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PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Interaction in the Nickel Perchlorate–Acetamide–Perchloric Acid–Water System at 25°C

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Abstract—Heterogeneous equilibria in the nickel perchlorate–acetamide–perchloric acid–water quaternary system at 25°C were studied by studying solubility. The crystallization regions were determined for the initial solid components, eutonic compositions of the ternary systems constituting the quaternary system, binary compounds of acetamide with nickel perchlorate and perchloric acid, and also two new coordination compounds containing simultaneously nickel perchlorate, acetamide, and perchloric acid: $Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4$ and $Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$.

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As a continuation of our study of the processes and products of the interaction of metal salts with amides in acid media, we investigated the solubility in the nickel perchlorate–acetamide–perchloric acid–water quaternary system at 25°C. This system is of interest for determining the formation conditions of new coordination compounds containing three physiologically active components. We previously explored systems in which similar compounds form [1–3]. These compounds may be promising as feed additives, microfertilizers, pesticides, and analytical reagents. The interest in these compounds is also due to the fact that they are comparatively poorly studied and, therefore, can be good objects of both practical and theoretical investigation of their structure and physical and chemical properties [4, 5].

Interactions in ternary aqueous systems that constitute the quaternary system, are based on acetamide with perchloric acid or nickel perchlorate, and contain binary compounds were investigated before [6, 7].

EXPERIMENTAL

The initial substances were special-purity grade acetamide, perchloric acid, and chemically pure nickel perchlorate. The solubility in the system was studied by saturating eutonic solutions of the ternary systems constituting the quaternary system—nickel perchlorate–acetamide–water and acetamide–perchloric acid–water—with increasing amounts of the fourth component. The components of the system were determined according to published procedures [4, 5].

The results of determining the solubility (wt %) in the system are presented in the Table 1 and plotted in Fig. 1 as the central projection of the spatial isotherm. The representative points in the projection of the solubility isotherm indicate the salt composition; the water content is expressed as the water number, which is the number of moles of water that is necessary for dissolving 1 mole of the sum of the salts in the solution.

RESULTS AND DISCUSSION

The isotherm branch including points 1–6 corresponds to saturated solutions in the $Ni(ClO_4)_2$–CH_3CONH_2–H_2O system that are in equilibrium with two solid phases, CH_3CONH_2 and $Ni(ClO_4)_2 \cdot 4CH_3CONH_2$. These compounds precipitate from solutions containing 46.30 to 45.82% acetamide, 27.65 to 24.05% nickel perchlorate, and 0 to 12.19% perchloric acid.

The water number in these solutions decreases from 1.62 to 1.01; this is indicative of a salting-in effect of perchloric acid, owing to which, at point 6, a new incongruently soluble chemical compound of the composition $Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4$ forms.

The isotherm at points 6–10 characterizes saturated solutions that are in equilibrium with two solid

Table 1. Solubility in the $Ni(ClO_4)_2$–CH_3CONH_2–$HClO_4$–H_2O system at 25°C

No. of point	Composition of liquid phase, wt %				Dry component composition of liquid phase, wt %			Water number ω	Equilibrium solid phase
	$Ni(ClO_4)_2$	CH_3CONH_2	$HClO_4$	H_2O	$Ni(ClO_4)_2$	CH_3CONH_2	$HClO_4$		
1	27.65	46.30	0.00	26.05	37.43	62.57	0.00	1.62	$Ni(ClO_4)_2 \cdot 4CH_3CONH_2 + CH_3CONH_2$
2	26.49	46.02	2.98	24.51	35.09	60.96	3.95	1.49	"
3	25.60	45.82	5.65	22.93	33.21	59.42	7.37	1.37	"
4	25.28	45.94	7.97	20.81	31.92	58.01	10.07	1.21	"
5	24.39	45.68	10.13	19.80	30.41	56.96	12.63	1.13	"
6	24.05	45.82	12.19	17.94	29.33	55.88	14.79	1.01	$Ni(ClO_4)_2 \cdot 4CH_3CONH_2 + CH_3CONH_2 +$ $Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4$
7	20.83	46.23	15.14	17.80	25.34	56.24	18.42	0.97	$Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4 + CH_3CONH_2$
8	17.46	46.76	18.15	17.63	21.19	56.78	22.03	0.94	"
9	14.27	47.59	20.75	17.39	17.27	57.61	25.12	0.90	"
10	11.84	48.35	22.64	17.17	14.30	58.39	27.31	0.87	$CH_3CONH_2 + 2CH_3CONH_2 \cdot HClO_4 +$ $Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4$
11	0.00	44.74	26.29	28.97	0.00	63.02	36.98	1.31	$CH_3CONH_2 + 2CH_3CONH_2 \cdot HClO_4$
12	2.94	45.93	26.32	24.81	3.92	61.08	35.00	1.58	"
13	5.57	47.45	26.28	20.70	7.02	59.84	33.14	1.06	"
14	9.09	48.26	24.81	17.84	11.06	58.71	30.23	0.90	"
15	12.47	45.87	24.92	16.74	14.97	55.07	29.96	0.87	$Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4 + 2CH_3CONH_2 \cdot HClO_4$
16	13.97	41.88	27.70	16.45	16.70	50.10	33.20	0.88	"
17	14.97	38.72	30.22	16.09	17.83	46.15	36.02	0.88	"
18	15.67	35.51	32.90	15.92	18.63	42.18	39.19	0.89	"
19	15.95	33.39	35.35	15.31	18.55	39.57	41.88	0.87	"
20	15.35	32.22	37.49	14.94	18.06	37.91	44.03	0.85	$2CH_3CONH_2 \cdot HClO_4 + CH_3CONH_2 \cdot HClO_4 +$ $Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$
21	0.00	32.53	39.50	27.97	0.00	45.14	54.86	1.64	$2CH_3CONH_2 \cdot HClO_4 + CH_3CONH_2 \cdot HClO_4$
22	2.96	32.46	39.77	24.81	3.94	43.17	52.89	1.44	"
23	5.54	32.72	39.90	21.84	7.08	41.84	51.08	1.25	"
24	9.29	32.33	38.53	19.85	11.59	40.31	48.10	1.14	"
25	12.11	32.69	38.49	16.71	14.54	39.25	46.21	0.94	"
26	15.39	28.49	39.42	16.70	18.48	34.20	47.32	0.99	$Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4 + CH_3CONH_2 \cdot HClO_4$
27	15.15	24.54	41.62	18.69	18.63	30.18	51.19	1.17	"
28	14.88	21.11	43.30	20.71	18.77	26.62	54.61	1.36	"
29	13.36	17.96	45.89	22.79	17.31	23.27	59.42	1.56	"

Table 1. (Contd.)

No. of point	Composition of liquid phase, wt %				Dry component composition of liquid phase, wt %			Water number ω	Equilibrium solid phase
	$Ni(ClO_4)_2$	CH_3CONH_2	$HClO_4$	H_2O	$Ni(ClO_4)_2$	CH_3CONH_2	$HClO_4$		
30	12.40	15.13	47.72	24.75	16.54	20.09	63.37	1.76	"
31	9.61	13.54	50.18	26.67	13.11	18.47	68.42	1.93	"
32	24.82	43.76	13.67	17.75	30.19	53.23	16.58	1.01	$Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4 + Ni(ClO_4)_2 \cdot 4CH_3CONH_2$
33	26.34	41.36	14.69	17.61	31.97	50.20	17.83	1.03	"
34	27.59	38.15	16.69	17.57	33.40	46.19	20.41	1.06	"
35	29.00	34.64	19.16	17.20	35.03	41.83	23.14	1.07	"
36	30.08	31.87	20.96	17.09	36.28	38.44	25.28	1.10	"
37	30.51	29.99	22.59	16.91	36.71	36.10	27.19	1.10	$Ni(ClO_4)_2 \cdot 4CH_3CONH_2 + Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4 +$ $Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4$
38	28.16	30.20	25.04	16.60	33.77	36.21	30.02	1.06	$Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4 +$ $Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$
39	25.33	30.64	27.82	16.21	30.23	36.57	33.20	1.01	"
40	21.02	32.23	31.94	14.81	24.97	37.09	37.94	0.87	"
41	18.98	31.57	34.36	15.09	22.35	37.18	40.47	0.88	"
42	30.66	27.65	24.99	16.70	36.81	33.19	30.00	1.11	$Ni(ClO_4)_2 \cdot 4CH_3CONH_2 + Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$
43	31.72	25.43	26.45	16.40	37.94	30.42	31.64	1.11	"
44	31.64	22.68	29.47	16.21	37.76	27.07	35.17	1.12	"
45	31.42	20.38	32.19	16.01	37.41	24.26	38.33	1.13	$Ni(ClO_4)_2 \cdot 4CH_3CONH_2 + Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4 +$ $Ni(ClO_4)_2 \cdot 4CH_3CONH_2 + Ni(ClO_4)_2$
46	63.49	11.53	0.00	24.98	84.62	15.38	0.00	3.14	"
47	60.11	12.12	3.96	23.81	78.89	15.91	5.20	2.77	"
48	57.20	12.24	7.81	22.75	73.86	16.02	10.12	2.49	"
49	50.50	13.92	13.96	21.62	65.08	16.98	17.94	2.10	"
50	46.13	13.98	17.66	22.23	59.28	17.97	22.75	2.09	"
51	39.99	15.79	22.67	21.55	50.89	20.19	28.92	1.85	"
52	37.69	17.20	25.41	19.70	46.94	21.42	31.64	1.58	"
53	34.80	18.56	28.83	17.81	42.34	22.58	35.08	1.34	"
54	31.88	16.46	33.81	17.85	38.78	20.03	41.19	1.34	$Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4 + Ni(ClO_4)_2$
55	31.93	12.77	35.46	19.84	39.82	15.96	44.22	1.59	"
56	31.55	9.28	37.40	21.77	40.30	11.87	47.83	1.85	"
57	31.07	6.13	39.01	23.79	40.77	8.04	51.19	2.16	"
58	29.15	4.14	42.92	23.79	38.26	5.43	56.31	2.16	"
59	24.49	2.13	47.54	25.84	33.00	2.87	64.13	2.37	"

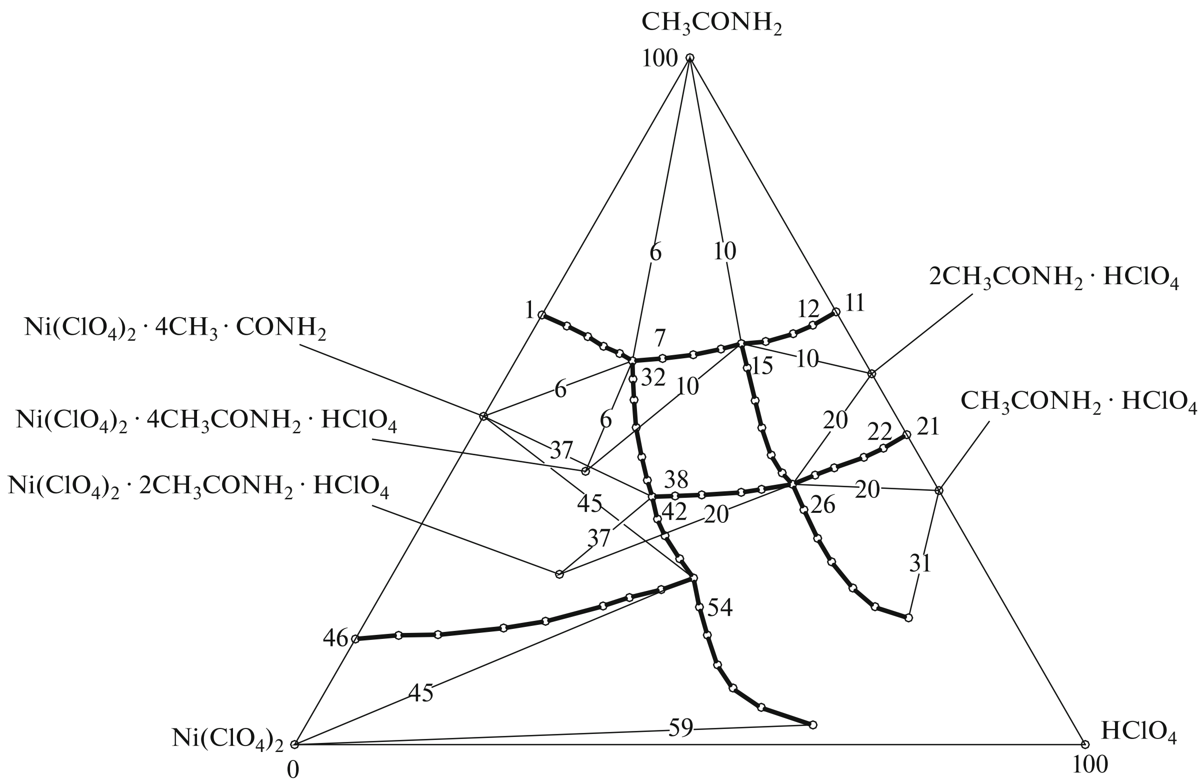

Fig. 1. Central projection of the solubility isotherm of the nickel perchlorate–acetamide–perchloric acid–water system at 25°C.

phases, CH_3CONH_2 and $Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4$.

With increasing perchloric acid concentration from 12.19 to 22.64%, the nickel perchlorate concentration decreases from 24.05 to 11.84%, and the acetamide concentration increases from 45.82 to 48.35%. The water number in these solutions decreases from 1.01 to 0.87, which suggests a salting-in effect of perchloric acid on the solubility of the ternary compound.

With supplementing a eutonic solution in the CH_3CONH_2–$HClO_4$–H_2O system with nickel perchlorate to 11.84% (isotherm points 10–14), the acetamide concentration increases from 44.74 to 48.35%, and the perchloric acid concentration decreases from 26.29 to 22.64%.

With increasing nickel perchlorate concentration, the water number decreases from 1.31 to 0.87; this shows a salting-in effect of nickel perchlorate on the solubility of CH_3CONH_2 and $2CH_3CONH_2 \cdot HClO_4$, which gives rise to a new compound, $Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4$ (point 10).

The isotherm branch at points 10 and 15–20 describes saturated solutions that are in equilibrium with two solid phases, $2CH_3CONH_2 \cdot HClO_4$ and $Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4$. Increasing nickel perchlorate concentration from 11.84 to 15.35% leads to a decrease in the acetamide concentration from 48.35 to 32.22% and to an increase in the perchloric acid concentration from 22.64 to 37.49%. The decrease in the water number from 0.87 to 0.85 is indicative of an insignificant salting-in effect of the acid, which leads to the formation of a new incongruently soluble chemical compound of the composition $Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$ at point 20.

If nickel perchlorate is added to a concentration of 15.35% to another saturated solution in the CH_3CONH_2–$HClO_4$–H_2O system that is in equilibrium with two solid phases, $CH_3CONH_2 \cdot HClO_4$ and $2CH_3CONH_2 \cdot HClO_4$ (isotherm points 20–25), the acetamide concentration insignificantly decreases (from 32.53 to 32.22%), and so does the perchloric acid concentration (from 39.50 to 37.49%). With increasing nickel perchlorate concentration, the water number decreases from 1.64 to 0.85; this suggests a salting-in effect of nickel perchlorate on the solubility in the system, because of which a new incongruently soluble chemical compound, $Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$, forms.

The isotherm branch at points 20 and 26–31 corresponds to saturated solutions that are in equilibrium with two solid phases, $CH_3CONH_2 \cdot HClO_4$ and $Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$. Increasing perchloric acid concentration in solution from 37.49 to 50.18% leads to a decrease in the acetamide concentration from 32.22 to 13.54% and in the nickel perchlorate concentration from 15.35 to 9.61%.

The increase in the water number from 0.85 to 1.93 in this case indicates a salting-out effect of perchloric acid on the solubility of the new ternary compound.

The isotherm branch at points 6 and 32–37 represents saturated solutions that are in equilibrium with two solid phases, $Ni(ClO_4)_2 \cdot 4CH_3CONH_2$ and $Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4$. Increasing perchloric acid concentration from 12.19 to 22.59% leads to a decrease in the acetamide concentration from 45.82 to 29.99%, whereas the nickel perchlorate concentration increases from 24.05 to 30.51%.

The increase in the water number from 1.01 to 1.1 points to an insignificant salting-out effect of perchloric acid on the solubility of the ternary compound.

The solubility isotherm branch at points 37 and 42–45 describes the crystallization of the compounds $Ni(ClO_4)_2 \cdot 4CH_3CONH_2$ + $Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$ from saturated solutions. Increasing perchloric acid concentration from 22.59 to 32.19% leads to a small decrease in the water number from 1.10 to 1.13, indicating an insignificant salting-out effect of the acid on the solubility of the ternary compound. In this case, the acetamide concentration decreases from 29.99 to 20.38%, and the nickel perchlorate concentration increases from 30.51 to 31.42%.

The isotherm portion at points 20 and 37–41 represents the crystallization of new compounds containing three initial components simultaneously: $Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$ and $Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4$. Increasing perchloric acid concentration from 22.59 to 37.49% leads to a decrease in the water number from 1.10 to 0.85, demonstrating a salting-in effect of perchloric acid on the solubility in the formed compounds. The acetamide concentration increases from 29.99 to 32.22%, and the nickel perchlorate concentration decreases from 30.51 to 15.35%.

The isotherm branch at points 45–53 corresponds to saturated solutions that are in equilibrium with two solid phases, $Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$ and $Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4$. Increasing perchloric acid concentration in solution to 32.19% brings about an increase in the acetamide concentration from 11.53 to 20.38%, whereas the nickel perchlorate concentration decreases from 63.49 to 31.42%.

The decrease in the water number from 3.14 to 1.13 shows a strong salting-in effect of perchloric acid on the solubility of the compound.

The isotherm branch at points 45 and 54–59 characterizes saturated solutions that are in equilibrium with two solid phases, $Ni(ClO_4)_2$ and $Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$. Increasing perchloric acid concentration in solution from 32.19 to 47.54% leads to a decrease both in the nickel perchlorate concentration (from 31.42 to 24.49%) and in the acetamide concentration (from 20.38 to 2.13%). With increasing perchloric acid concentration, the water number increases from 1.13 to 2.37, showing a strong salting-out effect of perchloric acid on the solubility of $Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$.

The acid–base interactions in the studied quaternary system that yield new coordination compounds containing three initial components simultaneously are possible by the following reactions:

—a new ternary compound is produced by a direct synthesis:

$$Ni(ClO_4)_2 + 2CH_3CONH_2 \cdot HClO_4 = Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4,$$

$$HClO_4 + Ni(ClO_4)_2 \cdot 4CH_3CONH_2 = Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4,$$

$$HClO_4 + Ni(ClO_4)_2 \cdot 2CH_3CONH_2 = Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4;$$

—with adding nickel perchlorate to a eutonic solution in the acetamide–acid–water system, a free acid molecule is displaced from amido acid:

$$Ni(ClO_4)_2 + 2[2CH_3CONH_2 \cdot HClO_4] = Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4 + HClO_4,$$

$$Ni(ClO_4)_2 + 2[2CH_3CONH_2 \cdot HClO_4] = Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4 + HClO_4;$$

—with adding perchloric acid to a eutonic solution in the acetamide–nickel perchlorate–water system, the binary compound reacts with the acid to yield a free acetamide molecule;

$$Ni(ClO_4)_2 \cdot 4CH_3CONH_2 + HClO_4 = Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4 + 2CH_3CONH_2.$$

Laboratory synthesis procedures were developed for the new compounds formed in the quaternary system.

$Ni(ClO_4)_2 \cdot 4CH_3CONH_2 \cdot HClO_4$. A mixture containing 16.8 g (0.065 mol) of nickel perchlorate and 15.3 g (0.259 mol) of acetamide was dissolved in 10 mL of concentrated (40%, d = 1300 kg/m^3) perchloric acid at 25–30°C while continuously stirring. The solution was left for a day, after which 26.9 g (0.045 mol) of light-green needle-like crystals of the compound was separated from the solution, with the yield being 87.0% of the theoretical one.

The density and the decomposition temperature of the synthesized compound are 1740 kg/m^3 and 175°C, respectively.

$Ni(ClO_4)_2 \cdot 2CH_3CONH_2 \cdot HClO_4$. A mixture containing 26.3 g (0.102 mol) of nickel perchlorate and 12.5 g (0.212 mol) of acetamide was dissolved in small portions in 10 mL of concentrated (60%, d = 1540 kg/m^3) perchloric acid at 25–30°C while continuously stirring. The solution was left for a day, after which 38.5 g (0.081 mol) of light-yellow crystals of the compound was separated from the solution, with the yield being 87.2% of the theoretical one.

The density and the decomposition temperature of the synthesized compound are 2080 kg/m^3 and 190°C, respectively.

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