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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

N,N-Dibutylhydrazide of Octanoic Acid as an Extragent for the Extraction of Copper(II) from Ammonium Media

V. J. Gusev, A. V. Radushev, T. A. Verkholantseva, and T. D. Batueva

Institute of Applied Chemistry, Ural Division, Russian Academy of Sciences, Perm, Russia

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Abstract—The solubility and the coefficient of copper(II) distribution between hexane and aqueous phase of *N,N*-dibutylhydrazide of octanoic acid were studied. The effects of ammonium, Co(II), Ni(II), and Zn(II) salts on the copper(II) extraction was studied. The extraction isotherm was constructed and the constant of copper extraction from ammonium solutions was calculated. The capacity of the organic phase with respect to copper and the conditions of its reextraction were determined.

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Ammonium media are used in hydrometallurgy for leaching copper(II) from copper concentrates [1] and also for processing secondary raw material of non-ferrous metals [2]. Ammonium-sulfate solutions are applied most widely, and ammonium-carbonate or mixed solutions, to a lesser degree. To isolate copper(II) from these solutions, various methods are used, of which the extraction-electrolysis method should be admitted to be the most economic [3]. Oxyoximes and β-diketones used in this method for copper(II) extraction from ammonium solutions have certain disadvantages limiting their application. For example, oxyoximes transfer ammonia together with an organic phase, they have a rather low capacity with respect to copper (no more than 12–17 g/l) whereas β-diketones are subjected to the action of ammonium salts, which reduce the degree of copper extraction. Therefore searching of alternative extragents for copper(II) extraction from ammonium media is actual.

N,N-Dialkylhydrazides of aromatic and aliphatic carboxylic acids extract copper(II) to 98–99% in the pH range corresponding to 6–1.5 M NH_3 concentrations [4–6], which makes them promising for copper(II) extraction from ammonium solutions. However, properties of the compounds important for their application, for example losses with an aqueous phase and influence of impurities on the extraction are scarcely considered in the specified publications. Constants of copper(II) extraction required for comparing the effectiveness of these compounds and known industrial reagents are not calculated. There is paper [7] devoted to the study of physicochemical properties of *N,N*-dialkylhydrazides. The authors have studied the solubility, resistance to hydrolysis, and ablation of *N,N*-dialkylhydrazides of 2-ethylhexane acid with an aqueous phase.

The aim of the present work was to fill this gap. We have studied certain properties of *N,N*-dibutylhydrazide of octanoic acid (DBHOA)- $C_7H_{15}CONHN(Bu)_2$ important from the viewpoint of industrial application.

EXPERIMENTAL

The reagent was prepared by the reaction of hydrazide of octanoic acid with butyl bromide in presence of KOH [6]. The content of the basic substance determined by the conductometric titration [8] was 96%. We used pure-grade $CuCl_2 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$. The other reagents were of analytical or chemically-pure grade, hexane was of chemically-pure grade.

The UV spectrum and optical density were recorded on an SF-26 spectrophotometer, pH values were measured on an I-160M ionometer with glass and silver-chloride electrodes. The conductometric titration was carried out on an OK 102/1 conductometer (Hungary).

Solubility was determined by the gravimetrical method. An aliquot (5 ml) of a DBHOA solution saturated at room temperature was placed in a weighing bottle and brought up to a constant weight. A solvent was evaporated

Table 1. Solubility of DBHOA and HOA in certain solvents
Extragent

Extragent	Solubility, g/L		
	in water	in 0.1 M HC1	in hexane
DBHOA	0.04	3.9	>500
HOA	1.8	19.8	insoluble

in a drying box at 110-115°C and the weighing bottle was brought up to a constant weight. The distribution of the reagent between organic and water phases was found as follows. To create a required ionic strength, 1 ml of 2 M $NaC1O_4$ solution was placed in a 50 ml separating funnel, a corresponding amount of an HC1 or NH_3 solution was added, and the volume was brought to 10 ml. A 0.1 M DBHOA solution in hexane (10 ml) was poured in and shaked for 3 min. The aqueous phase was filtrated, pH was measured, an aliquot of 5 ml was taken, and the DBHOA concentration was determined by titration with sodium lauryl sulfate.

The DBHOA content was determined with sodium lauryl sulfate by the following procedure. To 5 ml of a DBHOA aqueous solution 10 ml of 0.05 N HC1, 20 ml of chloroform, and three drops of a mixed indicator (20 ml of 0.1% dimethyl yellow alcohol solution and 10 ml of 0.1% methylene blue alcohol solution) were added. The titration was carried out with vigorous shaking using a 0.015 M sodium lauryl sulfate solution up to a rose-violet coloring of the chloroform layer. The substances reacted in the equimolar proportion.

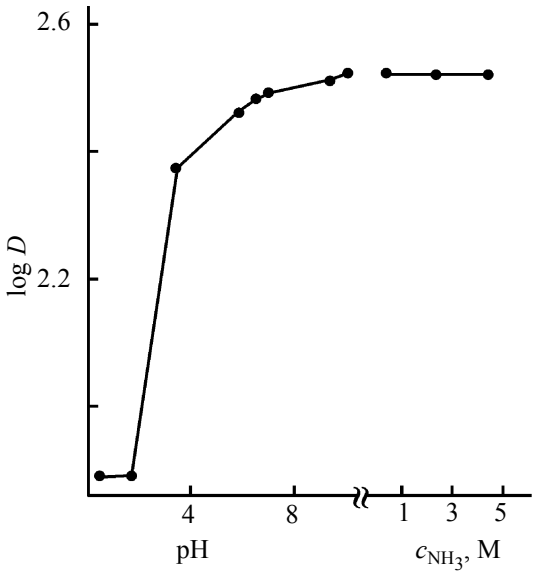

Fig. 1. Dependence of the coefficient log D of DBHOA distribution between organic and aqueous phases on the acidity of medium (c_{NH_3}, M). c_{DBHOA} = 0.1 M in hexane, i = 0.2 ($NaClO_4$), $V_0 : V_A$ = 1:1.

To construct an extraction isotherm, an aliquot of a $CuC1_2$ solution, 1 ml of 1 M KC1, and 0.5 ml of 13 M NH_3 solutions were placed in a 50 ml separating funnel, and the solution volume was brought to 10 ml. Copper(II) was extracted with 10 ml of 2.5×10^{-3} M DBHOA solution in hexane with mixing by shaking within 5 min. After separation of phases into layers the aqueous layer was taken off, pH was measured, and a copper(II) content was determined by the extraction-photometric method with sodium diethylthiocarbamate [9]. Copper was reextracted from the organic phase by shaking an aliquot with 10 ml of a 1.2 N H_2SO_4 within 5 min. The copper(II) content in the reextract was determined by the same method. The relative error in the resulting total copper content did not exceed 5%.

To take into account the effect of ammonium salts on the Cu(II) extraction, we added 0.5 ml of a 0.86 M ammonia solution and a corresponding amount of an ammonium salt solution to 2.5 ml of a 0.01 M $CuSO_4$ solution. The aqueous phase volume was brought to 10 ml. Copper(II) was extracted by 5 ml of a 0.05 M DBHOA solution in hexane within 3 min. The aqueous phase was filtrated and a residual copper content was determined by the extraction-photometric method with sodium diethylthiocarbamate.

The effect of metal cations on the copper(II) extraction was studied as follows. In a 50 ml separating funnel 2.5 ml of 0.01 M copper(II) solution, 2 ml of 5.3 M NH_3, and a corresponding amount of a 0.1 M solution of a salt of the metal under study were placed. The aqueous phase volume was brought to 20 ml. As in the previous experiments, copper(II) was extracted from a solution by shaking with 5 ml of a 0.05 M DBHOA solution in hexane for 3 min. The extract was filtrated, and its optical density was measured at λ = 460 nm.

The data on the DBHOA solubility are given in Table 1. To illustrate the effect of alkyl radicals in the hydrazide group on the solubility, the data [10] on the solubility of hydrazide of octanoic acid (HOA) are also shown in Table 1. It follows from Table 1 that the introduction of two butyl radicals decreases the solubility of the compound in water. DBHOA is highly soluble in hexane, in which HOA is practically insoluble. Solubility of a reagent in aliphatic hydrocarbon solvents is an important characteristic in view of their wide application

Table 2. Calculation of the coefficient Kex of copper(II) extraction by DBHOA. $c_{DBHOA} = 2.5 \times 10^{-3}$ M, $c_{NH_3} = 0.65$ M, pH 11.5, $i = 0.1$ (KCl)

$[Cu(NH_3)_4^{2+}] \times 10^4$,	$[CuL_2^+] \times 10^4$	$[HL^+] \times 10^3$	$[HL]^{2+} \times 10^6$,	$[NH_4^+] \times 10^3$,	$[NH_4^+]^2 \times 10^5$,	K_{ex}	log K_{ex}
mol l^{-1}			$mol^{-2}\ l^{-2}$	mol l	$mol^{-2}\ l^{-2}$		
0.29	5.85	1.33	1.77	4.79	2.29	110	2.04
0.60	7.55	0.99	0.98	5.13	2.63	142	2.15
0.84	8.15	0.87	0.76	5.25	2.76	148	2.17
1.35	8.65	0.77	0.59	5.35	2.86	130	2.11
2.43	9.40	0.62	0.38	5.50	3.02	129	2.11
3.54	9.71	0.56	0.31	5.56	3.09	115	2.06
6.00	10.42	0.42	0.18	5.70	3.25	132	2.12

in extraction processes. An important characteristic for an industrial extracting reagent is also the coefficient of its distribution between organic and aqueous phases. This value defines reagent losses with the aqueous phase during the extraction and thus influences its economic efficiency.

The coefficients D of the DBHOA distribution between hexane and aqueous phases are given in Fig. 1. In the pH interval 0–2 log D is ~1.9, and in the medium with pH > 5 it is about 2.5, which is connected with the existence of two forms of the reagent in solutions. As $pK_{a1} = 3.34$ for DBHOA [6], it means that at pH > 5 the reagent is in the neutral form, and at pH < 2 in the protonated form. It is obvious that the protonated form is more soluble in water than the neutral. For a solution of the industrial extragent of copper, 2-hydroxy-5-dodecylsalicylaldoxome (LIX 860), log D =3.95 at pH 5 in hexane [11]. Thus, this characteristic for DBHOA is much lower than for LIX 860. This characteristic can be improved by increasing the molecular weight of the *N,N*-dialkylhydrazide.

The reagent forms an extractable complex CuL2 (L is the deprotonated form of DBHOA) with copper(II) [6]. The isotherm of copper(II) extraction from ammonium media is shown in Fig. 2. A 2.5 M DBHOA solution in hexane saturated by the metal contains 1.28×10^{-3} M of copper(II), which practically corresponds to its theoretical value (1.25×10^{-3} M) for the complex of the composition [Cu(II)] : [DBHOA] =1 : 2.

The extraction of copper(II) from ammonium media can be described by the equation

$$Cu(NH_3)_{4(A)}^{2+} + 2HL_{(O)} = {}^*CuL_{2(O)} + 2NH_{4(A)}^+ + 2NH_{3(A)}. \quad (1)$$

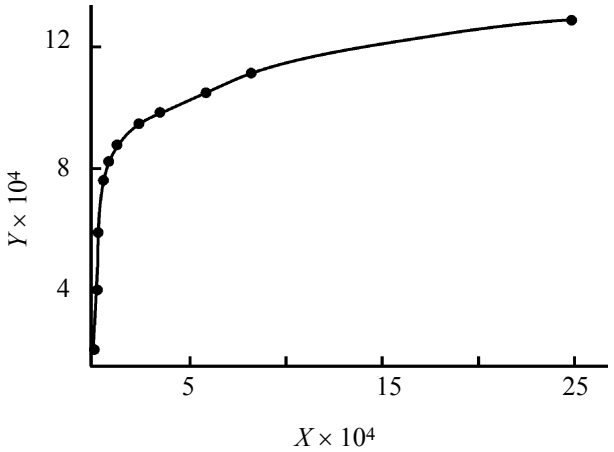

Fig. 2. Extraction isotherm of copper(II) chloride by DBHOA in hexane. $c_{DBHOA} = 2.5 \times 10^{-3}$, $c_{NH_3} = 0.65$ M; $i = 0.1$ (KCl); $\tau = 5$ min. X is concentration of copper(II) in aqueous phase (M), Y concentration of copper(II) in organic phase (M).

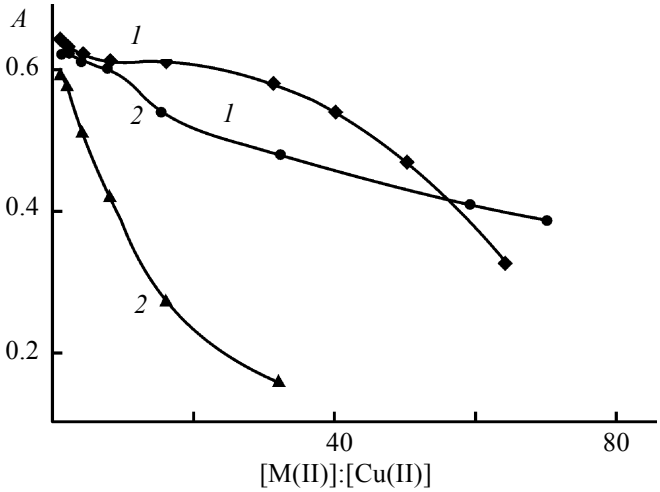

Fig. 3. Dependence of optical density A (relative units) of Cu(II)-DBHOA extract on the ratio [M(II)]:[Cu(II)] in aqueous phase. $c_{Cu(II)} = 1.25 \times 10^{-3}$; $c_{DBHOA} = 5 \times 10^{-2}$; $c_{NH_3} = 0.53$ M; $V_O = V_A$; $l = 1$ cm. (*1*) Ni(II), (*2*) Zn(II), (*3*) Co(II).

Here HL is *N,N*-dibutylhydrazide of octanoic acid; the indexes "A" and "O" correspond to aqueous and organic phases, respectively.

In terms of equation (1) the constant of copper(II) extraction is defined by the relation

$$K_{ex} = \frac{[CuL_2][NH_4^+]^2\,[NH_3]^2}{[Cu(NH_3)_4^{2+}][HL]^2}. \quad (2)$$

To simplify the calculation of the concentration extraction constant, we assumed that copper(II) in an aqueous phase is entirely in the form of $Cu(NH_3)_4^{2+}$. Copper(II) equilibrium concentrations in aqueous and organic phases were taken from the extraction isotherm data. As a considerable excess of ammonium was used in its constructing, the variation of its concentration during extraction can be neglected, and this value was taken to be constant and equal to the initial concentration. Remaining equilibrium concentrations were found as follows:

$$[NH_4] = [NH_4]_I + [NH_4]_{II}. \quad (3)$$

Here $[NH_4]_I$ is the concentration of ammonium ions liberated upon copper extraction (equal to $2[CuL_2]$); $[NH_4]_{II}$ the concentration of ammonium ions formed as a result of the dissociation of an aqueous ammonia solution, which was found from the expression for the dissociation constant by the formula

$$[NH_4]_{II} = \frac{K[NH_4OH]}{[OH^-]},$$

Here K is the dissociation constant (1.76×10^{-5} [12]) and $[NH_4OH]$ – the concentration of ammonia aqueous solution (0.65 M).

The solution after extraction has pH 11.5, at which $[OH^-] = 3.16 \times 10^{-3}$ M; whence it follows that $[NH_4]_n$ is 3.62×10^{-3} M.

$$[HL] = c_{DBHOA} - 2[CuL_2].$$

Here cDBHOA is the initial DBHOA concentration and $[CuL_2]$, the copper(II) concentration in the organic phase. The values of the logarithm of the extraction constant are given in Table 2.

The value of $\log K_{ex} = 2.11 \pm 0.04$ ($n = 7$, $P = 0.95$) was obtained. The thermodynamic extraction constant for the industrial extragent LIX 54 of the β-diketonate class extracting copper(II) from ammonium media was found by the same equation [13] The value of $\log K_{ex} = 2.89 \pm 0.03$ was obtained. These values show that DBHOA is a slightly less effective extragent than LIX 54.

Frequent copper satellites in ores are cobalt, nickel, and zinc. Therefore we have studied the influence of Co(II), Ni(II), and Zn(II) presence on the completeness of copper(II) extraction with DBHOA. We used the spectrophotometric method in this study. The absorption spectrum of the copper(II) extract with DBHOA in hexane is characterized by $\lambda_{max} = 460$ nm. The effect of admixtures was judged from the decrease in the optical density A of the complex CuL_2 extract at $\lambda = 460$ nm caused by the addition of foreign ions. This decrease can be assigned either to an element coextraction or to a suppression of copper(II) extraction. The effects of Co(II), Ni(II), and Zn(II) on the copper(II) extraction can be judged from Fig. 3. It is seen that the 30-fold excess of Ni(II) and 10-fold excess of Zn(II) affect copper(II) extraction only slightly (curves 1 and 2), as the decrease in the optical density of the complex extract is insignificant. The presence of Co(II) in a solution even in the ratio [Co(II)]:[Cu(II)] = 1:1 noticeably reduces the value of A (curve 3). Thus, Co(II) strongly affects the extraction of copper(II) with DBHOA.

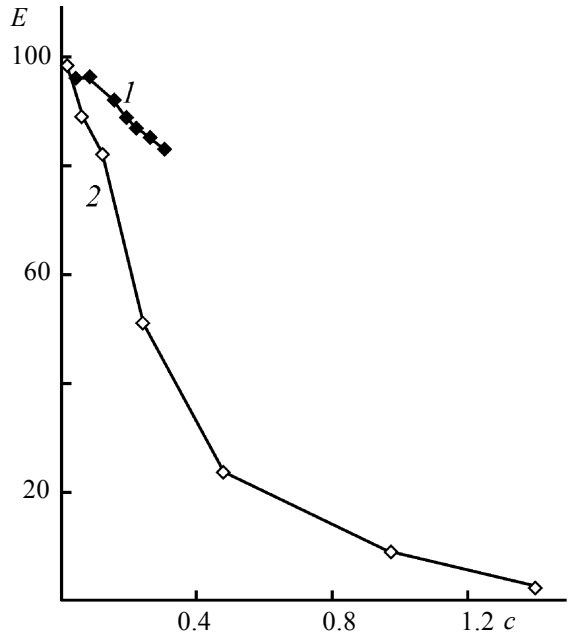

Fig. 4. Dependence of the degree of copper(II) extraction E by 0.05 M DBHOA solution in hexane on the contents of ammonium salts (M). $c_{NH} = 0.04$ M. (*1*) NH_4Cl, (*2*) $(NH_4)_2SO_4$.

As a number of industrial ammonium solutions can contain ammonium salts, it was of interest to study their influence on the copper extraction. The data obtained are shown in Fig. 4. It is seen that ammonium salts suppress the extraction. Ammonium sulfate renders a stronger effect: its content of 0.24 M reduces copper extraction from 98 to 49%. The same amount of NH_4C1 reduces the extraction only to 85%.

The maximum capacity of an 1.9 M DBHOA solution in hexane with respect to copper(II) is 28–32 g/l, thus it is comparable with β-diketones offered for the copper(II)extraction from ammonium media [2].

Copper(II) is readily reextracted from the organic phase by 1 N H_2SO_4. By this characteristic DBHOA outperforms oxyoximes which require a higher acid concentration (150–200 g l^{-1} [14]) for copper(II) reextraction. The base properties of DBHOA suggest that its molecules are protonated in the excess of acids and, therefore, a transfer of an inorganic acid is possible.

CONCLUSIONS

1. *N,N*-Dibutylhydrazide of octanoic acid is fairly high soluble in aqueous phases, especially at the reextraction in acid media.

2. *N,N*-Dibutylhydrazide of octanoic acid is slightly exceeded by the industrial reagent LIX 54 of the β-diketone class in the effectiveness of copper(II) extraction characterized by the extraction constant.

3. The presence of ammonium and Co(II) salts suppresses the copper(II) extraction. The 30-fold Ni(II) excess and the 10-fold Zn(II) excess influence its extraction only slightly.

4. The capacity of the 1.9 M solution of *N,N*-dibutylhydrazide of octanoic acid in hexane with respect to the copper(II) extraction from ammonium media is 28–32 g l^{-1}, which is comparable with the characteristics of β-diketones. Copper(II) is readily reextracted from the organic phase by the 1 N H_2SO_4 solution.

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