Equilibrium of the solubility isotherm in systems Cobalt(II) chloride-glutamic acid-water

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Abstract. The study is focused on the interaction between glutamic acid and hexavodic cobalt chloride. The solubility curve, influenced by the high solubility of the initial components, extends horizontally along a catheter corresponding to the cobalt chloride content. The secretion of glutamic acid exhibits a gradual increase over a relatively extended period. As the cobalt chloride concentration in the solution reaches 25.04%, a new phase emerges, resulting from the molecular interaction of the reactants, forming a double dihydrous compound comprising one molecule of glutamic acid and cobalt chloride: $C_5H_9NO_4 \cdot CoCl_2$.

1 Introduction

During the biotechnological extraction of precious metals (Au, Ag, Pt, Pd) from fossil raw materials, amino acids dissolve these metals and extract them from additional elements (Fe, Cu, Co, Ni, As, S, Si) and serve as ligands in the process of formation of their complex compounds. Research in this area began in the 50-60s of the last century and developed very quickly from the 70s to the present, leading to the creation of large hydrometallurgical enterprises based on biochemical technologies. Recently, preparations from amino acids are prepared in a harmonious state with trace elements, hormones, vitamins, antibiotics and other means. Amino acids are physiologically active substances and form the main links in the protein structure, so the study of their physicochemical properties is of great theoretical and practical interest. L-glutamic acid is a structural element of the protein molecule and has a number of properties that allow it to be used as a physiologically active drug [1-5].

The solubility of many amino acids has not been sufficiently studied to date, which hinders the development of technological schemes for their production. Solving the problem of increasing the solubility of–amino acids causes the need to create complex production of-amino acids and their water-soluble biologically active derivatives and compounds. In this connection, we will study the chemical interactions of L-glutamic acid with cobalt salts in aqueous solutions by the classical method of physic-chemical analysis [6-9].

This paper presents experimental data on the solubility isotherm of L-glutamic acid-cobalt chloride-water at 25°C. This issue has not been studied before.

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2 Materials and methods

The interaction of glutamic acid with the selected substances was studied using the classical isothermal solubility method [10-12]. As practice has shown, this method of studying ternary systems is the simplest, most convenient, and provides reliability and reproducibility of the obtained data, especially when isolating new double and complex compounds, hydrate forms, and phases of variable composition in solid solutions.

L-glutamic acid was determined by nitrogen, and its quantitative content can be found by the Kjeldahl semimicromethod [13-16]. The L-glutamic acid concentrations found in solutions and solid residues are calculated by the equation:

$$\% \, C_5H_9NO_4 = K \cdot 100 \cdot T \cdot 100 / V \cdot m$$

Cobalt is determined by trilonometric methods as simpler, more accurate and faster. Trilon B was used as the synthesized solution B, and the murexide indicator was used to determine cobalt [17-21]. The content of cobalt ions in solutions and solid residues was calculated by the equation:

$$\% \, Co^{2+} = K \cdot 100 \cdot T \cdot 100 / Vm$$

3 Results and discussion

When studying the chemical interaction of L-glutamic acid with cobalt chloride, the formation of a double molecular compound $C_5H_9NO_4 \cdot CoCl_2 \cdot 2H_2O$.

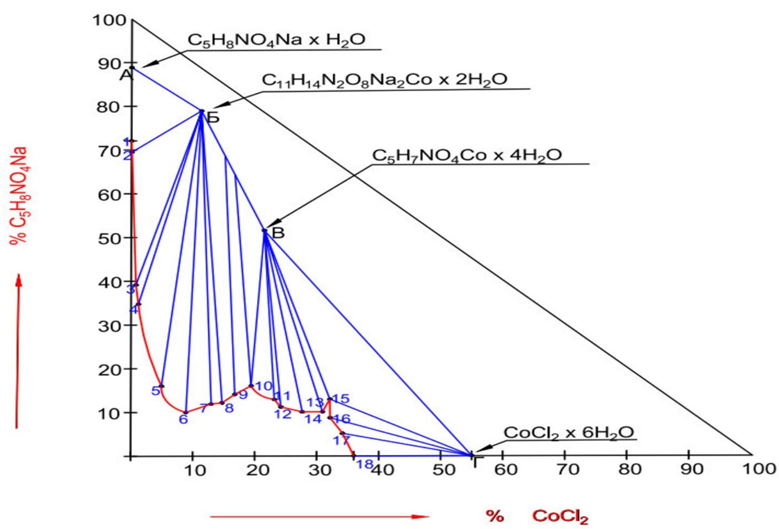

Fig. 1. Diagram of solubility of sodium L-glutamate and cobalt chloride in water at 25°C.

After making sure that the acid with reacting components does not form the expected substituted salts, in further studied, sodium hydroglutamine, which is well soluble in water (133 g per 100 ml of water at 25 °C), was used instead of poorly soluble in water (0.6-0.9%).

The solubility diagram of this system at 25°C consists of four branches, the first of which corresponds to the solid phase crystallization of monohydrate sodium L-glutamate (Table 1,2 and Figure 1)

Point 2 is a transition point, the solubility of the sodium salt decreases sharply from 72.10% to 11.22% in the presence of 8.94% cobalt chloride. This is probably due to the high chemical affinity of the reacting components.

The second branch (points 2-10) is characterized by the formation of a double compound in the bottom phase – disodium monocobalt diglutaminate.

Table 1. Data of chemical analysis of equilibrium solutions and solid phases of the $C_5H_9NO_4Na$–$CoCl_2$ – H_2O system at 25°C.

Point number	Liquid phase, %						True solid phase (chemical formula)
	Monosodium Sodium glutamate	$CoCl_2$	Co^{++}	Cl^-	Sum of salts	H_2O	
1.	72.10	-	-	-	72.10	28.58	$C_5H_8NO_4Na·H_2O$
2.	69.54	0.24	0.11	0.13	69.78	30.22	$C_{11}H_{14}N_2O_8Na_2Co·H_2O$
2[a].	69.54	0.24	0.11	0.13	69.78	30.22	$C_{11}H_{14}N_2O_8Na_2Co·H_2O$
3.	39.15	0.88	0.40	0.48	40.03	59.97	$C_{11}H_{14}N_2O_8Na_2Co·H_2O$
4.	34.73	1.27	0.58	0.69	36.00	64.00	$C_{11}H_{14}N_2O_8Na_2Co·H_2O$
5.	16.03	4.97	2.26	2.71	21.00	79.00	$C_{11}H_{14}N_2O_8Na_2Co·H_2O$
6.	11.22	8.94	4.06	4.88	20.16	79.84	$C_{11}H_{14}N_2O_8Na_2Co·H_2O$
7.	11.89	12.99	5.90	7.09	24.88	75.12	$C_{11}H_{14}N_2O_8Na_2Co·H_2O$
8.	12.16	14.76	6.70	8.06	26.92	73.08	$C_{11}H_{14}N_2O_8Na_2Co·H_2O$
9.	14.09	16.80	7.63	9.17	30.89	69.11	$C_{11}H_{14}N_2O_8Na_2Co·H_2O$
10.	16.03	19.43	8.82	10.61	35.46	64.54	$C_{11}H_{14}N_2O_8Na_2Co·H_2O$
10[a].	16.03	19.43	8.82	10.61	35.36	64.54	$C_5H_7NO_4Co·4H_2O$
11.	12.89	23.19	10.53	12.66	36.08	63.92	$C_5H_7NO_4Co·4H_2O$
12.	11.16	24.23	11.00	12.23	35.39	64.61	$C_5H_7NO_4Co·4H_2O$
13.	10.08	27.68	11.66	16.02	37.76	62.24	$C_5H_7NO_4Co·4H_2O$
14.	10.70	30.94	12.23	18.71	41.64	58.36	$C_5H_7NO_4Co·4H_2O$
15.	12.96	32.14	12.32	19.82	45.10	54.90	$C_5H_7NO_4Co·4H_2O$
15[a].	12.96	32.14	12.32	19.82	45.10	54.90	$C_5H_7NO_4Co·4H_2O$
16.	8.70	32.18	14.61	17.57	40.88	59.12	$CoCl_2·6H_2O$
17.	5.13	34.19	15.46	18.73	39.32	60.68	$CoCl_2·6H_2O$
18.	-	35.99	16.34	19.65	35.99	64.02	$CoCl_2·6H_2O$

Rectilinear rays coming from the figurative points intersected at point B, indicating the following content of components in the solid phase: L-sodium hydroglutaminate -77.97%, cobalt-13.68%, water-8.36%, which corresponds in terms of the chemical equation:

$$NaOOCCH(NH_2)\text{-}(CH_2)_2COOCoOOC(CH_2)_2CH(NH_2)COONa\cdot 2H_2O$$

Point 10 is a transition point with the composition of equilibrium solutions: L sodium L-hydroglutaminate-16.03%, cobalt chloride-19.43%.

The beam coming from the 11th point intersects between poles B and C, indicating the accumulation and formation of a double compound in the solution –sodium cobalt diglutaminate. However, due to the accumulation of hydrochloric acid in the solution to the limit content, the interaction process takes on the opposite direction. The chlorine ion, which is more active than the glutamation, cleaves sodium cobalt diglutaminate to form sodium chloride in the liquid phase and release cobalt hydroglutaminate in the solid phase.

Table 2. Data of chemical analysis of equilibrium solutions and solid phases of the $C_5H_9NO_4Na$–$CoCl_2$–H_2O system at 25°C.

Point number	**Percentage of solutes dissolved to the sum of salts**		**Solid residue, mass %**				**True solid phase (chemical formula)**
	Monosodium H_2O Sodium glutamate	**$CoCl_2$**	**Monosodium Sodium glutamate**	**$CoCl_2$**	**Co^{++}**	**Cl^-**	
1.	100	-	100	-	-	-	$C_5H_8NO_4Na\cdot H_2O$
2.	99.65	0.35	88.86	0.48	0.21	0.27	$C_{11}H_{14}N_2O_8Na_2Co\cdot H_2O$
2[a].	99.65	0.35	77.12	-	13.21	-	$C_{11}H_{14}N_2O_8Na_2Co\cdot H_2O$
3.	97.87	2.13	75.28	-	12.82	-	$C_{11}H_{14}N_2O_8Na_2Co\cdot H_2O$
4.	96.47	3.53	76.43	-	13.10	-	$C_{11}H_{14}N_2O_8Na_2Co\cdot H_2O$
5.	76.33	23.67	72.37	-	12.90	-	$C_{11}H_{14}N_2O_8Na_2Co\cdot H_2O$
6.	55.65	44.35	70.92	-	14.50	-	$C_{11}H_{14}N_2O_8Na_2Co\cdot H_2O$
7.	47.79	52.21	70.38	-	17.80	-	$C_{11}H_{14}N_2O_8Na_2Co\cdot H_2O$
8.	45.20	54.80	69.84	-	17.00	-	$C_{11}H_{14}N_2O_8Na_2Co\cdot H_2O$
9.	45.45	54.55	68.37	-	16.90	-	$C_{11}H_{14}N_2O_8Na_2Co\cdot H_2O$
10.	45.20	54.80	70.51	-	16.80	-	$C_{11}H_{14}N_2O_8Na_2Co\cdot H_2O$
10[a].	45.20	54.80	72.14	-	19.80	-	$C_5H_7NO_4Co\cdot 4H_2O$
11.	35.72	64.28	58.14	-	20.33	-	$C_5H_7NO_4Co\cdot 4H_2O$
12.	31.52	68.48	58.49	-	21.45	-	$C_5H_7NO_4Co\cdot 4H_2O$
13.	26.70	73.30	57.82	-	22.98	-	$C_5H_7NO_4Co\cdot 4H_2O$
14.	25.70	74.30	60.14	-	23.56	-	$C_5H_7NO_4Co\cdot 4H_2O$

15.	28.80	71.20	56.98	-	23.92	-	$C_5H_7NO_4Co{\cdot}4H_2O$
15[a].	28.80	71.20	30.22	52.87	24.00	28.87	$C_5H_7NO_4Co{\cdot}4H_2O$
16.	28.29	71.71	5.02	53.04	24.11	28.93	$CoCl_2{\cdot}6H_2O$
17.	13.00	87.00	2.21	54.42	24.74	29.68	$CoCl_2{\cdot}6H_2O$
18.	-	100	-	55.00	25.00	30.00	$CoCl_2{\cdot}6H_2O$

The third branch (points 11-15) corresponds to the process of cobalt glutaminate formation (neutral salt). Rectilinear rays connecting the compositions of equilibrium solutions and solid residues converge in the diagram at point B, corresponding to the constant composition of the solid phase.

According to the diagram, this point is characterized by the following solid phase content: glutamateion -52.55%, cobalt-21.37%, water-26.08% and corresponds to the chemical formula $HOOCHNH_2CH_2CH_2COO\ CoCl{\cdot}4H_2O$. In the resulting compound, the cobalt ion is bound to one molecule - glutamic acid.

The fourth branch (points 15-18) responds with a solution in equilibrium with bottom sediment of pure cobalt chloride.

Thus, when studying the solubility isotherm, two compounds with $Co(C_5H_7NO_4Na)_2{\cdot}2H_2O$ and $CoC_5H_7NO_4{\cdot}4H_2O$.

4 Conclusion

The solubility isotherm at 25°C of the ternary system $CoCl_2$-$C_5H_{14}NO_4$-H_2O was studied. Based on the results obtained, solubility diagrams for equilibrium solutions of the above systems were compiled.

Based on the solubility diagram, the composition of the formed compounds in the solid phase was established.

When studying the solubility isotherm, two compounds were identified: $Co(C_5H_7NO_4Na)_2{\cdot}2H_2O$ and $CoC_5H_7NO_4{\cdot}4H_2O$.

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