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Physio-Chemical Interactions of Manganese Sulfate/Acetate with Amides in Water

Aishakan Suiunbekova[1], Gulnara Omurzakova[2], Kalipa Salieva[3], Bakyt Borkoev[3], Zhypargul Abdullaeva[4]*, Mamatkadyr Iarmatov[1], Gulumkan Sartova[3], Zhyldyz Kamalov[2], Ziyadat Salieva[5]

[1]Department of Chemistry and Chemical Technologies, Osh State University, Osh, Kyrgyzstan

[2]Department of Natural Sciences Disciplines, Osh State University, Osh, Kyrgyzstan

[3]Department of Chemical Engineering, Kyrgyz-Turkish Manas University, Bishkek, Kyrgyzstan

[4]Science and Research Department, Osh State University, Osh, Kyrgyzstan

[5]Department of Food production technology, Kyrgyz State Technical University named after I. Razzakov, Bishkek, Kyrgyzstan

Abstract. This article is investigating physio-chemical characteristics in manganese sulfate/acetate and amide compounds including thioacetamide, thiocarbamide, thiosemicarbazide in water at 25 °C by isothermal solubility method. System equilibrium was established within 8-10 hours via continuous stirring. For the determination of manganese ion content and nitrogen ions in thiocarbamide, thioacetamide and thiosemicarbazide compounds, trilonometric, Kjeldahl and Duma methods were used.

Keywords: Physio-chemical interactions, Manganese sulfate, Acetate, System equilibrium, Kjeldahl method, Isothermal solubility method.

1. INTRODUCTION

Physio-chemical interactions in manganese salts with their complex formation [1-3] abilities were studied recently and formation of a new complex with various compositions revealed [4].

Synthesis, assessment of biological activity and toxicity for N-(β-D-glycopyranosyl) thiosemicarbazides with their carbohydrate derivatives [5-10] were analyzed.

Interactions between thiocarbamide and carbamide with nickel cobalt salts were studied. Cobalt chloride complex formation with semicarbazide, thiosemicarbazide and formate system of cobalt and nickel complexes with a molar ratio of 1:2 were investigated [11-13].

In this work physio-chemical interactions, solubility and composition of solid phase manganese sulfate/acetate -thioacetamide - water system was analyzed at 25°C.

1. RESEARCH METHODS AND MATERIALS

Study of physio-chemical interactions in systems carried out by physicochemical solubility method. Equilibrium in the systems controlled by the constancy content of components, which was established within 7 hours, the temperature was maintained in a water thermostat, its fluctuations did not exceed +0.02 °C. Compositions of true solid phases were found by the Skreinemakers method [14], magnesium cation was determined by trilonometrical method [15].

Analyses were carried out for amides according to the Kjeldahl method, which is based on sample reaction with sulphuric acid, after that organic matter is decomposed by oxidation and organic nitrogen is reduced to ammonium sulfate, which is distilled with sodium hydroxide to liberate gaseous ammonia [16]. Combustion or Dumas method is widely accepted for total protein determination in which combustion of food sample occurs at temperatures between 900 and 1300 °C in oxygen rich atmosphere, followed by released combustion gases (O_2, CO_2, H_2O, N_2, and NO_x), passed through gas and water sensitive traps/membranes to remove non-nitrogen containing gases [17].

New compounds have been isolated and their physicochemical constants have been studied. Compounds were identified by IR spectroscopy, X-ray phase analysis and thermogram analyzes. Analyzed compounds showed individual IR absorption spectra, X-ray pattern, and thermogram different from original substance. Further compounds were tested for biological activity properties.

2. RESULTS AND DISCUSSIONS

2.1. Manganese sulfate thioacetamide water system at 25°C. As can be seen from Table 1, the system consists of three solubility curves, one new compound and two original components. The smallest area is manganese sulfate solubility curve, since addition of thioacetamide to a saturated solution of manganese sulfate increases the solubility of salt from 39.59 % to 42.49 %.

With a further increase in amide concentration, a new compound with composition $MnSO_4CH_3CSNH_2$ crystallized from a saturated solution. This compound dissolved in water with decomposition due to incongruently soluble compound. It should be noted that aqueous solutions of thioacetamide were hydrolyzed with formation of H_2S, NH_3. This was evidenced by change in solution pH environment and the isolation of metal sulfide from solution of undissolved precipitate. This had a noticeable effect on accuracy of chemical analysis of components. To obtain reliable data, each time a new composition was prepared for analysis since the new compositions were stable during the first and second days.

Therefore, only samples from the first day were used for analysis. The composition of new compound contains 35.95% thioacetamide, 64.32 % manganese sulfate, corresponding to a molecular ratio of 1:1. Table 1 shows the solubility and composition of solid phases in the system manganese sulfate - thioacetamide - water at 25°C.

TABLE I

SOLUBILITY AND COMPOSITION OF SOLID PHASES IN THE SYSTEM MANGANESE SULFATE - THIOACETAMIDE - WATER AT 25 °C

Point No.	Liquid phase composition wt %		"Residue" composition wt%		Crystallizing phase
	$MnSO_4$	CH_3CSNH_2	$MnSO_4$	CH_3CSNH_2	CH_3CSNH_2
1	-	34.86	-	100.0	-/ /-
2	-	32.21	-	70.97	-/ /-
3	2.25	21.20	1.49	94.90	-/ /-
4	7.51	10.50	1.60	86.00	-/ /-
5	21.35 27.59	7.00	4.40 4.18	90.00	CH_3CSNH_2 + $MnSO_4^*$ CH_3CSNH_2
6	29.15	6.10	27.25	55.00	CH_3CSNH_2 + $MnSO_4^*$ CH_3CSNH_2 $MnSO_4^*$ CH_3CSNH_2 -/ /-
7	31.35	6.20	41.10	49.00	-/ /- -/ /-
8	31.48	6.71	60.12	33.04	CH_3CSNH_2 $MnSO_4$+ $MnSO_4$
9	33.79	4.59	54.00	26.15	$MnSO_4^*4H_2O$
10	39.40 43.12	2.50	60.54 62.10	31.70	-/ /-
11		2.19		33.20	-
12	42.49	1.89	75.25	14.85	
13	44.20	2.00	60.00	0.85	
14	39.59	-	67.75	-	

The largest solubility curve corresponds to thioacetamide compound. When manganese sulfate was added to a thioacetamide saturated solution the solubility of thioacetamide sharply decreases from 34.86% to 6.20%, as the solubility of a new compound is less than solubility of original components.

Thus, in the system $MnSO_4$-CH_3CSNH_2-H_2O, a new compound is formed, which was delimited by two eutonic compounds [18, 19]. The complex compound was isolated in an individual crystalline form.

Accordingly, we have obtained a new compound of manganese sulfate with thioacetamide complex.

2.2. Manganese sulfate-thiosemicarbazide-water system at 25 °C. As shown by the solubility data in Table 2, the solubility of interacting components characterized by absence of new phases separating into solid phase. The solubility of manganese sulfate

after adding thiosemicarbazide was decreases from 39.59% to 34.61%. At the eutonic points, the solubility of thiosemicarbazide increases slightly from 2.65% to 3.08%.

Absence of a complex formation process in studied system is explained by relatively weak complexing ability of cation, since polarization is difficult in thiosemicarbazide. In this system, the amide has slight salting out effect. Table 2 shows solubility and composition of solid phases in the system manganese sulfate - thiosemicarbazide - water at 25 °C.

TABLE 2

SOLUBILITY AND COMPOSITION OF SOLID PHASES IN THE SYSTEM MANGANESE SULFATE THIOSEMICARBAZIDE - WATER AT 25 °C

Point No.	Liquid phase composition wt %		"Residue" composition wt%		Crystallizing phase
	CH_5N_3S	$MnSO_4$	CH_5N_3S	$MnSO_4$	CH_5N_3S
1	-	100.00	-	-/ /-	
2	2.35	2.71	78.07	0.78	-/ /-
3	1.74	4.20	78.61	0.99	-/ /-
4	1.83	7.37	84.82	1.01	-/ /-
5	1.81	1.68	64.01	3.69	-/ /-
6	1.33	1337	82.56	2.64	-/ /-
7	1.81	16.33	71.80	6.22	-/ /-
8	1.58	19.31	56.66	9.25	-/ /-
9	1.17	21.33	73.62	6.06	-/ /-
10	1.63	24.78	81.22	4.80	-/ /-
11	1.36	26.83	53.37	13.53	-/ /-
12	1.23	36.08	65.57	14.06	$MnSO_4+CH_5N_3S$
13	1.83	36.03	27.49	60.88	
14	1.64	35.21	18.57	57.71	-/ /-
15	1.64	35.40	0.83	62.34	-/ /-
16	1.94	36.51	0.79	61.26	$MnSO_4+4H_2O$
17	1.41	39.59	-	67.75	-/ /-
	-				-/ /-

Manganese acetate thiocarbamide-water system at 25°C. Experimental data on solubility of system is shown in Table 3. As can be seen from the solubility, the system belongs to a simple eutonic system, and formation of a new compound under these conditions was not detected. The composition of the eutonic dots is 7.26% thiocarbamide and 22.03% manganese acetate.

TABLE 3

SOLUBILITY AND COMPOSITION OF SOLID PHASES IN THE MANGANESE ACETATE-THIOCARBAMIDE-WATER SYSTEM AT 25°C

Point No.	Liquid phase composition wt %		"Residue" composition wt%		Crystallizing phase
	$Mn(CH_3COO)_2$	**CH_4N_2S**	**$Mn(CH_3COO)_2$**	**CH_4N_2S**	**CH_4N_2S**
1	-	14.20	-	100.0	-/ /-
2	7.71	8.78	0.86	98.06	-/ /-
3	21.31	7.63	3.14	87.22	$Mn(CH_3COO)_2+CH_4N_2S$
4	22.03	7.26	25.49	63.75	
5	22.53	8.92	30.12	50.94	-/ /-
6	25.22	6.17	38.27	46.74	-/ /-
7	27.54	4.07	52.13	32.26	-/ /-
8	29.40	3.77	66.00	18.81	$Mn(CH_3COO)_2+4H_2O$
9	35.60	2.44	66.84	0.56	-/ /-
10	43.20	-	71.20	-	-/ /-

Near the eutonic points, the solubility of thiocarbamide decreases from 14.20% to 7.63%, and the solubility of manganese acetate also decreases. The absence of a complex between thiocarbamide and manganese acetate is explained by a decrease in the electron-donor capacity of the amide due to the replacement of the oxygen atom in urea by a sulfur atom.

In studied system, formation of a solid phase is observed, which is delimited by two eutonic points.

Concentration limits of components in solid solution region vary from 4.07% to 8.92% thiocarbamide and from 27.54% to 22.53% manganese acetate.

The shape of crystals viewed under a microscope in the region of solid solution crystallization does not change, but the chemical composition of solid solutions was changed. A decrease in mutual solubility observed in the system, which additionally indicates a decrease in chemical activity of components in aqueous solution.

CONCLUSION

Manganese sulfate/acetate systems with amide (thioacetamide, semicarbazide, thiocarbamide) compounds were studied in an aqueous medium by isothermal solubility method at 25 °C. Formation of a new compound in the system of manganese sulfate with thioacetamide in a molecular ratio of 1:1 was revealed. Solubility of manganese sulfate when thiosemicarbazide was added decreases from 39.59% to 34.61%. At eutonic points, the solubility of thiosemicarbazide increases slightly from 2.65% to 3.08%. In the system $MnSO_4$-CH_3CSNH_2-H_2O, a new compound is formed, which is delimited by two eutonic compounds.

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