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Abstract

Full Text

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CHEMISTRY

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A SYSTEM OF ARSENATES AND CARBONATES OF COPPER AND SODIUM

In previous works ([1,2]) we published data on the study of an aqueous system of arsenates and sulfates of copper and sodium. In the interaction of these salts, the formation of a double trihydrated compound—copper sulfate-arsenate—was established. The presence of the double compound provided grounds for clarifying the behavior of copper arsenate with carbonates, nitrates, and chlorides of sodium and potassium.

The present work is devoted to the study of the system consisting of copper arsenate, sodium carbonate, and water. Chemically pure copper arsenate salt was prepared for the work. The sodium carbonate used in the work was purified by recrystallization.

The study was carried out by the widely known isothermal method in an aqueous thermostat at 50°, with regulation of the water temperature to ±0.1°. The system of copper arsenate and sodium carbonate in an aqueous medium is a reciprocal (quaternary) one; however, since copper arsenate and carbonate are sparingly soluble, while the analogous sodium salts have high solubility, the system under study, with some convention, may be regarded as a simple ternary system: copper arsenate—sodium carbonate—water.

The equilibrium state of the system between the liquid and solid phases was established relatively slowly; samples were kept in the thermostat from two to ten days, and at transition points twice as long. When preparing the mixture in the reaction vessel, copper arsenate (about 10–15 g) and sodium carbonate (2 g) were first charged and treated with water. Then, in subsequent investigations, after each sampling, 1–2 g of sodium carbonate was added to the mixture. The establishment of equilibrium was monitored by chemical analysis; it was considered established when the last two analyses showed the same or a close content of arsenate ion in the solution. The homogeneity of the solid phases was checked under a microscope. Samples of the solutions and of the solid phases in equilibrium with them were taken simultaneously.

In the liquid and solid phases, the content of the following ions was determined: arsenate, carbonate, and copper. The arsenate ion was determined iodometrically by the method of Shakhtakhtinskii (³). The carbonate ion was established by the widely known calcimetric method. The content of copper ion was found gravimetrically in the form of copper oxide (CuO); sodium was calculated by difference.

The data obtained in the study of the solubility of the system copper arsenate —sodium carbonate—water are presented in Table 1. The solubility of copper arsenate is low: it amounts to only 0.001%.

The solubility of sodium carbonate is 32.16%. The limiting concentration of pure sodium arsenate at this temperature reaches 49.06% (²). As can be seen from Table 1, when the concentration of sodium carbonate is increased to 7.08%, the amount of arsenic-acid salts of copper and sodium in the solution increases to 19.82%. These solutions are in equilibrium with the given precipitate—copper arsenate.

For the purpose of obtaining the clearest representation of the nature of the change in the equilibrium state of the solutions of the system under study, we constructed

Table 1

Chemical composition of the solutions and solid phases of the system $Cu_3(AsO_4)_2$—Na_2CO_3—H_2O **at** 50°

No.	Liquid phase: Na_2CO_3, wt. %	Liquid phase: $Cu_3(AsO_4)_2$, wt. %	Liquid phase: Na_3AsO_4, wt. %	Liquid phase: $CuCO_3$, wt. %	Liquid phase: sum of salts, wt. %	Liquid phase: H_2O, wt. %	Liquid phase: Na_2CO_3, % of total salts	Liquid phase: $Cu_3(AsO_4)_2$, % of total salts	Liquid phase: Na_3AsO_4, % of total salts	Solid precipitates: Na_2CO_3, wt. %	Solid precipitates: $Cu_3(AsO_4)_2$, wt. %	Solid precipitates: Na_3AsO_4, wt. %	Solid precipitates: $CuCO_3$, wt. %	Solid precipitates: sum of salts, wt. %	Solid precipitates: Na_2CO_3, % of total salts	Solid precipitates: $Cu_3(AsO_4)_2$, % of total salts	Solid precipitates: Na_3AsO_4, % of total salts	Solid precipitates: $CuCO_3$, % of total salts	Solid phase
1	—	0,001	—	—	0,001	99,999	—	100	—	—	—	—	—	—	—	100	—	—	$Cu_3(AsO_4)_2 \cdot 4H_2O$
2	7,08	19,7	0,12	—	26,90	73,10	26,32	73,23	0,45	12,23	38,21	—	21,87	72,31	16,91	52,84	—	30,25	$Cu_3(AsO_4)_2 \cdot 4H_2O + CuCO_3$ (?)
3	13,05	5,31	10,75	—	29,11	70,89	44,83	18,24	36,93	9,33	38,79	—	31,75	49,87	18,71	17,63	—	63,66	$Cu_3(AsO_4)_2 \cdot 4H_2O + CuCO_3$ (?)

No.	Liquid phase: Na_2CO_3, wt. %	Liquid phase: $CuCO_3$, wt. %	Liquid phase: Na_3AsO_4, wt. %	Liquid phase: $Cu_3(AsO_4)_2$, wt. %	Liquid phase: sum of salts, wt. %	Liquid phase: H_2O, wt. %	Liquid phase: Na_2CO_3, % of total salts	Liquid phase: $CuCO_3$, % of total salts	Liquid phase: Na_3AsO_4, % of total salts	Solid precipitates: Na_2CO_3, wt. %	Solid precipitates: $CuCO_3$, wt. %	Solid precipitates: Na_3AsO_4, wt. %	Solid precipitates: $Cu_3(AsO_4)_2$, wt. %	Solid precipitates: sum of salts, wt. %	Solid precipitates: Na_2CO_3, % of total salts	Solid precipitates: $CuCO_3$, % of total salts	Solid precipitates: Na_3AsO_4, % of total salts	Solid precipitates: $Cu_3(AsO_4)_2$, % of total salts	Solid phase
4	11,25	2,78	16,22	—	30,25	69,75	37,19	9,19	53,62	29,73	18,72	—	25,41	73,86	40,25	25,34	—	34,41	$CuCO_3$(?) +0,1$Cu_3(AsO_4)_2\cdot$ $2CuCO_3\cdot$ 1,5$Na_2CO_3\cdot$ $4H_2O$
5	15,58	1,60	18,47	—	35,65	64,35	43,70	4,49	51,81	38,22	18,03	—	16,59	72,84	52,47	24,75	—	22,78	0,1$Cu_3(AsO_4)_2\cdot$ $2CuCO_3\cdot$ 1,5$Na_2CO_3\cdot$ $4H_2O$
6	16,02	1,74	12,71	—	30,47	69,53	52,58	5,71	41,71	35,06	12,11	—	22,85	70,02	50,07	17,30	—	32,63	0,1$Cu_3(AsO_4)_2\cdot$ $2CuCO_3\cdot$ 1,5$Na_2CO_3\cdot$ $4H_2O$
7	18,42	1,20	14,79	—	34,41	65,59	53,53	3,49	42,98	27,31	7,50	—	23,85	58,64	46,58	12,78	—	40,64	0,1$Cu_3(AsO_4)_2\cdot$ $2CuCO_3\cdot$ 1,5$Na_2CO_3\cdot$ $4H_2O$
8	14,46	0,98	10,16	—	26,10	73,90	57,32	3,75	38,93	32,82	12,83	—	25,18	70,83	46,34	18,11	—	35,55	0,1$Cu_3(AsO_4)_2\cdot$ $2CuCO_3\cdot$ 1,5$Na_2CO_3\cdot$ $4H_2O$
9	16,98	1,52	9,41	—	27,91	72,09	60,84	5,45	33,71	38,14	12,90	—	26,91	77,95	48,93	16,55	—	34,52	0,1$Cu_3(AsO_4)_2\cdot$ $2CuCO_3\cdot$ 1,5$NaCO_3\cdot$ $4H_2O$
10	29,85	—	2,29	—	32,14	67,86	92,87	—	7,13	42,76	9,98	—	25,53	78,27	54,63	12,75	—	32,62	0,1$Cu_3(AsO_4)_2\cdot$ $2CuCO\cdot$ 1,5$Na_2CO_3\cdot$ $4H_2O$
11	32,16	—	—	—	32,16	67,84	100	—	—	—	—	—	—	—	100	—	—	—	$Na_2CO_3\cdot$ H_2O

solubility diagram (Fig. 1). The diagram consists of two isosceles triangles

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Fig. 1. Solubility diagram of arsenates and carbonates of copper and sodium at 50°

Figure 1: Fig. 1. Solubility diagram of arsenates and carbonates of copper and sodium at 50°

placed base to base along the line sodium carbonate—copper arsenate. The general form of the diagram is a rhombus. In the upper triangle the data on the solubility of the salts were plotted. At the vertices of the triangle are placed the salts: sodium and copper arsenates and sodium carbonate. Copper carbonate is absent in the upper triangle, since this salt is practically insoluble in water. In the lower triangle are shown the compositions of the solid phases. At the vertices of the triangle are placed copper arsenate, and sodium and copper carbonates.

Fig. 1. Solubility diagram of arsenates and carbonates of copper and sodium at 50°

Owing to the fact that sodium arsenate has high solubility and does not precipitate into the solid phase, the point indicating its presence in the bottom sediment is absent from the triangle of solid-phase composition. The figurative points of equilibrium solutions and solid residues were plotted on the composition triangle by the method proposed by Roseboom. For this purpose the salt content in the solution and in the solid residue was recalculated as percentages of the sum of salts. Such a type of diagram is new and is being constructed for the first time, and it seems to us that it will be quite appropriate for characterizing reciprocal systems when the components have sharply differing solubilities, and, moreover, of the reciprocal pairs one or two salts are almost insoluble.

Solubility diagrams constructed according to this principle are characterized by a curve consisting of two branches. The first branch, from point *1* to *4*, corresponds to crystallization into the solid phase of tetrahydrate copper arsenate. The hydration state of copper arsenate was established by chemical analysis. Water, as a constituent part of the separating solid phases, is not shown on the diagram. The concentration of the solutions with respect to the content of copper and sodium arsenates varies from 0.001 to 19.82%. At the transition point *4* the sum of arsenates is 19.00%. The straight-line rays connecting the figurative points of the solutions and residues indicate the presence of a mixture in the solid phases consisting of copper arsenate and copper carbonate. The solubility branch in this concentration interval is represented by a curve convex toward the copper arsenate—sodium carbonate side. Point *4* is a transition point and is characterized by the maximum distance from the base toward the sodium arsenate vertex.

The composition of the solution at the transition point is characterized by the following salt content: copper arsenate 2.78%; sodium carbonate 11.25%; sodium arsenate 16.22%, and water 69.75%. The second branch of the solubility curve, extending from point *4* to point *10*, corresponds to crystallization of a ternary salt containing copper and sodium carbonates and copper arsenate.

This new salt separates in the form of well-formed crystals having a clearly expressed habit of the hexagonal system. Under the microscope the crystals are seen as hexagonal plates.

or low bipyramids. According to the data of the solubility diagram, the new salt is characterized by the following content of the principal components: copper carbonate 47.07%; sodium carbonate 30.28%; copper arsenate 8.92%; water 13.73%. These theoretical data on the composition of the triple salt were repeatedly confirmed by us by chemical analysis. In the analysis of the salt, the following composition was found: copper carbonate 47.42%, sodium carbonate 29.46%, copper arsenate 8.72%, water 14.40%, which closely agrees with the theoretical calculations.

On the basis of the experimental data obtained, we calculated for this salt the molecular ratio of the principal components, which is expressed by the following chemical formula: $20CuCO_3 \cdot 15Na_2CO_3 \cdot Cu_3(AsO_4)_2 \cdot 40H_2O$.

For the most convenient expression of the salt, the coefficients of its constituent components may be reduced tenfold, and the formula takes the following form: $0.1\,Cu_3(AsO_4)_2 \cdot 2CuCO_3 \cdot 1.5\,Na_2CO_3 \cdot 4H_2O$. The composition of the triple salt plotted on the physicochemical diagram is anhydrous: copper arsenate 10.34%, sodium carbonate 35.11%, copper carbonate 54.55% (Fig. 1).

The straight-line rays connecting the figurative points of the solutions (from *5* to *10*) and of the solid residues intersect on the diagram at a single point. Such a regular intersection of straight-line rays makes it possible to suppose that a new solid phase is formed in the system in the form of a triple salt of constant composition. Indeed, sodium carbonate is almost completely absent from the diagram because of the formation of a triple salt that is sparingly soluble in water. The newly established triple hydrated salt from copper arsenate and the carbonates of copper and sodium may also find practical application. This new salt, at our suggestion, was tested at the Kirghiz Scientific-Research Institute of Animal Husbandry as a medicinal agent for domestic animals. N. E. Shkodin and D. K. Teslennikov established that this preparation is an effective agent in the treatment of sheep affected by monieziasis (tapeworms).

Testing of the triple salt as a medicinal preparation is continuing.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.

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