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Extraction of Cobalt(II) and Zinc Ions by the Molten Mixtures of Diantipyrylalkanes and Benzoic Acid

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Abstract—The extraction of cobalt(II) and zinc ions with the molten mixtures of diantipyrylalkanes and benzoic acid from thiocyanate solutions was studied. Optimum conditions for phase separation, the formation of a melt, and the extraction of the metal ions were determined. The composition of the extracted complex compounds was found, and the mechanism of extraction was proposed.

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Phase-separation systems with water as the only liquid component are currently in increasing use for the extraction of various substances. These systems are free of the main disadvantage of liquid extraction—the use of toxic and flammable organic solvents [1, 2].

Organic bases and organic or inorganic acids are used as the constituents of these systems. The formation of the second phase is explained by salt formation reactions occurring in the system. In this case, the resulting chemical compounds are sparingly soluble in water to result in phase separation.

However, the formation of the second (organic) phase sometimes occurs only on heating extraction system components. After extraction, the organic phase solidified to form a compact mass, which can be easily separated from the aqueous phase. In this case, we are dealing with extraction by molten organic substances.

The extraction of scandium and bismuth with the melts of tributyl phosphate in paraffin was studied [3, 4]. Studies on the extraction of metal ions with the melts of chelating reagents (8-hydroxyquinoline, β -diketones, pyridylazonaphthol, and ditizone) [5–7] and with molten carboxylic acids [8–10] are well known.

Antipyrine and its condensed derivatives are widely used in liquid extraction because of their high extraction power. However, the applicability of these compounds to melt extraction and their properties are not understood.

Here, we report data on the extraction of Co(II) and Zn ions from thiocyanate solutions with the molten mixtures of diantipyrylalkanes (DAAs) and benzoic acid (BA).

EXPERIMENTAL

The standard solutions of Co and Zn sulfates (0.1 mol/L) were prepared by dissolving the weighed portions of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water. The concentrations of these solutions were determined by titration with EDTA [11]. The mixtures of BA (analytical grade) with the following reagents of the DAA group were used as extractants: diantipyrylmethane (DAM), propyldiantipyrylmethane (PDAM), butyldiantipyrylmethane (BDAM), isobutyldiantipyrylmethane (IBDAM), and hexyldiantipyrylmethane (HDAM). The reagents were synthesized in accordance with a published procedure [12].

The effects of various factors on the formation of a melt, the mutual solubility of phases, and the distribution of chemical elements between phases were studied in graduated test tubes with glass stoppers on heating to 80–90°C for 10 min. It was preliminarily found that this time was sufficient for chemical equilibration.

The required concentration of hydrogen ions was produced by adding certain amounts of a corresponding inorganic acid (HX). The concentration of thiocyanate ions was adjusted by adding a 2 M solution of NH_4SCN (chemically pure).

After reaching an extraction equilibrium, the test tubes were cooled to room temperature, and the solidified extract was separated mechanically.

The concentrations of cobalt and zinc ions in the organic phase were determined by titrimetry [11]. The monitoring was performed by the same technique using an aqueous phase.

A bilogarithmic method and the chemical analysis of extracts were used to determine the composition of the extracted compounds. In the latter case, the concentrations of the reagent, metal ions, hydrogen ions, and thiocyanate ions were determined in the aliquot

Table 1. Effect of inorganic acid concentration on the volume of the melt ($n_{\text{DAM}} : n_{\text{BA}} = 1 : 1$; $\Sigma n = 0.004$ mol, $c_{\text{SCN}^-} = 0.25$ mol/L)

Acid concentration, mol/L	V_{melt} , mL		
	HCl	H ₂ SO ₄	H ₃ PO ₄
0.01	0.5	1.1	0.8
0.25	1.1	1.2	1.0
0.5	1.2	1.2	0.9
1.0	1.2	1.3	0.9
2.0	1.2	1.2	0.9
4.0	1.2	1.2	0.9

portions of the extract (extraction was performed under preliminarily determined optimum conditions). The concentrations of metal ions were determined in accordance with a published procedure [11]; the concentration of hydrogen ions was determined by alkalimetry; and the reagent concentration was found as described elsewhere [13]. The concentration of thiocyanate ions was found by argentometry. The concentrations of all of the components were calculated taking into account the values obtained in a blank experiment.

RESULTS AND DISCUSSION

The aqueous phase of the test systems underwent separation on heating to 80–90°C over a range of hydrogen ion concentrations from 0.01 to 5 mol/L. In this case, the second liquid phase (a melt) was formed on heating; that is, a version of ordinary liquid-phase extraction occurred.

In operations with phase-separation systems containing no organic solvents, the most important parameters are the following: the occurrence of a

phase-separation region in the absence or the presence of an inorganic acid, the ratio between extraction system components, and the concentration of inorganic substances affecting the ionic strength of solution.

To optimize phase-separation conditions, we studied the effects of these parameters on the formation of a melt and on its volume.

To determine the boundaries of the occurrence of phase separation, the effect of inorganic acid concentration should be studied. In addition, the nature of the inorganic acid affects not only the formation but also the volume of the melt (Table 1).

In Table 1, it can be seen that the phase-separation region in the DAM–BA–HX–NH₄SCN–H₂O system occurs over a wide range of inorganic acid concentrations. In this case, the concentration of H₂SO₄ or HCl had almost no effect on the volume of the resulting melt, and this was true of all of the above diantipyrylalkanes. In the presence of phosphoric acid, the volume of the melt was noticeably smaller than that in the presence of hydrochloric and sulfuric acids. This can be explained by the fact that H₃PO₄ is a weaker acid ($K_{\text{H}_3\text{PO}_4}^I = 7.6 \times 10^{-3}$) [14], which interacted with the reagent to a smaller extent with the formation of a monosubstituted salt (LH)H₂PO₄.

The effect of the ratio between organic reagents on the formation of a melt was studied by the isomolar series method (Table 2).

It was found that the melt was not formed in the absence of thiocyanate ions; on the contrary, a maximum melt volume was formed at an NH₄SCN concentration of 0.25 mol/L and a DAM : BA ratio of 1 : 1.

At a thiocyanate ion concentration of 0.25 mol/L and a DAM : BA ratio of 3 : 2, a precipitate was separated because of the formation of the sparingly soluble DAM · 2HSCN salt.

Table 2. Effect of the ratio between DAM and BA concentrations on the volume of the melt $\Sigma n = 0.004$ mol, $c_{\text{H}^+} = 0.25$ mol/L)

n_{DAM} , mol	n_{BA} , mol	DAM : BA	HCl		H ₂ SO ₄	
			[SCN [−]] = 0.05 mol/L	[SCN [−]] = 0.25 mol/L	[SCN [−]] = 0.05 mol/L	[SCN [−]] = 0.25 mol/L
			V_{melt} , mL			
0.0008	0.0032	1 : 4	1 – s*	0.6	0.4	0.3
0.0010	0.0030	1 : 3	0.6	0.7	0.9	0.4
0.0016	0.0024	2 : 3	1.0	1.1	0.7	1.0
0.0020	0.0020	1 : 1	1.1	1.2	1.0	1.2
0.0024	0.0016	3 : 2	1.1	1 – s**	1.1	1.0
0.0030	0.0010	3 : 1	0.8	1 – s**	0.4	1 – s**
0.0032	0.0008	4 : 1	0.6	1 – s**	0.7	1 – s**

Note: 1 – s*, benzoic acid is separated as a precipitate in the extraction system; 1 – s**, the reagent is separated as a precipitate in the extraction system.

Table 3. Effect of the total amount of DAM and BA on the volume of the melt ($n_{\text{DAM}} : n_{\text{BA}} = 1 : 1$; $c_{\text{H}^+} = 0.25 \text{ mol/L}$; $c_{\text{SCN}^-} = 0.25 \text{ mol/L}$)

$n_{\text{DAM}}, \text{mol}$	$n_{\text{BA}}, \text{mol}$	$\Sigma n, \text{mol}$	$V_{\text{melt}}, \text{mL}$	n_{DAM} in the melt, mol
0.001	0.001	0.002	0.4	0.00100
0.002	0.002	0.004	1.1	0.00200
0.003	0.003	0.006	1.5	0.00273
0.004	0.004	0.008	2.2	0.00368
0.005	0.005	0.010	2.5	0.00383
0.007	0.007	0.014	3.5	0.00658

At a constant ratio between DAA and BA, the dependence of the melt volume on the total amount of the above substances was studied.

As follows from Table 3, the melt volume increased with the total amount of DAM and BA. Note that the reagent concentration in the melt was much higher than that in ordinary extraction in the presence of an organic solvent.

The effect of the total volume of an aqueous phase on the formation and volume of a melt was studied in order to determine the possibility of the absolute pre-concentration of the trace amounts of metals. It was found that the phase-separation region was retained as the aqueous-phase volume was increased from 20 to 100 mL. In this case, the recovery of metal ions remained unchanged; however, the extraction equilibration time increased.

The results of preliminary experiments indicated that extraction systems as the melt of an organic reagent with an organic acid are suitable for the extraction of both trace and macro amounts of metal ions. Optimum conditions for the formation of a melt (of volume $\sim 1 \text{ mL}$) should be consider as follows: $n_{\text{DAA}} : n_{\text{BA}} = 1 : 1$, $\Sigma n = 4 \times 10^{-3} \text{ mol}$, and the concentration of hydrogen ions in a range from 0.01 to 5 mol/L.

We studied the effect of mineral acid concentration on the distribution coefficient of cobalt and found that cobalt was quantitatively extracted with DAM at an HCl concentration of 0.25–2.0 mol/L. For PDAM and BDAM, this range was expanded to 3.0 mol/L, whereas in the case of HDAM, on the contrary, the recovery decreased with the acidity of the aqueous phase (Fig. 1).

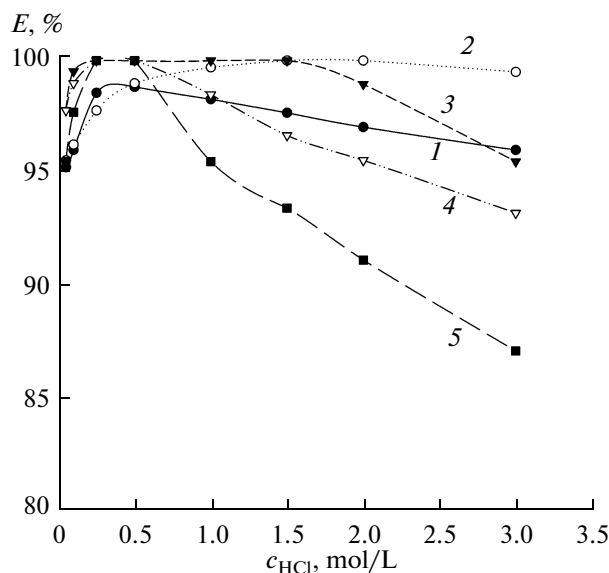
This was likely due to a high reagent protonation constant ($\text{p}K_{\text{H}^+}$ is 3.55 for HDAM in water [15]) and, as a consequence, the ability of the reagent to extract superstoichiometric amounts of thiocyanic acid (HSCN), which exerts a competing effect on the extraction of the cobalt complex. The curves of cobalt extraction in the presence of H_2SO_4 and H_3PO_4 differ only slightly from that of cobalt extraction from HCl solutions.

The maximum distribution of Zn ions (99.6%) was observed in the H_2SO_4 concentration range of 0.1–

1.0 mol/L; in this case, the chain length of the aldehyde radical in the DAA molecule had no effect on the extraction (Fig. 2).

Under the optimum conditions of cobalt(II) extraction, we constructed the $\log D_{\text{Co(o)}} - \log D_{\text{Co(b)}}$ plot. The slope of this plot was 1; this suggests that cobalt was extracted as a monomer into the melt. Using the extraction isotherms of cobalt (85°C), we calculated the capacities of 0.1 M melts of the reagents ($c_{\text{SCN}^-} = 0.25 \text{ mol/L}$; $c_{\text{H}^+} = 0.25 \text{ mol/L}$), (g Co)/(L melt): DAM (56.05) > PDAM (57.74) > BDAM (62.74) > HDAM (61.68). Note that the capacity was sufficiently high, as compared with the extraction capacity of reagent solutions in organic solvents.

As noted above, the melt was not formed in the absence of thiocyanate ions. The introduction of even a small amount of NH_4SCN ($8 \times 10^{-4} \text{ mol}$) into the system facilitated the formation of 1.0 mL of a melt. A

**Fig. 1.** Dependence of the extraction of cobalt on HCl concentration: (1) DAM, (2) PDAM, (3) BDAM, (4) IBDAM, and (5) HDAM ($n_{\text{L}} = n_{\text{BA}} = 0.002 \text{ mol}$; $c_{\text{M}} = 0.01 \text{ mol/L}$; and $c_{\text{SCN}^-} = 0.25 \text{ mol/L}$).

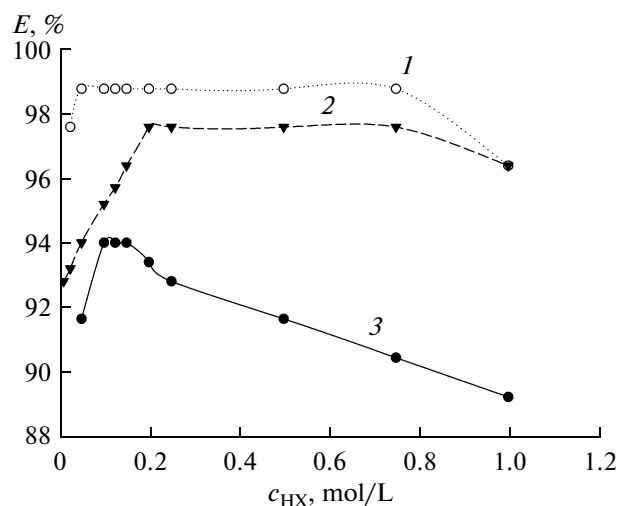


Fig. 2. Dependence of the extraction of zinc with dianthiopyrilmethane on inorganic acid concentration: (1) H_2SO_4 , (2) H_3PO_4 , and (3) HCl ($n_{\text{DAM}} = n_{\text{BA}} = 0.002$ mol; $c_{\text{M}} = 0.01$ mol/L; and $c_{\text{SCN}^-} = 0.25$ mol/L).

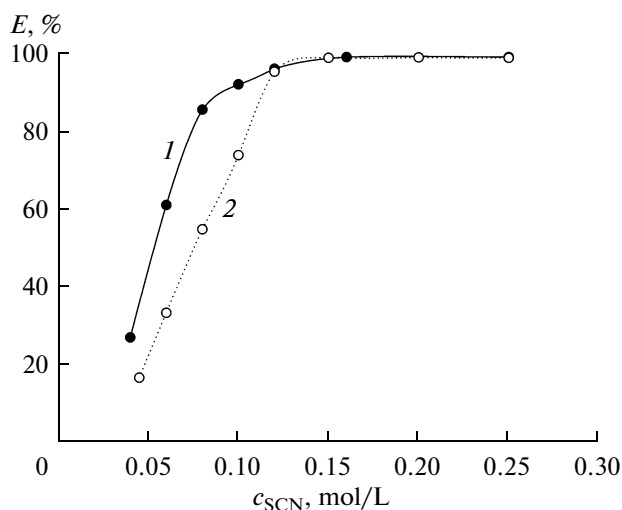
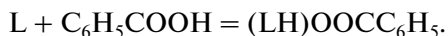


Fig. 3. Dependence of the extraction of metal ions on the concentration of thiocyanate ions: (1) cobalt and (2) zinc ($n_{\text{DAM}} = n_{\text{BA}} = 0.002$ mol; $c_{\text{M}} = 0.01$ mol/L; and $c_{\text{SCN}^-} = 0.25$ mol/L).

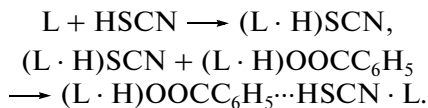
further increase in the concentration of thiocyanate ions to 5×10^{-3} mol or higher had no effect on the melt volume. However, the recovery of metal ions increased in this case (Fig. 3). Therefore, a thiocyanate ion concentration of 0.2–0.25 mol/L should be considered an optimum for extraction.

Table 4 summarizes the results of the chemical analysis of an extract saturated with a metal.

From the above, it follows that a chemical compound between DAA as a base and BA is formed in the DAA–BA–water system; this compound is sparingly soluble in water to result in the separation of the second liquid phase.



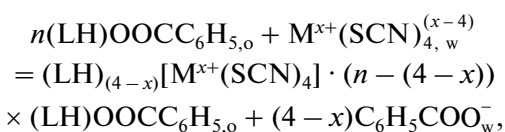
In addition, the salt of the reagent with an inorganic acid is formed; in turn, this salt is dissolved in the salt of the reagent with BA to form a complex microphase.



On the addition of small amounts of metal ions to the system, the resulting complex $(\text{LH})_{(4-x)}[\text{M}^{x+}(\text{SCN})_4]$ was completely dissolved in the phase formed by the solvate $(\text{L} \cdot \text{H})\text{OOC}\text{C}_6\text{H}_5 \cdots \text{HSCN} \cdot \text{L}$.

Note that the melt changed to a crystalline state as the concentration of metal ions and, correspondingly, the concentration of the resulting complex compound was increased; that is, the complex compound of the thiocyanate metal complex with DAM was sparingly soluble in the resulting solvate.

In this context, we can hypothesize that, on the complexation of the reagent with a metal ion, a portion of the chemical compound between DAM and BA decomposed and the following process occurred in the system:



that is, benzoate ions ($\text{C}_6\text{H}_5\text{COO}^-$) were released into an aqueous solution. Next, upon the saturation of the reagent with the metal ion, only the complex

Table 4.

Test element	Co		Zn	
	for $(\text{DAMH})_2[\text{Co}(\text{SCN})_4]$		for $(\text{DAMH})_2[\text{Zn}(\text{SCN})_4]$	
	found, %	calculated, %	found, %	calculated, %
M (II)	5.36	5.48	5.98	6.00
SCN^-	23.06	22.28	22.09	22.16
DAM	71.40	72.05	71.75	71.66
H^+	0.18	0.19	0.18	0.18

$(\text{LH})_{(4-x)}[\text{M}^{x+}(\text{SCN})_4]$ was formed and separated as a precipitate because its solvated moiety $(\text{LH})\text{OOCCH}_2\text{CH}_3$ decomposed with the complete release of BA into the aqueous phase.

The experimental results were used to develop a procedure for the determination of cobalt trace impurities in materials containing zinc ions. Cobalt ions form a colored complex compound, which absorbs at $\lambda = 625 \text{ nm}$, in a thiocyanate system with DAA, whereas zinc forms a colorless complex. Therefore, zinc will not cause interference with the photometric determination of cobalt.

Additionally, we developed a procedure for the simultaneous extraction-photometric determination of cobalt(II) and iron(III). These metal ions form colored complexes in the thiocyanate system. However, the maximum absorption wavelengths of these complexes are strongly different ($\lambda_{\text{max}}(\text{Co}) = 625 \text{ nm}$; $\lambda_{\text{max}}(\text{Fe}) = 480 \text{ nm}$). Because of this, both iron and cobalt can be simultaneously determined at different wavelengths.

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