method (Мойжес, И.Б., 1973).

The content of elemental carbon and hydrogen was carried out according to the method (Климова, В.А., 1975).

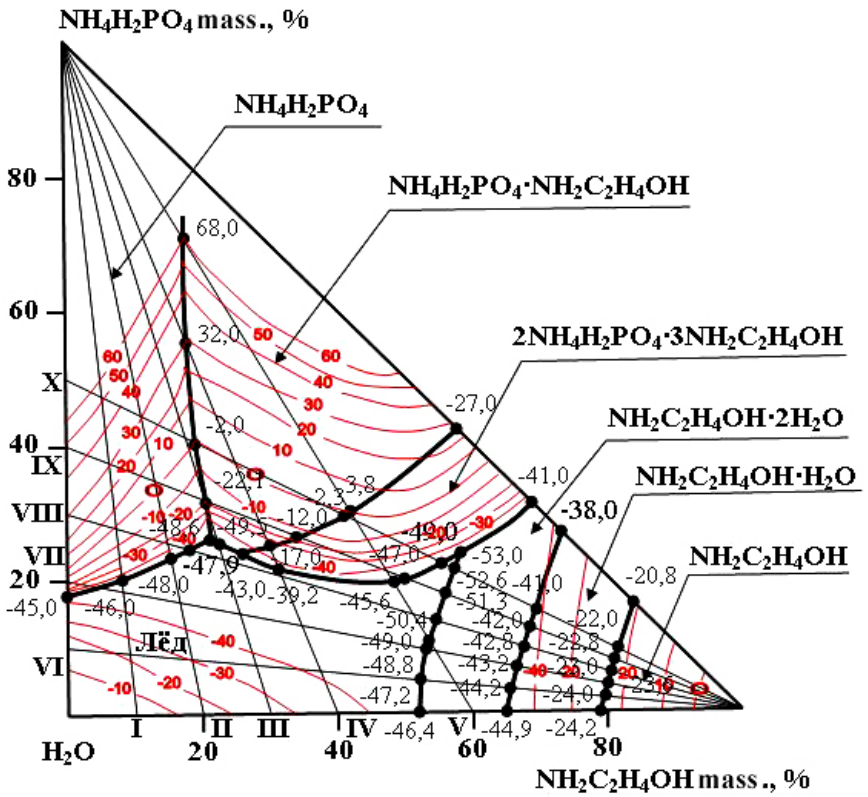
Solid phases were identified by chemical and various methods of physicochemical analysis. Thermal analysis of the new phases under study was carried out on a derivatograph of the Paulik-Paulik-Erdey system.

X-ray phase analysis was carried out on a Dron-3.0 diffractometer. The values of interplanar distances were found from the reference book (Диллер, Я.Л., 1966; Недома, И., 1975), according to the angle of reflection, and the intensity of diffraction lines was assessed on a 100-point scale.

Results and discussion

We studied the solubility of the $(NH_4)_2HPO_4$-$NH(C_2H_4OH)_2$-H_2O system (Ergashev D.A., Xamdamova Sh. Sh., 2022; Adiljonovich, E.D., & Sherzodovna, K.S., 2021; Adiljanovich, E.D., 2020; Эргашев Д.А., Асқарова М.К., Тухтаев С., 2015; Эргашев Д.А., Асқарова М.К., Тухтаев С., 2015; Ergashev Dilmurod Adiljonovich, Askarova Mamura Kamilovna, Tukhtaev Saidahral, 2016) using ten internal cuts. Of these, sections IV were studied from the side $NH_2C_2H_4OH$-H_2O to the top of $NH_4H_2PO_4$, sections VI–IX from the side $NH_4H_2PO_4$-H_2O to the top of $NH_2C_2H_4OH$.

Figure 1. *Solubility diagram for the system* $NH_4H_2PO_4$-$NH_2C_2H_4OH$-H_2O



Based on the results of studying binary systems and internal sections, a polythermal solubility diagram of a ternary system was constructed, on which the fields of crystalli-

zation of ice, mono ammonium phosphate, compounds of the compositions $NH_4H_2PO_4 \cdot NH_2C_2H_4OH$, $2NH_4H_2PO_4\ 3NH_2C_2H_4OH$, two aqueous, one aqueous and anhydrous monoethanolamine are delimited (Fig. 1, Table. 1).

These fields converge at four triple nodal points of the system, for which the chemical compositions of equilibrium solutions and the corresponding crystallization temperatures are determined (Table 1).

Table 1. *Double and triple points of the $NH_4H_2PO_4$-$NH_2C_2H_4OH$-H2O system*

Composition of the liquid phase, wt.%			*Crystal temperature,* °C	Solid phase
$NH_4H_2PO_4$	$NH_2C_2H_4OH$	H_2O		
18.0	–	82.0	–45.0	Ice + $NH_4H_2PO_4$
20.0	8.0	72.0	–46.0	Same
23.4	15.5	61.1	–48.0	—
24.6	18.3	57.1	–48.6	—
26.0	23.1	50.9	–49.5	Ice + + $NH_4H_2PO_4$ + $NH_4H_2PO_4$·N-$H_2C_2H_4OH$
71.0	17.8	11.2	68.0	$NH_4H_2PO_4$ + $H_4H_2PO_4$·N -$H_2C_2H_4OH$
55.4	18.0	26.6	32.0	Same
40.2	19.2	40.6	–2.0	—
31.6	20.5	47.9	–22.1	—
25.5	22.6	51.9	–47.9	Ice + $NH_4H_2PO_4$·$NH_2C_2H_4OH$
23.9	25.9	50.2	–43.0	Ice + $NH_4H_2PO_4$·$NH_2C_2H_4OH$ + +$2NH_4H_2PO_4$·$3NH_2C_2H_4OH$
25.3	29.0	45.7	–17.0	$NH_4H_2PO_4 \cdot NH_2C_2H_4OH$ + $2NH_4H_2PO_4$·$3NH_2C_2H_4OH$
26.2	33.8	40.0	–12.0	Same
29.5	41.2	29.3	–2.3	—
30.0	42.1	27.9	3.8	—
42.0	58.0	–	27.0	—
21.7	31.5	46.8	–39.2	Ice + $2NH_4H_2PO_4 \cdot 3NH_2C_2H_4OH$
19.8	48.3	31.9	–45.6	Same
20.0	50.0	30.0	–47.0	—
22.3	55.5	22.2	–49.0	—
23.9	58.5	17.6	–53.0	Ice + $2NH_4H_2PO_4 \cdot 3NH_2C_2H_4OH$ + +$NH_2C_2H_4OH \cdot 2H_2O$
31.0	69.0	–	–47.7	$2NH_4H_2PO_4 \cdot 3NH_2C_2H_4OH$ + + $NH_2C_2H_4OH$·$2H_2O$
21.5	57.5	21.0	–52.6	Ice + $NH_2C_2H_4OH \cdot 2H_2O$
17.8	56.0	26.2	–51.3	Same
13.9	54.6	31.5	–50.4	—
11.0	53.5	35.5	–49.0	—
9.4	53.0	37.6	–48.8	—
5.0	52.3	42.7	–47.2	—
–	52.0	48.0	–46.4	—

Composition of the liquid phase, wt.%			*Crystal temperature, °C*	Solid phase
$NH_4H_2PO_4$	$NH_2C_2H_4OH$	H_2O		
26.2	73.8	–	–38.0	$NH_2C_2H_4OH \cdot 2H_2O$ + + $NH_2C_2H_4OH \cdot H_2O$
15.7	69.5	14.8	–41.0	Same
12.7	68.7	18.6	–42.0	—
9.9	67.8	22.3	–42.8	—
7.0	66.5	26.5	–43.2	—
5.8	65.8	28.4	–44.2	—
–	65.0	35.0	–44.9	—
16.0	84.0	–	–20.8	$NH_2C_2H_4OH \cdot H_2O + NH_2C_2H_4OH$
9.7	81.8	8.5	–22.0	Same
7.9	81.0	11.1	–22.8	—
6.0	80.8	13.2	–23.0	—
4.2	80.3	15.5	–23.6	—
2.2	79.8	18	–24.0	—
–	79	21	–24.2	—

The polythermal diagram plots solubility isotherms every 10 °C. To clarify the nodal triple points, projections of polythermal solubility curves onto the corresponding lateral water sides of the concentration triangle were constructed.

Analysis of the solubility diagram of the studied system shows that the formation of the compound $2NH_4H_2PO_4 \cdot 3NH_2C_2H_4OH$ occurs in the temperature range –53.0 ÷ ÷ 27.0 °C. The minimum concentration of ammonium phosphate causing crystallization of $2NH_4H_2PO_4 \cdot 3NH_2C_2H_4OH$ into the bottom phase is 19.8%, and monoethanolamine is 24.0%. The formation of a compound with the composition $NH_4H_2PO_4 \cdot NH_2C_2H_4OH$ is observed at a higher temperature range –49.5 ÷ 68.0 °C and at higher concentrations of ammonium phosphate 24.1 ÷ 70.8%

From the data presented, it is clear that in the system under study, two chemical compounds are formed based on the initial components, i.e. $NH_4H_2PO_4 \cdot NH_2C_2H_4OH$, $2NH_4H_2PO_4 \cdot 3NH_2C_2H_4OH$, which are isolated from the expected areas and identified by chemical, thermogravimetric and X-ray phase analysis methods.

Chemical analysis of the isolated compounds gave the following results:

for $2NH_4H_2PO_4 \cdot 3NH_2C_2H_4OH$;

found,%: N= 15.01; H= 6.98; C = 16.87; P_2O_5= 35.02;

calculated,%: N= 16.95; H= 7.51; C = 17.43; P_2O_5= 34.38;

for $NH_4H_2PO_4 \cdot NH_2C_2H_4OH$;

found,%: N= 15.13; H= 6.79; C= 13.07; P_2O_5= 40.51;

calculated,%: N= 15.9; N= 7.38; C = =13.64; P_2O_5= 40.33;

A comparison of the data from X-ray diffraction and thermogravimetric analyses of the starting substances and $2NH_4H_2PO_4 \cdot$ $\cdot 3NH_2C_2H_4OH$, $NH_4H_2PO_4 \cdot NH_2C_2H_4OH$ showed that the isolated compounds have their own inherent crystal lattices and are characterized by specific transformations. The values of interplanar distances and intensities are given in Table 2.

According to thermal analysis data, in the range of 20–600 °C, five endothermic effects are observed on the heating curve of the compound $2NH_4H_2PO_4 \cdot 3NH_2C_2H_4OH$, corresponding to the melting and decomposition of the compound. The total mass loss at 600 °C is 68.7%. On the heating curve of the compound $NH_4H_2PO_4 \cdot NH_2C_2H_4OH$, four endothermic and one exothermic effect are observed. That is, the thermal analysis data are identical to the literature data [6].

Table 2. *Values of interplanar distances* $NH_4H_2PO_4$ $2NH_4H_2PO_4 \cdot 3NH_2C_2H_4OH$ и $NH_4H_2PO_4 \cdot NH_2C_2H_4OH$

$NH_4H_2PO_4$		$2NH_4H_2PO_4 \cdot 3NH_2C_2H_4OH$		$NH_4H_2PO_4 \cdot NH_2C_2H_4OH$	
d, Å	J/J1,%	d, Å	J/J1,%	d, Å	J/J1,%
5.32	100	8.35	77	8.99	100
3.75	64	5.00	72	5.40	63
3.07	89	4.51	63	4.71	93
3.06	75	4.00	95	4.18	66
2.66	18	3.65	100	3.86	73
2.65	15	2.82	45	2.91	26
2.37	8	2.59	36	2.63	23
2,009	29	2.31	18	2.40	20
2,004	22	2.27	22		
1.77	5				

In addition, in the studied system, the salting effect of the components on each other is observed. With increasing concentration and temperature, the salting-in effect of monoethanolamine on ammonium phosphate increases. So, with a 10% content of monoethanolamine in solution, the solubility of monoammonium phosphate at temperatures is 0.0; 10.0; 20.0; and 30.0 °C increases by 11.2 accordingly; 14.0; 18.0 and 20.9% compared to its solubility in water. Monoammonium phosphate has a lesser ability to increase the solubility of monoethanolamine than the latter does to the solubility of ammonium phosphate.

Conclusions

The results of the studied system indicate the technological possibility of obtaining compounds with physiologically active properties by joint dissolution of the initial components at their optimal ratios, also identified from the data of agrochemical tests.

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submitted 22.08.2023;
accepted for publication 20.09.2023;
published 8.10.2023

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