SOLUBILITY POLYTEREME OF THE SYSTEM AMMONIUM SULPHATE - MAGNESIUM CHLORATE DEFOLIANT - WATER

Shukhrat Yakubov, Mohira Adilova, Doniyorjon Obidjonov,
Jamshid Shukurov, Bakhrom Kucharov, Bakhtiyor Zakirov

Institute of General and Inorganic Chemistry
Academy of Sciences of the Republic of Uzbekistan,
77 Mirzo Ulugbek St., Tashkent, 100170 Uzbekistan
Email: doniyor_obidjonov94@mail.ru

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ABSTRACT

The mutual influence of components in an aqueous system consisting of ammonium sulfate and magnesium chlorate defoliant was studied in a wide concentration range at a temperature of -27.0 to 4.5°C. On the state diagram of the system, the fields of crystallization of ice, magnesium chlorate hexahydrate, ammonium sulfate, and the compound $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$ are delimited, which was identified and characterized by chemical, X-ray phase, thermal, and IR spectroscopic methods of analysis.

Keywords: solubility chart, ammonium sulfate, magnesium chlorate, temperature, defoliation.

INTRODUCTION

In Uzbekistan, in recent years, scientific research to find new types of defoliants has been significantly expanded and deepened. This need is due to the great national economic importance of the use of defoliants, as one of the most important conditions for the successful mechanized and high-quality harvesting of raw cotton in the pre-frost period [1 - 6]. A significant problem of cotton growing in our Republic is the lack of local, mild defoliants that ensure a high degree of cotton leaf fall [7 - 19]. In case of chemical impact on cotton to remove leaves, highly effective defoliants are needed, providing more than 80 % fall of cotton leaves in one treatment at low consumption rates, acting on plants gently, i.e. not negatively affecting the oil content and quality of cotton fibre. In the Republic, the widely used cotton defoliant magnesium chlorate does not fully meet the modern requirements of cotton growing, its rigidity on plants and high doses of application requires the creation of new effective, mild, that do not negatively affect the oil content of seeds, productivity, quality of cotton fibre and do not clog defoliants on plants.

From the foregoing, the need for the search and development of low - toxicity, highly effective and mildly acting defoliants concentrated in terms of the active substance is obvious.

One of the promising ways to solve these urgent problems is the selection of the most accessible and effective synergists to the known existing range of defoliants, the synthesis and use of complex compounds of the latter with the active components of defoliants. The most accessible and effective synergists for defoliants of the chlorate group are the components of nitrogen, nitrogen - sulfur and nitrogen-phosphorus fertilizers. Ammonium sulfate is a synergist for magnesium chlorate, which enhances the efficiency of the defoliation process and eliminates the negative effects of chlorates on plants [20, 21]. At the same time, it is possible to reduce the consumption rates of their active components, thereby reducing the harshness of the action on cotton. Ammonium sulfate to serve as an additional foliar top dressing for plants.

For the physicochemical substantiation of the process of obtaining mild defoliants, it is necessary to know the solubility of salts in systems that include the studied components and the interaction of the initial components in a wide range of temperatures and concentrations [22 - 24].

Based on the foregoing, we studied the interaction of components in an aqueous system with the participation of magnesium chlorate defoliant and ammonium sulfate in a wide range of temperatures and concentrations using the visual-polythermal method [25, 26].

EXPERIMENTAL

The objects of study are ammonium sulfate, magnesium chlorate-chloride.

Magnesium chlorate was obtained based on the exchange reaction of sodium chlorate with magnesium sulfates and chlorides in aqueous and acetone media [27, 28]. For the study, ammonium sulfate grade "ch" was used.

In quantitative chemical analysis, the following methods were used: the content of chlorate ion was determined by the volumetric permanganometric method [29], elemental analysis for nitrogen and hydrogen was carried out according to [30].

In the course of the work, a visual-polythermal method was used using a TN-6 glass mercury thermometer with a measurement range from -30 to 60°C [25, 31].

RESULTS AND DISCUSSION

For the physicochemical substantiation of the process of obtaining a new defoliant with mild properties, we studied the solubility of the components in the system ammonium sulfate-magnesium chlorate defoliant-water, the composition of which is $(NH_4)_2SO_4$ - {55 % [79 % $Mg(ClO_3)_2$ + 21 % $MgCl_2$] + 45 % H_2O} - H_2O visual-polythermal method in a wide temperature range.

The behaviour of magnesium chlorate and ammonium sulfate in the system $(NH_4)_2SO_4$ - {55 % [79 % $Mg(ClO_3)_2$ + 21 % $MgCl_2$] + 45 % H_2O} - H_2O studied under polythermal conditions from - 27.0 to 4.5^{o}C.

On the state diagram of the system, the fields of crystallization of ice, magnesium chlorate hexahydrate, ammonium sulfate, and a compound of the composition $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$ are delimited (Fig. 1).

The fields converge at two triple nodal points of coexistence of three different solid phases (Table 1).

From the system solubility diagram $(NH_4)_2SO_4$ - {55 % [79 % $Mg(ClO_3)_2$ + 21 % $MgCl_2$] + 45 % H_2O} - H_2O It can be seen that the temperature range -14.5 to 4.5°C corresponds to the joint crystallization of the compound $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$ with ice, ammonium sulfate, and magnesium chlorate hexahydrate.

In the temperature range -26 to 27.0°C, magnesium chlorate hexahydrate with ice crystallizes from an equilibrium solution, in the temperature range -19.0 to -17.0°C, ammonium sulfate with ice crystallizes.

The field of crystallization of the ternary compound occupies a large part of the polythermal diagram, which indicates its low solubility relative to other components of the system.

The synthesized compound was isolated from the expected region of crystallization, identified and confirmed by modern methods of chemical and physico-chemical analysis.

The results of the chemical analysis of the solid phase isolated from the crystallization region of the compound are given in Table 2.

The formation of a ternary compound in the system is apparently the result of the following reactions in solution

$Mg(ClO_3)_2 + (NH_4)_2SO_4 = 2NH_4ClO_3 + MgSO_4$

$2MgSO_4 + 2NH_4ClO_3 + (NH_4)_2SO_4 + H_2O =$

$= (NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$

Each compound, as a rule, has its own specific crystal lattice inherent only to it. Therefore, to establish the crystallinity and identify the obtained compounds, X-ray phase analysis was performed [32].

X-ray phase analysis showed that the obtained compound of the composition $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$ is characterized by its own values of interplanar distances, confirming its individuality (Fig. 2).

One of the important characteristics of chemical compounds is their thermal stability, the knowledge of which makes it possible to select temperature intervals for the use of certain substances, as well as to determine methods for their preparation.

Thermal analysis or the method of heating and cooling curves, as one of the methods of physicochemical analysis, makes it possible to study phase transformations in solid and liquid systems, accompanied by the release or absorption of heat, and is one of the methods for identifying individual chemical compounds [33, 34].

Usually, the location of thermal effects on a thermogram and even the general shape of the theoretical curve is often so typical only for a given substance that the thermograms of many substances

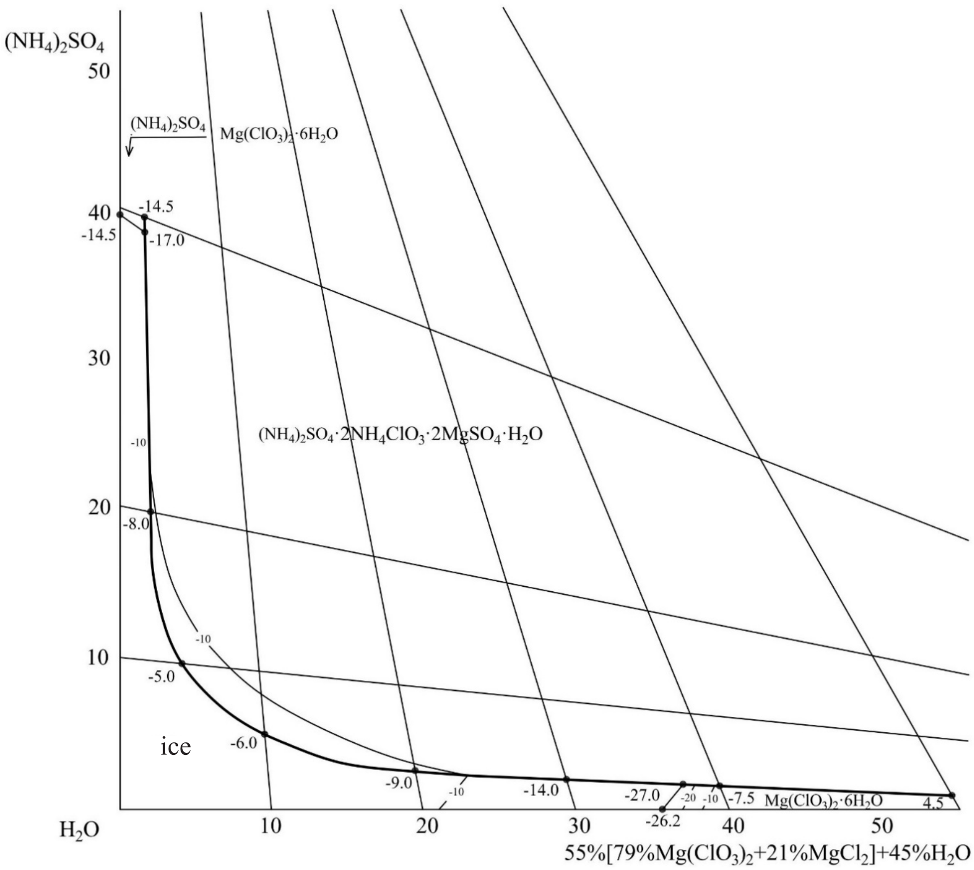

Fig. 1. Solubility polytherm of the $(NH_4)_2SO_4$ - {55 % [79 % $Mg(ClO_3)_2$ + 21 % $MgCl_2$] + 45 % H_2O} - H_2O system.

Table 1. Double and triple points of $(NH_4)_2SO_4$ - 55 % [79 % $Mg(ClO_3)_2$ + 21 % $MgCl_2$] + 45 % H_2O} - H_2O system.

Liquid phase composition, %			T cris. ˚C	Solid phase
$(NH_4)_2SO_4$	{55 % [79 % $Mg(ClO_3)_2$ + + 21 % $MgCl_2$] + 45 % H_2O}	H_2O		
39.5	1.6	58.9	- 14.5	$(NH_4)_2SO_4$ + $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$
38.3	1.7	60.0	- 17.0	Ice + $(NH_4)_2SO_4$ + $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$
39.5	-	60.5	- 19.0	$(NH_4)_2SO_4$ + Ice
19.6	2.0	78.4	- 8.0	Ice + $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$
9.6	4.0	86.4	- 5.0	
5.0	9.5	85.5	- 6.0	
2.5	19.5	78.0	- 9.0	
2.0	29.4	68.6	- 14.0	
1.6	37.0	61.4	- 27.0	Ice + $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$ + $Mg(ClO_3) \cdot 6H_2O$
-	35.5	64.5	- 26.2	Ice + $Mg(ClO_3) \cdot 6H_2O$
1.5	39.5	59.0	- 7.5	$Mg(ClO_3) \cdot 6H_2O$ + + $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$
1.0	55.0	44.0	4.5	

Table 2. The results of the chemical analysis of $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$ compound.

Compound	$MgSO_4$		$(NH_4)_2SO_4$		NH_4ClO_3		H_2O	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$	40.8	40.61	22.02	22.33	33.86	34.85	3.32	2.71

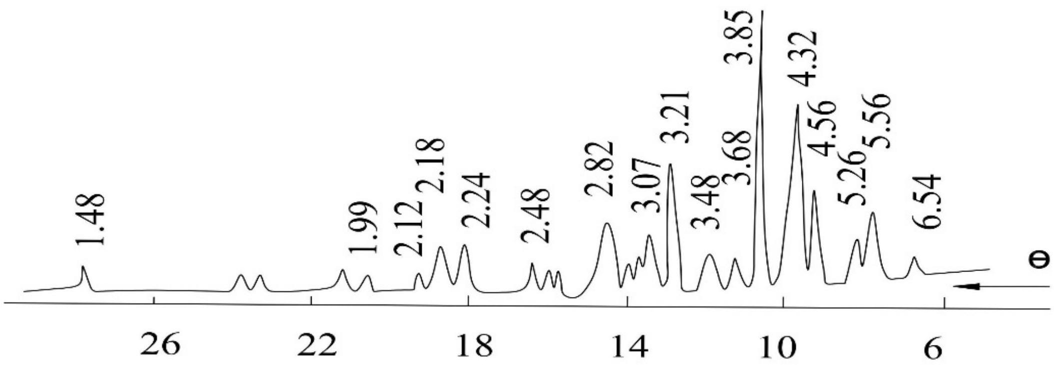

Fig. 2. Radiograph pattern of $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$.

can be considered as their thermal spectra [35]. The most general information on the thermal properties of the components of mineral fertilizers and inorganic compounds is reflected in the literature [36].

The derivatogram of $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$ shows several endothermic effects (Fig. 3).

The effects at 135°C and 150°C correspond to the stepwise decomposition of ammonium chlorate, which is part of the ternary compound. At 190°C, water of crystallization is given. The total weight loss, according to the TG curve of the derivatogram, is 37.3 %. The endothermic effect at 305°C is the result of the incongruent melting of the decomposition products of the ternary compound to form a melt of the binary compound $(NH_4)_2SO_4 \cdot MgSO_4$. At 390°C, ammonium sulfate in the composition of this double compound $(NH_4)_2SO_4 \cdot MgSO_4$ partially decomposes with the formation of an acid salt of ammonium sulfate, the final decomposition of which occurs at 405°C. The total weight loss is 59.2 %. The product of the decomposition of the ternary compound is magnesium sulfate.

IR spectroscopy is one of the methods used for qualitative determination of the structure and identification of new complex compounds. By studying the vibrational spectra of compounds obtained in the form of solutions and in the crystalline state, it is possible to elucidate the types of chemical bonds, the place and method of coordination of the ligand with the complexing agent [37 - 39].

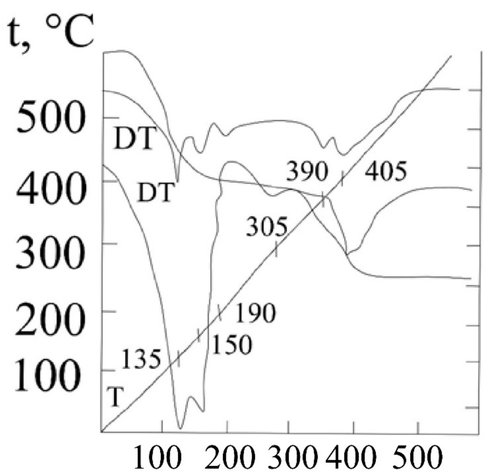

Fig. 3. Derivatogram of the compound $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$.

The IR spectrum of $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$ shows a shift in a number of absorption bands (Fig. 4).

The absorption bands νs and νas of the sulfate ion are shifted to the low-frequency region by 10 and 30 - 50 cm^{-1}, respectively, νs by 50 - 90 cm^{-1} compared to the free molecule of the initial components.

This indicates that the coordination of molecules

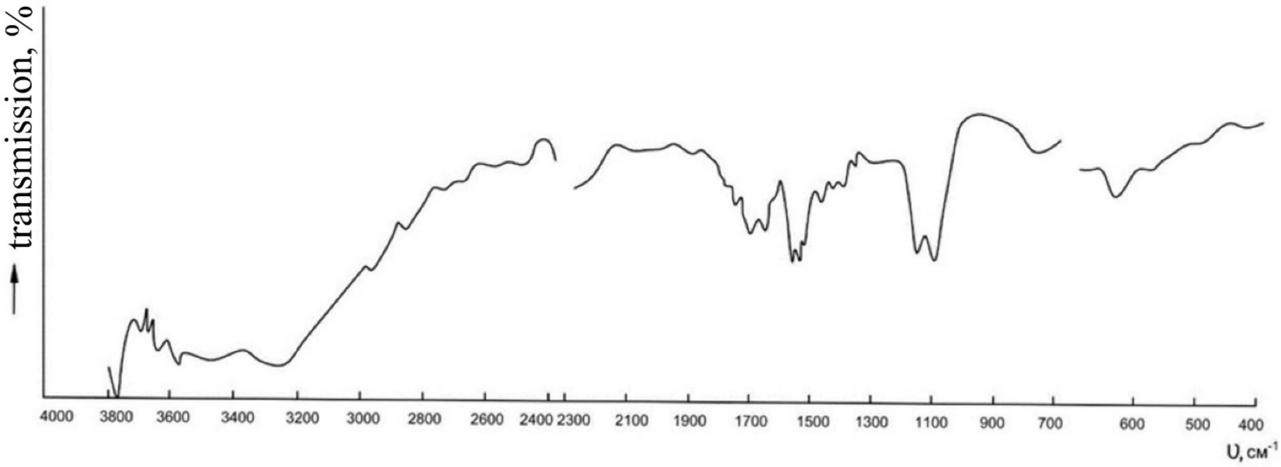

Fig. 4. IR spectra of the compound $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$.

in the compound under study is carried out through the SO_4^{2-} magnesium sulfate groups and the NH_4^+ group of ammonium chlorate and sulfate as a result of the formation of an anionic complex. The absorption bands of the chlorate ion change insignificantly; apparently, this group does not participate in the specific interaction in the newly formed bond. The absorption bands of stretching vibrations of water of crystallization, usually observed in the region of 3355 - 3445 cm^{-1} in free magnesium sulfate hepthydrate in the spectrum of the compound, are aligned with the vibrations νas (NH_4), and δ (H_2O) we found at 1630 - 1633 cm^{-1}.

CONCLUSIONS

Thus, in the studied system $(NH_4)_2SO_4$ - {55 % [79 % $Mg(ClO_3)_2$ + 21 % $MgCl_2$] + 45 % H_2O} - H_2O the formation of a compound of the composition $(NH_4)_2SO_4 \cdot 2NH_4ClO_3 \cdot 2MgSO_4 \cdot H_2O$ was established, which was identified by methods of chemical and physicochemical analysis. The data obtained are of interest and are the physicochemical basis for further development of a technology for obtaining a physiologically active, mild defoliant based on $(NH_4)_2SO_4$ and 55 % [79 % $Mg(ClO_3)_2$ + 21 % $MgCI_2$] + 45 % H_2O.

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