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PREPARATION OF PHYSIOLOGICAL ACTIVE SUBSTANCE BASED ON SULFURIC ACID AND MONOETHANOLAMINE

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ПРИГОТОВЛЕНИЕ ФИЗИОЛОГИЧЕСКОГО АКТИВНОГО ВЕЩЕСТВА НА ОСНОВЕ СЕРНОЙ КИСЛОТЫ И МОНОЭТАНОЛАМИНА

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ABSTRACT

A number of studies were carried out to determine the optimal conditions for the synthesis of monoethanolammonium sulfate solution. The different modes of important parameters of the process of obtaining a saturated solution of monoethanolammonium sulfate were used, differences of the enthalpy (ΔH), pH of the medium, decomposition of raw materials and the appearance of the finished product were established, and a diagram was constructed based on the obtained data.

АННОТАЦИЯ

Был проведен ряд исследований по определению оптимальных условий синтеза раствора сульфата моноэтаноламмония. Использованы разные режимы важных параметров процесса получения насыщенного раствора сульфата моноэтаноламмония, установлены различия энтальпии (ΔH), pH среды, разложения сырья и внешнего вида готового продукта, а также диаграмма был построен на основе полученных данных.

Keywords: synthesis, sulfate, monoethanolammonium, process, enthalpy, diagram.
Ключевые слова: синтез, сульфат, моноэтаноламмоний, процесс, энтальпия, диаграмма.

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A number of works are known from the literature on the preparation and use of salts based on ethanolamine and mineral acids [1-4], which have physiological activity [5]. One of the representatives of this class of compounds, the triethanolammonium salt of 2-methylphenyloxyacetic acid (the drug "Trecrezan") [6], showed significantly higher growth-regulating activity for plants than the original acid [7].

Depending on the purpose of use, such compounds are used in practice directly or as an additive.

It is known from world experience that the use of physiologically active substances in the chemical processing of agricultural crops gives effective results [8]. Their use in defoliation also gives positive results.

As already mentioned, physiologically active substances can increase the physiological activity of the initial product by using them as additives to existing drugs. It is in this way that cotton defoliants are obtained, which have physiological activity. Defoliants and desiccants are classified as crop-promoting chemicals because they are commonly used to facilitate mechanical harvesting [9].

It is important to remove the cotton foliage before harvesting to improve the quality of the cotton fiber with less debris during harvesting by machines [10]. Thus, harvesting aids, such as chemical defoliants or desiccants, are now considered important components of modern cotton production [11]. Removing leaves before harvesting cotton leaves using certain defoliants can facilitate mechanical cleaning and improve the quality of the collected cotton lint [12-14]. Hence, defoliation is an important management practice associated with this high yield and high quality cotton [15].

The role of physiologically active substances in defoliation is to increase yields by accelerating the opening of young bolls after the fall of cotton leaves.

Ultra-small hectare doses of these drugs (to achieve a result per hectare, it is enough to add a few grams or milligrams of these substances) "vote" for more active and widespread use of a physiologically active substance in rural production [16], and therefore, their low cost, comparative safety for humans and the natural environment [17], the ability to heal plants in the most rational and ecological way, enhancing their natural capacity to withstand various kinds of stress [18].

Accordingly, the acquisition of valuable drugs containing physiologically active substances plays an increasingly important role in the development of modern innovative technologies.

To substantiate the process of obtaining a physiologically active substance in the form of a concentrated solution of monoethanolammonium sulfate was studied the processes of neutralization of monoethanolamine with the introduction of 98% sulfuric acid.

The reaction of adding inorganic acids to ethanolamines, as we know, proceeds with an explosion, and this is an exothermic process, in which a large amount of heat is released. herewith the higher the pace of sulfuric acid inning, the greater the increase in the temperature of the solution. The sudden increase of temperature in the process can lead to the decomposition of the reaction participants. Which will inevitably interfere the achievement of the desired result. To prevent this, a number of necessary measures are taken, such as controlling the temperature of process, the acid inning pace and the mixing pace of the solution.

The chemical reagents were used of analytical purity grade. These are sulfuric acid (H_2SO_4, 94.0%, mass fraction), monoethanolamine ($NH_2C_2H_4OH$, 98.0%, mass fraction).

The pH value was measured by a high precision pH meter (FE 20 pH meter, Mettler-Toledo International Inc., USA) with a precision of ±0.01.

For save stability of temperature uring conditions of experiment, a Polyscience cooled circulating water bath was used (precision of ± 0.05).

An overhead stirrer (OS20-S, DLAB Sci-entific Co., Ltd, China) was used to regularly stir the solution while adding sulfuric acid to monoethanolamine during the synthesis of monoethanolamine sulfate.

A chemical dispenser pump (541-0125NT, Analytical Scientific Instruments US, Inc.) was used to control acid temperature and feed rate with a precision of ± 1% or ± 2 μL / min.

The hydrometric and refractive index methods were used to determine the concentration of the initial materials. A digital refractometer (PAL-BX/RI ATAGO CO., LTD, Japan) was used to determine the refractive index.

For the IR spectral analysis of the initial and obtained materials, an MIRacle10 IR spectrometer (Shimadzu Scientific Instruments) was used.

To find the optimal ratio of sulfuric acid and monoethanolamines, which provides a neutral pH of the medium (pH = 6-7), during the neutralization process, the acid was added in stages and at each stage the pH of the medium, the reaction temperature (ΔH) and the ratio of the components corresponding to the concentration of the acid in the solution and the results obtained are presented in table 1.

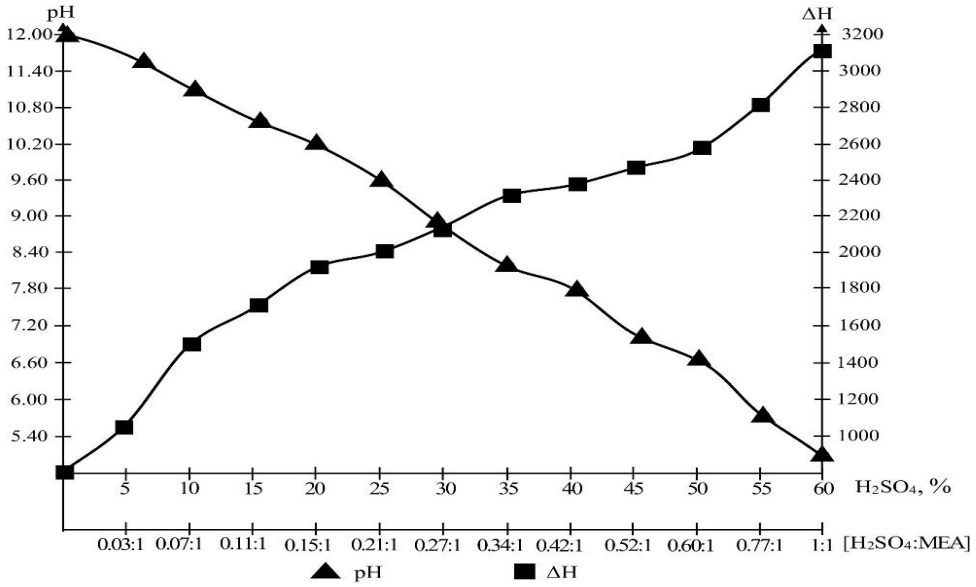

Figure 1. Mutual change of ΔH and pH medium of the solution during neutralization of monoethanolamine with sulfuric acid

Table 1.

Determination of the optimal ratio of the concentrations of monoethanolamine and sulfuric acid.

№	Concentration H_2SO_4, %	Ratios H_2SO_4:MEA	ΔH	pH
1	-	MEA	-	12.55
2	5.21	0.03:1	1051.2	11.91
3	10.44	0.07:1	1445.4	11.23
4	15.63	0.11:1	1708.2	10.62
5	20.74	0.15:1	1930.9	9.97
6	26.05	0.21:1	2041.0	9.60
7	31.31	0.27:1	2194.3	8.98
8	36.47	0.34:1	2305.8	8.34
9	41.68	0.42:1	2394.5	7.78
10	46.89	0.52:1	2462.0	7.19
11	**50.12**	**0.60:1**	2498.0	**6.61**
12	56.31	0.77:1	2810.8	5.89
13	62.61	1:1	3156.6	5.33

Table 1 shows that the optimal ratio of sulfuric acid and monoethanolamine, providing a neutral pH of the medium (pH = 6-7) in solution, is 0.60: 1.

To determine the optimal mode that allows maintaining the process temperature (ΔH) at a constant level, the experiment was carried out using the following modes of the sulfuric acid inning rate in the MEA: 1 ml/min., 0.5 ml/min. and 0.17 ml/min.

The heat of reaction (ΔH), the pH of the mixture medium, the evolved gases, and the change in the color of the mixture with time were determined for each mode (Table 2).

Table 2.

Determination of the optimal acid inning mode and the optimal stirring speed of the solution (Ratio H_2SO_4: MEA (0.60: 1))

Mode of inning	Speed of stirring	ΔH	pH	Separated gases	Color of the solution
0.17 ml/min.	500 rpm	2628.0	5.25	H_2O	Leaky gray
	700 rpm	2490.8	6.61	-	Transparent brown
	1000 rpm	2430.9	6.77	-	The same
0.5 ml/min.	500 rpm	4599.0	4.89	H_2O	Leaky gray
	700 rpm	4467.6	5.21	-//-	The same
	1000 rpm	4336.2	5.34	-//-	-//-
	500 rpm	4993.2	4.51	H_2O	Leaky gray

Mode of inning	Speed of stirring	ΔH	pH	Separated gases	Color of the solution
1.0 ml/min.	700 rpm	5256.0	4.43	-//-	The same
	1000 rpm	5518.8	4.13	-//-	-//-

The study showed that saturated solution of monoethanolammonium sulfate with 6-7 pH of medium can be obtained at sulfuric acid inning rate of 0.17 ml/min. and mixing speeds of 700 and 1000 rpm. The optimal mixing speed mode, which allows you to achieve the desired result at minimal cost, was accepted as 700 rpm. As a result of the interaction of sulfuric acid with monoethanolamine, a 95.8% saturated solution of monoethanolammonium sulfate is formed with a pH value 6.61 and a crystallization temperature of -52.4 ° C.

The study found that in the process of neutralization, the temperature and pH values of the newly formed solutions increase. Herewith, the higher the sulfuric acid inning rate, the greater increase in the temperature of the solution and the degree of water separation. The maximum separation of water is observed at a sulfuric acid inning rate of 2.25 ml/s. An increase in the temperature of the solution also results in the loss of one water molecule. Thus, at 40 °C and a sulfuric acid inning rate of 1.17 ml/s. the water separation is 1.154%. At 20 and 30 °C, this index is 0.273%; 0.512% (Table 3).

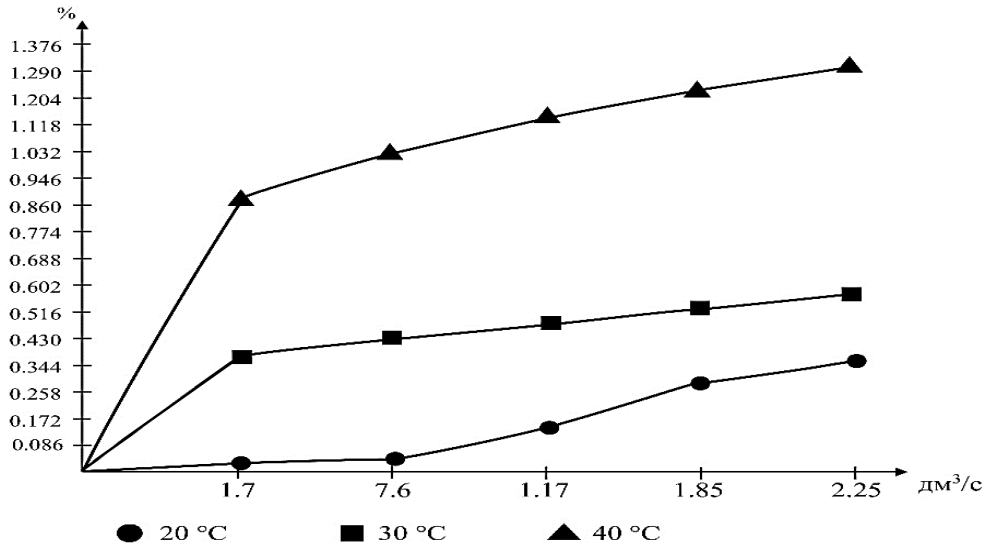

Figure 2. Diagram of the dependence of water losses on the rate of sulfuric acid inning at temperatures of 20, 30 and 40 °C

Table 2.

Dependence of water losses on the rate of sulfuric acid inning in the process of obtaining a solution of neutralized monoethanolamine sulfate

№	Sulfuric acid inning rate, ml / s.	Temperature, °C	Water separation degree, % (rel.)
1.	1.7	20	0.032
2.	7.6	-//-	0.049
3.	1.17	-//-	0.157
4.	1.85	-//-	0.273
5.	2.25	-//-	0.353
6.	1.7	30	0.408
7.	7.6	-//-	0.428
8.	1.17	-//-	0.492
9.	1.85	-//-	0.512
10.	2.25	-//-	0.596
11.	1.7	40	0.908
12.	7.6	-//-	1.072
13.	1.17	-//-	1.102
14.	1.85	-//-	1.154
15.	2.25	-//-	1.296

From the results of these studies, it follows that to obtain a saturated solution of monoethanolamine sulfate, it is expedient to carry out the process with a sulfuric acid inning rate of 1.7-7.6 ml/s. with intensive mixing and at 20 °C, where the loss of water is minimal and does not exceed 0.049 %.

To identify the difference between the substances synthesized in different modes of sulfuric acid supply, IR spectral analysis was performed.

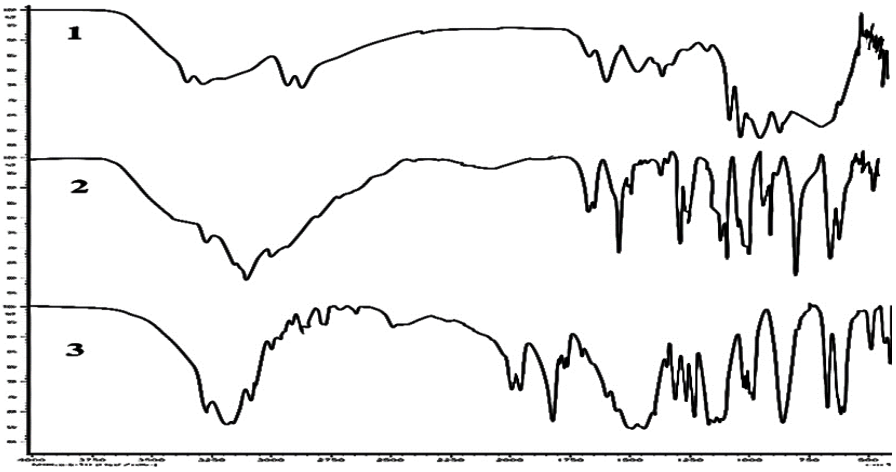

Figure 3. IR spectra: (1) monoethanolamine; (2) the compound synthesized at 700 rpm and in the mode of inning sulfuric acid: 0.17 ml/min; (3) a compound synthesized at 500 rpm and in the mode of inning sulfuric acid: 0.5 ml/min

Depending from the rate of addition of monoethanolamine to sulfuric acid, two reactions occur: with the slow addition of monoethanolamine, monoethanolammonium sulfate is formed.

$$H_2SO_4+NH_2C_2H_4OH= HSO_4 \cdot NH_3C_2H_4OH$$

At high rates of monoethanolamine addition, one water molecule is lost form ethanolamine sulfate.

$$H_2SO_4+NH_2C_2H_4OH= C_2H_7NO_4S+H_2O$$

If the supply of monetanolamine is high, one water molecule will be lost and ethanolamine sulfate will be formed. In the IR spectra of the compound, with the addition of 0.17 ml/min of monethanolamine to sulfuric acid, several stretching vibration frequencies are observed in the bands of the NH and OH bond. The high frequency of triethanolammonium sulfate with hydrogen bonds is 137 cm^{-1}, the difference in stretching vibrations of the OH-group in monethanolamine and stretching vibrations in monoethanolamine is 134 cm^{-1}, the highest frequency of stretching vibrations of the N-H bond is 1049-758 cm^{-1}. The bands of 3078-2966 cm^{-1} are linked by stretching vibrations of the CH_2 bond. The 613 and 432 cm^{-1} bands correspond to SO_4 vibrations (Fig. 3).

In the IR spectra of the compound obtained by adding monoethanolamine to sulfuric acid at a rate of 0.50 ml / min, ethanolamine sulfate is formed due to the loss of the OH group in monoethanolamine. In the new compound, stretching vibrations were observed corresponding to the NH_2 group in the range of 3081-2968 cm^{-1}. Vibrations in the range 2483-2268 cm-1 are symmetric and asymmetric stretching vibrations of the CH_2 bond, and the 768 and 416 cm^{-1} bands are asymmetric and symmetric stretching vibrations of the SO_4 group. Vibrations in the range 2483-2268 cm^{-1} are symmetric and asymmetric stretching vibrations of the CH_2 bond, and the 768 and 416 cm^{-1} bands are asymmetric and symmetric stretching vibrations of the SO_4 group. Thus, there was a loss of stretching vibrations of OH lines in the region of the absorption spectra of the compound (Fig. 4).

Thus, the research results showed the following:

1. The optimal ratio (0.60:1) of sulfuric acid and monoethanolamines was determined, providing an environment with a neutral pH;
2. The optimal parameters of the acid injection mode and the solution stirring speed have been determined;
3. The levels of water loss were studied depending on the rate of delivery of sulfuric acid at different temperatures.

These data are the scientific basis for the development of technology for the obtaining of physiologically active substances based on sulfuric acid and monoethanolamine.

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