YUGATO

ISSN: 0387-5695, eISSN: 0387-5695
Vol. 75 No. 2 (2023)

Received: October 16, 2023 / Revised: November 11, 2023 / Accepted: November 29, 2023 / Published: December 16, 2023

STUDYING THE SOLUBILITY OF THE SYSTEM $MnSO_4$ - KCl - H_2O

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ABSTRACT

The solubility of the components in the system KCl - $MnSO_4$ - H_2O was studied by the visual-polythermal method in the temperature range from -6.0° C to 13.0° C. The phase diagram limits the crystallization regions of ice, KCl, $MnSO_4$ and K_2SO_4. A solubility diagram was plotted and a new compound, K_2SO_4, was isolated. The new compound was identified by chemical, X-ray diffraction, thermogravimetric and IR spectroscopic analyses.

Key words: potassium chloride, manganese sulfate, solubility diagram, visual polytherm, X-ray phase analysis, IR spectrum, thermogravimetric analysis.

INTRODUCTION

The solubility of the KCl - $MnSO_4$ - H_2O system has been studied in connection with the practical importance of micronutrient fertilizers in agriculture.

At present, it has been found out that microelements are part of a large number of enzymes, the role of which in plant life is great: they accelerate biochemical reactions ensuring their occurrence at normal body temperature [I]. The content of trace elements in plants is thousandths of a percent, but their importance in plant nutrition is great. The lack or excess of microelements in the soil causes significant deviations in growth and development in plants, stimulating or inhibiting them, because all processes in a living organism occur with the assistance of biologically active substances - enzymes, vitamins, hormones, of which microelements are an integral part [II]. Manganese is an essential nutrient for plants and animals. It also affects the synthesis of amino acids, polypeptides and cell proteins [III]. Manganese contributes to the selective absorption of ions from the external environment; when it is excluded, the content of a number of microelements increases. Manganese influences the promotion of phosphorus from aging leaves to young ones. [IV]. The main part of manganese is concentrated in leaves and chloroplasts. It activates the conversion reactions of di- and tricarboxylic acids, is part of about 30 metal-enzyme complexes. Takes part in redox processes, being an integral part of many enzymes, such as hydroxylamine reductase; reducing hydroxylamine to ammonia and an assimilation enzyme that reduces carbon dioxide during photosynthesis; increases the content of sugars, their outflow from the leaves to the roots, enhances respiration. Using plants nitrogen in the form of nitrates, it acts as a reducing agent and, conversely, when using ammonium nitrogen – as oxidizer. It activates the action of indomylacetic acid on the growth of plant cells [V]. With a lack of manganese, the synthesis of organic substances decreases, the content of chlorophyll in plants decreases, and they become ill with chlorosis [VI]. Well-known phosphorus fertilizers containing manganese are manganese superphosphate, manganese sulfate use technical manganese salts, which increases the cost of fertilizers. Therefore, the study of the possibility of manganese-containing industrial waste in the production of phosphate fertilizers enriched with trace elements is an urgent task

[VII]. The application of micro fertilizers with solid macro fertilizers includes the following three main procedures: simple mechanical mixing, incorporation into the composition of macro fertilizers during the production process, and application of ready-made fertilizer granules to the surface. The addition of trace elements in the production of granular NPK fertilizers or the preparation of fertilizer mixtures can significantly reduce costs and create various combinations [VIII, C. 15-19; IX, p. 22]. To solve the problem of obtaining highly effective complex NPK fertilizers, deep physicochemical studies of the interaction of microelements with fertilizer components during their production and storage are necessary. For the purpose of physical and chemical substantiation of the process of obtaining NPK fertilizers containing, depending on the ratio of N: P_2O_5: K_2O and solubility in water, potassium chloride, potassium and ammonium sulfates, monoammonium phosphate, urea or ammonium nitrate, the interaction of potassium chloride and in order to identify the possibility of using manganese-containing wastes and middlings of non-ferrous metallurgy, as well as the chemical industry in the production of mineral fertilizers with the addition of the trace element manganese, the solubility of the components in the KCl - $MnSO_4$ - H_2O system was studied visually by the polythermal method in the temperature range from -6.0° C to 13.0° C.

EXPERIMENTAL PART

The objects of study are water, potassium chloride and manganese sulfate monohydrate. In our studies, chemically pure potassium chloride (GOST 4568-95) and salt of manganese sulfate monohydrate (GOST TU 6-47-53028-10-93, CAS 10034-96-5) were used. Our experimental measurements included X-ray phase analysis (LabX XRD-6100, Japan) [X], infrared spectroscopic analysis (Specord IR-75) [XI], and thermal analysis (DTG-60, Japan). The studies used the visual-polythermal method [XII] using a TN-6 glass mercury thermometer with a measurement range from -30° C to 60° C, as well as the pycnometric method (GOST 31992.1-2012) [XIII]. To measure the viscosity of the solutions, a VPZh viscometer was used; to measure the pH value of the solutions, a FE20 METTLER TOLEDO pH meter was used.

RESULTS AND DISCUSSION

The solubility and properties of the components of the KCl-$MnSO_4$-H_2O system have been studied at various temperatures and concentrations to demonstrate the physicochemical interactions between manganese sulfate and potassium chloride. The KCl-$MnSO_4$-H_2O system was studied on nine internal sections (Fig. 1). Of these, sections I-IV from the KCl side to the $MnSO_4$ peak, and sections V-IX from the $MnSO_4$ - H_2O side to the KCl peak were studied. Based on binary systems and internal sections, a solubility diagram of the KCl-$MnSO_4$ - H_2O system was constructed in the temperature range from -6.0° C to 13.0° C. On the phase diagram of the state of the system, the fields of crystallization of ice, potassium chloride, manganese sulfate and potassium sulfate are delimited. These fields converge at two triple points of the system. The equilibrium composition of solutions at the double and triple points of the system and the corresponding crystallization temperatures were determined (Table 1). The first triple point corresponds to 20% manganese sulfate, 6.2% potassium chloride and 73.8% water with a crystallization temperature of -7.0° C. In this case, the solid phase will consist of manganese sulfate, ice and potassium sulfate.

The second triple point corresponds to 4.3% manganese sulfate, 12.0% potassium chloride and 83.7% water with a crystallization temperature of -9.7° C, the composition of the solid phase consists of ice, potassium chloride and potassium sulfate.

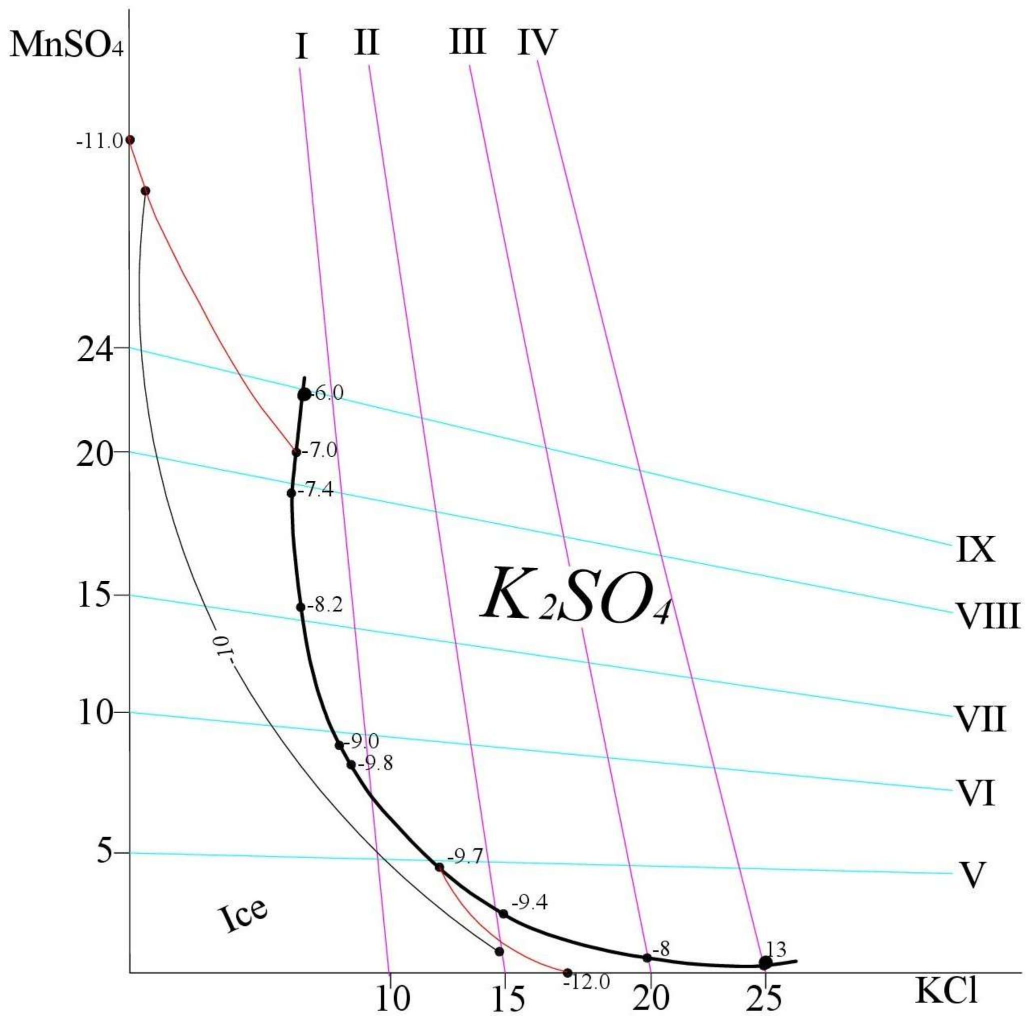

Fig. I. Solubility polytherm of the KCl - $MnSO_4$ - H_2O system.

On the polythermal diagram, the solubility isotherm of the system is expressed at 10° C. The results obtained show that a new K_2SO_4 phase has formed in the system. To identify a new compound in the system, physicochemical analyzes were carried out, such as X-ray phase, IR spectroscopic and thermal.

Table I. Double and triple nodal points of the $MnSO_4$ - KCl - H_2O system.

Composition of the liquid phase , %			Crystallization temperature , °C	Solid phase
$MnSO_4$	KCl	H_2O		
22,2	6,3	71,5	-6,0	$MnSO_4·H_2O+K_2SO_4$
20,0	6,2	73,8	-7,0	$MnSO_4·H_2O+K_2SO_4$
18,4	6,1	75,5	-7,4	$MnSO_4·H_2O+K_2SO_4$
14,0	6,4	79,6	-8,2	$MnSO_4·H_2O+K_2SO_4$
8,6	8,2	83,2	-9,0	ice + $MnSO_4$ + K_2SO_4
8,0	8,6	83,4	-9,8	ice + KC l+ K_2SO_4

4,3	12,0	83,7	-9,7	ice + KC l+ K_2SO_4
2,4	14,4	83,2	-9,4	ice + KC l+ K_2SO_4
0,6	18,9	80,5	-8	KC l+ K_2SO_4
0,3	24,4	75,3	13	KC l+ K_2SO_4

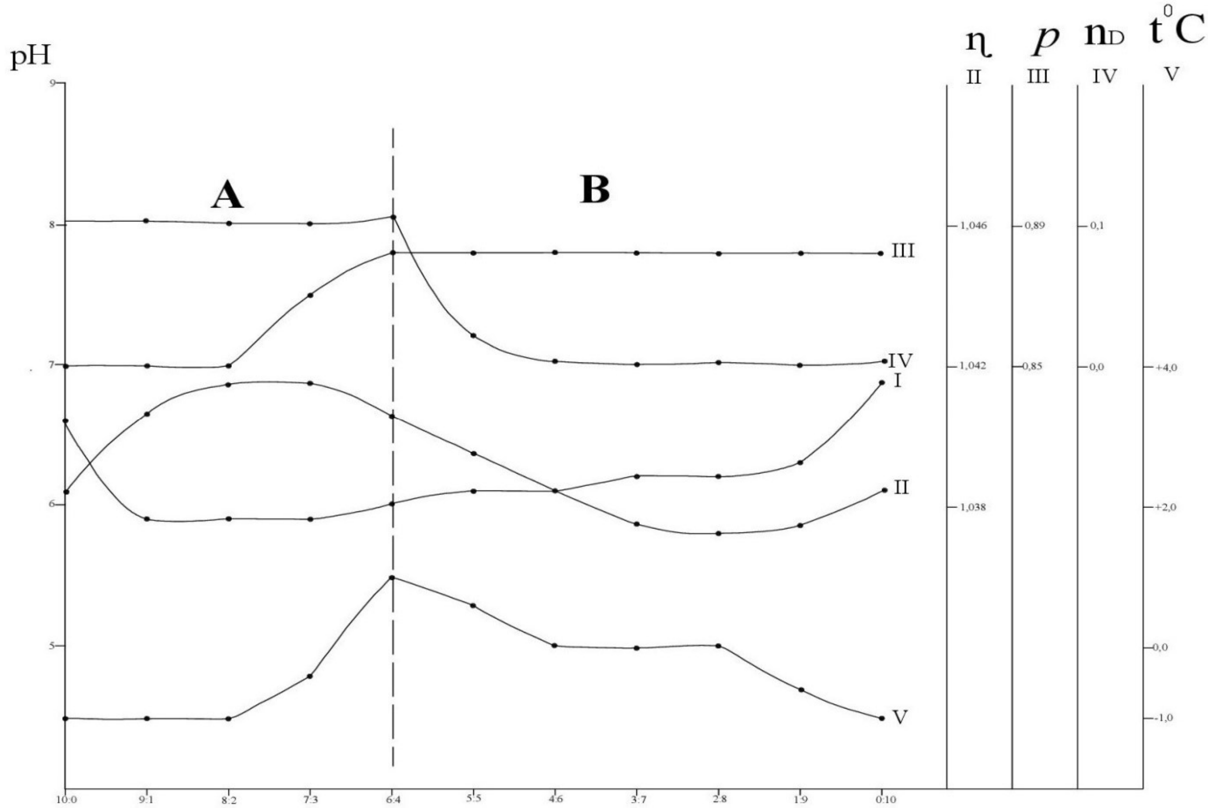

Fig. II. Changes in pH (1), density (2), viscosity (3) and crystallization temperature (4) of solutions depending on the composition of components in the KCl - $MnSO_4$ - H_2O system.

Changes in viscosity, density, pH, and crystallization temperature were studied after preparing 0.01 M solutions of the MnSO4 and KCl components. To establish the possible course of the reaction in the KCl - MnSO4 - H2O system, the change in the viscosity characteristics, pH, and crystallization temperature of a mixture of various ratios of 0.01 M solutions of potassium chloride and manganese sulfate were determined.

Table II. Changes in the physicochemical properties of solutions depending on the composition of the components in the system [MnSO4 (0.01 M)] and [KCl (0.01 M)].

№	Composition of components		pH	Density g cm-3	Viscosity	Crystallization temperature
	$MnSO_4$, ml	KCl, ml				
1	30	0	6.3	1.039	0.85	-1.0
2	27	3	5.9	1.041	0.85	-1.0
3	24	6	5.9	1.042	0.85	-1.0
4	21	9	5.9	1.042	0.87	-1.0
5	18	12	6.0	1.041	0.88	+1.0

6	15	15	6.1	1.040	0.88	+0.6
7	12	18	6.1	1.039	0.88	0.0
8	9	21	6.2	1.038	0.88	0.0
9	6	24	6.2	1.03636	0.88	0.0
10	3	27	6.3	1.037	0.88	-0.6
11	0	30	6.9	1.039	0.88	-1.0

Analysis of the data obtained, the ratio of components - pH 0.01 M solutions shows that with an increase in the proportion of a 0.01 M solution of potassium chloride from 3 ml to 30 ml and a decrease in the content of a 0.01 M solution of manganese sulfate from 30 ml to 0 ml, the pH value decreases from 6.3 to 6.0. Up to a ratio of 15:15, the pH of the mixtures increases along the curve, then it is seen that the pH value increases again as the amount of potassium chloride in the mixture increases. The linear dependence of pH indicates an increase in pH values in proportion to the increase in the proportion of potassium chloride, since the pH of 0.01 M potassium chloride is higher than the pH of 0.01 M manganese sulfate (Fig. II).

The crystallization temperature of a 0.01 M MnSO4 solution rises from -1°C to 0°C, respectively, with an increase in the proportion of KCl solution. The viscosity increases linearly from 0.85 mm^2 to 0.88 mm^2 with an increase in the content of 0.01 M solutions of potassium chloride in the mixture and a decrease in manganese sulfate.

Chemical analysis of the new compound gave the following results: found, wt. %:

K=44,9; S=18,4; O=36,7.

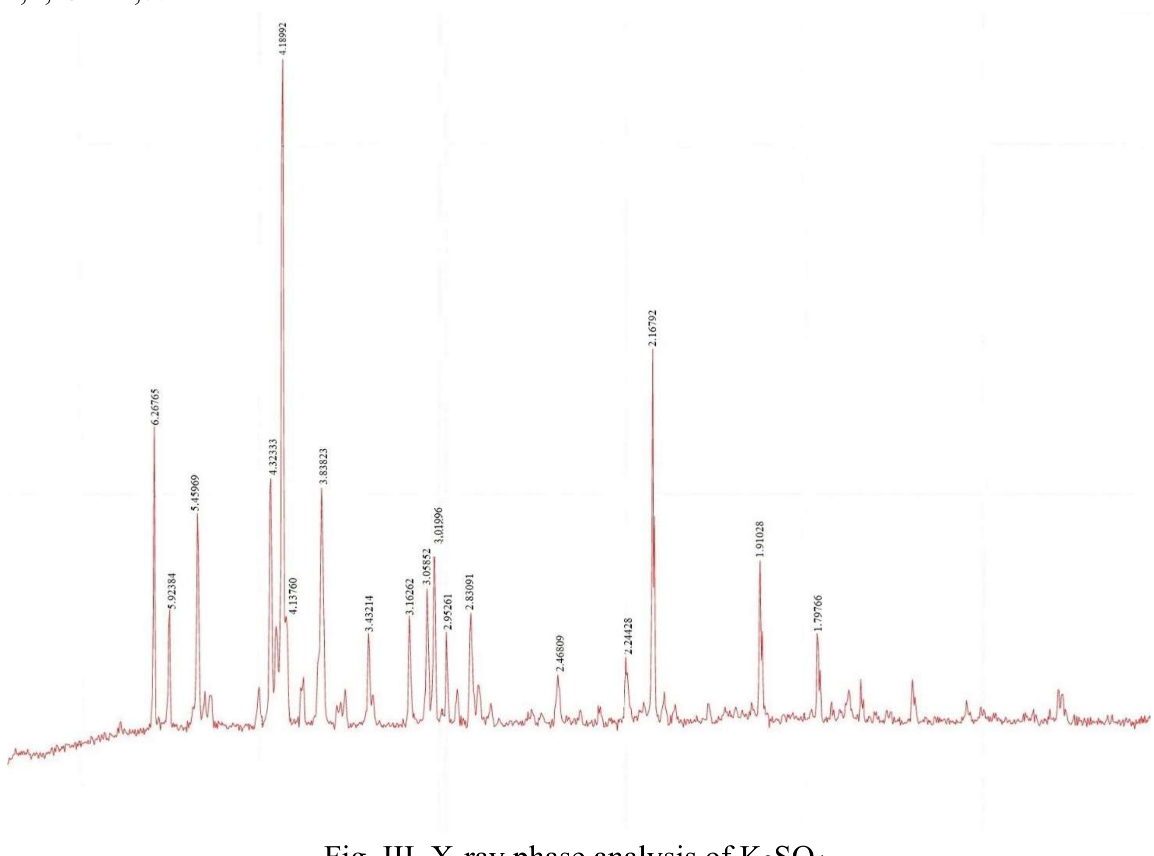

Fig. III. X-ray phase analysis of K_2SO_4.

As can be seen from the X-ray phase analysis, all changes in the diffraction patterns, as well as the activation of their reflection angles, a set of interplanar distances and diffraction lines, confirm that the new compound is K_2SO_4 (Fig.III). In order to confirm the individuality of the obtained compound, an analysis was carried out using modern physicochemical methods of analysis.

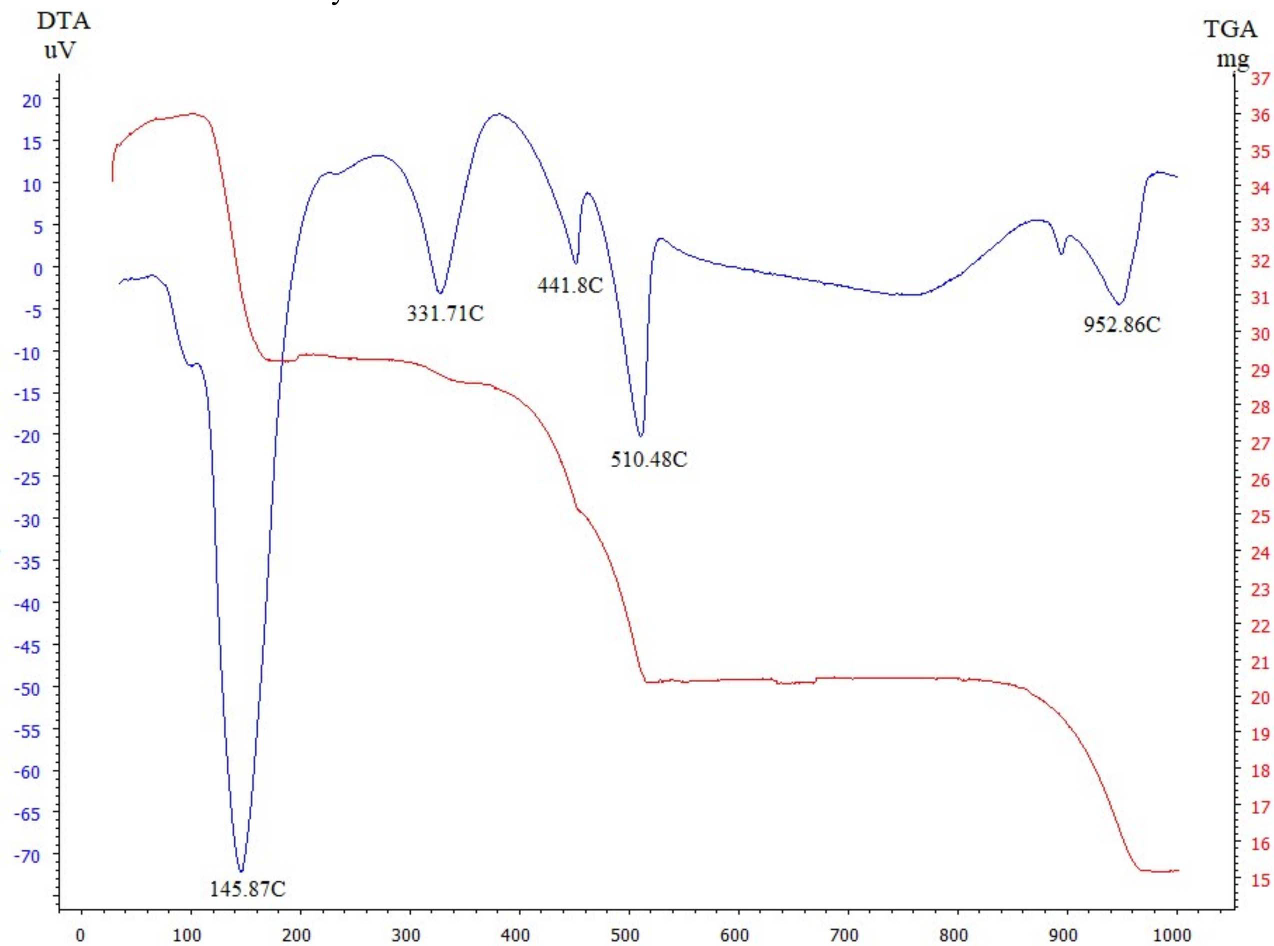

Fig. IV. Derivatogram of K_2SO_4 formation.

The test temperature started from 44 ^{0}C and the lowest endo effect was observed at 580 0C. Until the end of the test, no significant changes were observed. The mass decreased by 4% from the initial state by the end of the process. The measurements were carried out in an oxidizing environment at a rate of 20 s min.

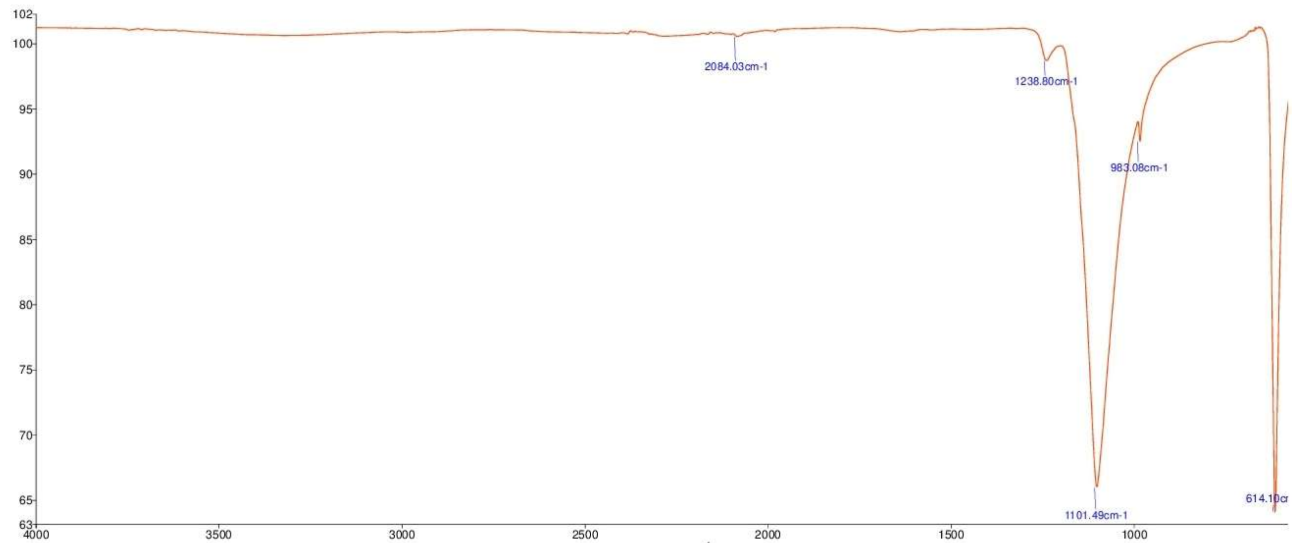

Fig. V. IR Fourier spectrum of K_2SO_4.

When observing the IR spectrum of the KCl+MnSO4+H2O crystal structure, it can be seen that this medium is strong in the region of 1045-1170 cm-ring compounds. And in the range of 983.08 cm-1 in the middle part it represent SO_4 chain compounds. (Fig V). The description of the IR spectra shown confirms that the new compounds is potassium sulfate.

CONCLUSIONS

By changing the solubility of the components and the physicochemical properties of the solutions (density, viscosity, crystallization temperature, pH), the optimal conditions for obtaining potassium sulfate in this system are determined. The isolated potassium sulfate was analyzed on the basis of physicochemical analysis. In future studies, manganese sulfate and ammonium nitrate will be studied for their solubility and interactions.

Thank you for taking the time to reviem my article. I wish you success in science.

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