

Conference Paper

# Hydrazides in the Processes of Extraction of Non-ferrous Metals from Ammonia Solutions

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## Abstract

The extraction of copper and other non-ferrous metals from ammonia solutions with hydrazides of Versatic acids (C<sub>15</sub>–C<sub>19</sub> fraction) is discussed in this article. Hydrazide group has been known to be a selective extractant for non-ferrous metals. Introducing the alkyl radical of  $\alpha$ -branched tert-carboxylic acids into the reagent structure may lead to new properties important for an extractant, such as chemical stability and good compatibility with solvents properties. The optimal extraction conditions, the effect of ammonium salts and the regularities of re-extraction are assessed.

**Keywords:** extraction, hydrazides,  $\alpha$ -branched tert-carboxylic acids, non-ferrous metals

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Published: 31 December 2020

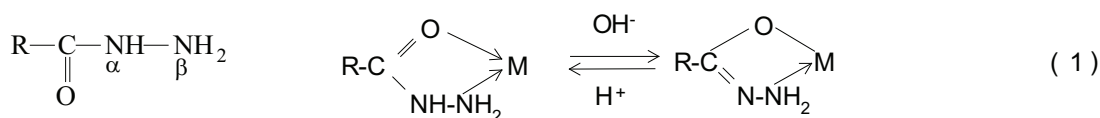
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Selection and Peer-review under the responsibility of the TECHNOGEN-2019 Conference Committee.

Hydrazides are a class of organic compounds characterized by a nitrogen-nitrogen covalent bond with four substituents with at least one of them being an acyl group (-C(O)NHNH<sub>2</sub>). Hydrazides draw attention of the researchers owing to specific properties of this functional group. Hydrazides can act as bidentate ligands (1) and form stable chelate complexes of various composition and structure with d-elements [1], therefore they are of interest as reagents for non-ferrous metal concentration processes.



At the same time, targeted transformation of the hydrazide group is possible. The introduction of substituents can result in a pronounced change in the ligand properties (acid-base, dentation, etc.), so practical application of the reagents is possible. For example, N, N-alkylation of  $\beta$ -nitrogen atom of the functional group, which is one of the coordination centers, significantly changes the physicochemical and extraction properties of the initial hydrazides. Unlike hydrazides, N',N'-dimethylhydrazides were shown to be efficient both in extraction of copper (II) ions from ammonia solutions [2, 3] and in extraction of acid complexes of vanadium (V), molybdenum (VI), rhenium (VII) [4, 5].

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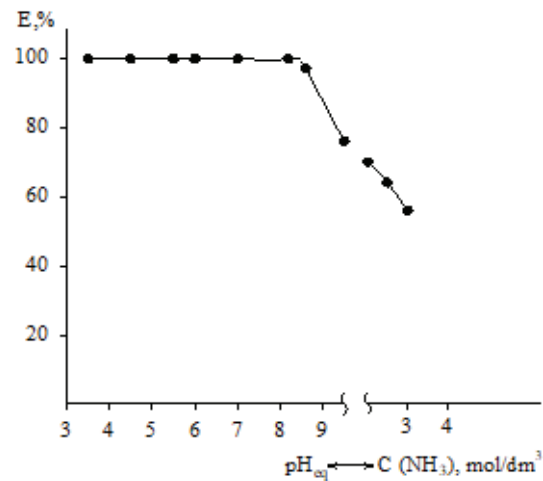
A proper choice of acyl structure allows such properties as compatibility with organic solvents, water solubility, resistance to hydrolysis to be regulated. For example, the reagent (HVA 1519) was synthesized via acylation of hydrazides by  $\alpha$ -branched tertiary carboxylic acid Versatic (fraction  $C_{15}$ - $C_{19}$ ). The reagent is used for extraction of copper (II) and accompanying non-ferrous metals from sulfuric acid solutions [6]. Such solutions are usually obtained upon leaching in hydrometallurgical processing of oxidized, poor copper ores and industrial waste. The HVA 1519 is well compatible with hydrocarbon solvents and modifiers, resistant to hydrolysis and oxidation in the extraction – re-extraction cycles. The organic phase capacity is 13,2 g copper (II)/dm<sup>3</sup> is about two times higher than that of the industrial extractant LIX 984N - 7 g copper (II)/dm<sup>3</sup>. Moreover, the advantage of HVA 1519 is that selective extraction of copper (II) can be carried out in presence of iron (III), nickel (II), cobalt (II), zinc (II) in more acidic media, at pH <1. Thus, it can be used for recycling of copper-containing raw materials (cement copper, copper-based alloys).

The aim of this work was to study the extraction of copper (II) and other non-ferrous metals from ammonia solutions with HVA 1519.

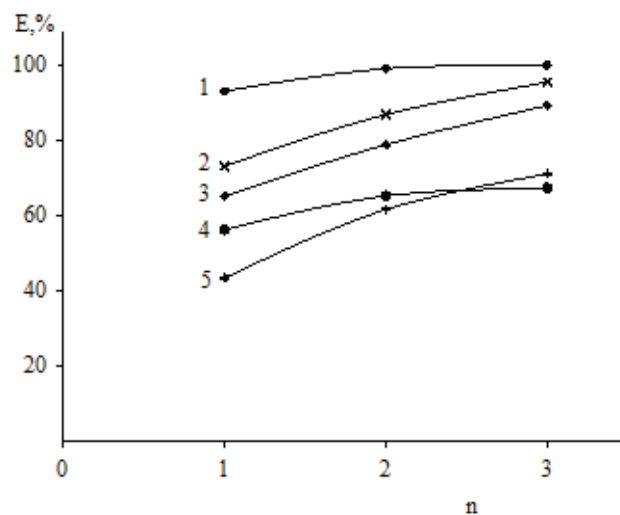
Figure 1 shows the dependence of Cu (II) extraction with HVA 1519 (in kerosene solution) on the pH value of solution and ammonia concentration. It is seen that the reagent extracts copper (II) most completely ( $E = 99\%$ ) in the pH range 4,0-9,0; then the degree of extraction begins to decrease and at a concentration of ammonia 3 mol/dm<sup>3</sup> is 56 %. In the pH range 3,5-6,0 simultaneous extraction and formation of a beard-shaped copper hydroxide precipitate at the interface is observed.

A three-step extraction procedure can lead to a significant increase in copper extraction degree at higher ammonia concentrations (Figure 2). Thus, at  $C_{NH_3} = 1$  mol/dm<sup>3</sup>, the extraction degree for one step is 65 %, and for three - 90 %.

Copper-containing ammonia solutions usually contain ammonium salts. Therefore, the effect of ammonium salts on the extraction of Cu (II) ions was studied. No effect of the presence of ammonium salts on copper extraction degree was found up to  $pH_{eq}$  value 7 ( $pH_{initial}$  7.5). At higher pH values a decrease in extraction degree was observed. In case of ammonium salt concentration over 10 g/dm<sup>3</sup>, the  $pH_{eq}$  range of copper extraction is narrower. To some extent, the presence of ammonium salts improves copper(II) extraction at concentrations over 50 g/dm<sup>3</sup>, since in this case no third phase appears in the extraction process. The data, illustrating the effect of ammonium sulfate concentration on the extraction of Cu(II) from a solution with the  $pH_{initial}$ -value equal to 8, are given in Table 1. A decrease in the extraction degree of Cu (II) is shown to be negligible at ammonium sulfate concentration of 200 g/dm<sup>3</sup>.



**Figure 1:** Dependence of Cu (II) extraction degree ( $E$ , %) on the  $pH_{eq}$  value of solution and ammonia concentration.  $V:V_{aq}=1:1$ ,  $C_{HVA1519}=0,4 \text{ mol/dm}^3$ ,  $\tau=3 \text{ мин.}$ ,  $C_{Cu}=883 \text{ mg/dm}^3$ .

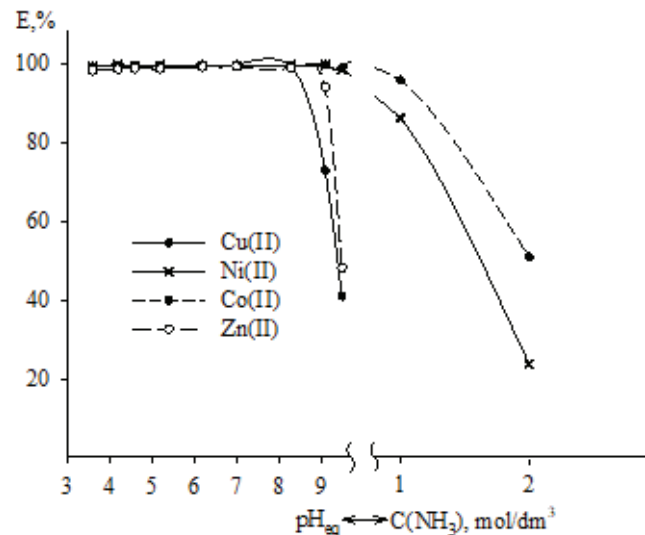


**Figure 2:** Dependence of Cu (II) extraction degree ( $E$ , %) on the number of extraction steps ( $n$ ) and ammonia concentration,  $\text{mol/dm}^3$ : 1-0,1; 2-0,5; 3-1,0; 4-3,0; 5-5,0  $V:V_{aq} = 1:1$ ,  $C_{HVA1519}=0,4 \text{ mol/dm}^3$ ,  $\tau=3 \text{ мин.}$ ,  $C_{Cu}=1382 \text{ mg/dm}^3$ .

**TABLE 1:** The effect of ammonium sulfate concentration on the extraction of copper(II) with of HVA 1519 (in kerosene solution).  $V : V_{aq}=1:1$ ,  $C_{HVA1519}=0,4 \text{ mol/dm}^3$ ,  $\tau=3 \text{ мин.}$ ,  $C_{NH_3}=0,05 \text{ mol/dm}^3$ ,  $Cu=1033 \text{ mg/dm}^3$ .

$C_{(NH_4)_2SO_4}, \text{ g/dm}^3$	$pH_{eq}$	$E, \%$
0	7,2	98,7
10	7,2	98,8
50	7,1	95,9
100	7,0	93,2
200	7,0	91,8

The curves describing joint extraction of Cu (II), Ni (II), Co (II) and Zn (II) ions with HVA 1519 are shown in Figure 3. The extraction degree for Cu (II) and Zn (II) starts to decrease at pH 8.5, the extraction degree for Ni(II) and Co(II) is high up to ammonia concentration of 1 mol/dm<sup>3</sup>. This makes possible the extraction separation of not only Ni and Cu, Co and Cu, but also Zn and Ni, Co and Zn ions.



**Figure 3:** The joint extraction of Cu (II), Ni (II), Co (II) and Zn (II) ions with HVA 1519 (in kerosene solution).  $V : V_{aq} = 1:1$ ,  $C_{HVA1519} = 0,4 \text{ mol/dm}^3$ ,  $\tau = 5 \text{ min}$ ,  $t = 20-22 \text{ }^\circ\text{C}$ ;  $C_{Cu}$ -553,  $C_{Ni}$ -440,  $C_{Co}$ -558,  $C_{Zn}$ -494 mg/dm<sup>3</sup>.

The separation coefficients of metal pairs at their joint presence are given in the Table 2.

**TABLE 2:** The coefficients of metal distribution ( $D_i$ ) and separation coefficients ( $\beta$ ) of metal pairs at their joint extraction with HVA 1519 (in kerosene solution).  $V : V_{aq} = 1:1$ ,  $C_{HVA1519} = 0,4 \text{ mol/dm}^3$ ,  $\tau = 5 \text{ мин.}$ ,  $t = 20-22 \text{ }^\circ\text{C}$ ;  $C_{Cu}$ -553,  $C_{Ni}$ -440,  $C_{Co}$ -558.

pH <sub>eq</sub>	E, %			D <sub>i</sub>			$\beta_{Ni/Cu}$	$\beta_{Co/Cu}$
	Cu (II)	Ni (II)	Co (II)	Cu (II)	Ni (II)	Co (II)		
7,3	88,0	99,9	99,3	7,32	1569,6	134,7	214	18
7,6	79,7	99,9	99,1	3,93	1046,0	113,1	266	29
7,8	68,7	99,9	99,0	2,20	1021,7	98,3	464	45
8,7	27,7	99,6	98,9	0,38	270,5	88,1	711	232
$C_{NH_3}=100 \text{ g/dm}^3$	2,3	73,2	95,5	0,02	2,7	21,5	137	1072

The re-extraction of copper in sulphuric acid solutions was studied. The re-extraction degree was 99-100% under the following conditions: H<sub>2</sub>SO<sub>4</sub> concentration - 147 g/dm<sup>3</sup>, phase contact time - 3 min, phase volume ratio -  $V : V_{aq} = 1:10$ .

This work was financially supported by the Program of the Ural branch of RAS (project № 18-3-3-24).

## References

- [1] Machkhoshvili, R. I. (1983). Coordination Compounds of Metals with Hydrazines. (Doctoral Thesis, Institute of General and Inorganic Chemistry, 1983).
- [2] Radushev, A. V., Batueva, T. D. and Gusev V. Y. (2007). Copper(II) Complexation and Extraction with 2-Ethylhexanoic Acid *N',N'*-dialkylhydrazides. *Russian Journal of Inorganic Chemistry*, vol. 52, issue 8, pp. 1317–1320.
- [3] Gusev, V. Y., *et al.* (2012). *N',N'* - dialcylhydrazine p-tertbutylbenzene acid. Patent RF, № 2448174.
- [4] Batueva, T. D., Baigacheva, E. V. and Nasrtdinova, T. Y. (2016). Vanadium(V) Extraction from Sulfuric and Hydrochloric Acid Solutions with Hydrazides and *N',N'*-Dialkylhydrazides of Versatic Acids. *Russian Journal of Inorganic Chemistry*, vol. 61, issue 3, pp. 397–401.
- [5] Batueva, T. D. and Shcherban, M. G. (2017). Rhenium(VII) extraction with Versatic hydrazides and *N',N'*-Dialkylhydrazides. *Russian Journal of Inorganic Chemistry*, vol. 62, issue 10, pp. 1409-1413.
- [6] Vaulina, V. N., *et al.* (2018). Method of copper(II) extraction from aqueous sulfuric acid solutions containing other metals. Patent RF, № 2668238.