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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

1,2-Dibenzoyl- and 1-Benzoyl-2-acetylhydrazines as Reagents for Recovering Cu(II) Ions from Alkaline Solutions

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Abstract—The conditions of complexation of 1,2-diacylhydrazines (H_2L) $C_6H_5C(O)NHNHC(O)R$, where R = C_6H_5 or CH_3, with Cu(II) ions in alkaline solutions were studied. The composition of the complexes formed by precipitation of Cu(II) from alkaline solutions, $(CuOH)_2L$ and CuL, was determined. The possibility of afterpurification of solutions with a low Cu(II) content by pneumatic flotation using H_2L was examined.

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1,2-Diacylhydrazines RC(O)NHNHC(O)R (H_2L) are tetradentate ligands and form stable flotation-active complexes ML with ions of Cu(II) and other nonferrous metals in ammonia or alkaline solutions [1, 2]. Replacement of alkyl radicals in symmetrical 1,2-diacylhydrazine molecules by phenyl radicals enhances the acid properties of the reagent, so that poorly soluble complexes of 1,2-dibenzoylhydrazine (DBzH) with Cu(II) are formed in ammonia solutions at pH 5–8 [3].

The goal of this study was to examine the conditions of complexation of 1,2-diacylhydrazines $C_6H_5 \cdot C(O)NHNHC(O)R$, where R = C_6H_5 or CH_3, with Cu(II) ions in alkaline solutions and the possibility of using these reagents for afterpurification of wastewater to remove Cu(II) after precipitation of the major amount of Cu(II) in the form of $Cu(OH)_2$.

EXPERIMENTAL

1,2-Dibenzoylhydrazine was prepared as described in [4], by thermal decomposition of $2C_6H_5COOH \cdot N_2H_4 \cdot H_2O$ [4]; 1-acetyl-2-benzoylhydrazine (BAH) was prepared similarly by the reaction of benzhydrazide with concentrated acetic acid. The main substance content in the reagent samples was 97% as determined by conductometric titration on an OK-102/1 conductometer (Hungary) with a bell-shaped OK-0902P electrode [5]. The optical density of solutions was measured on SF-26 and KFK-2 spectrophotometers, and pH, on an EV-74 pH meter with glass and silver chloride electrodes. The IR spectra were recorded in mineral oil on a Specord M 80 spectrophotometer. The derivatograms were taken on an MOM Q-1500D derivatograph (Hungary). The Cu(II) concentration in solution was determined by an extraction-photometric method with sodium diethyldithiocarbamate [6].

Complexation of reagents with Cu(II) ions was studied by the precipitation method, because the precipitates formed are insoluble in water and common solvents. Figure 1 (curve *4*) shows that the maximal

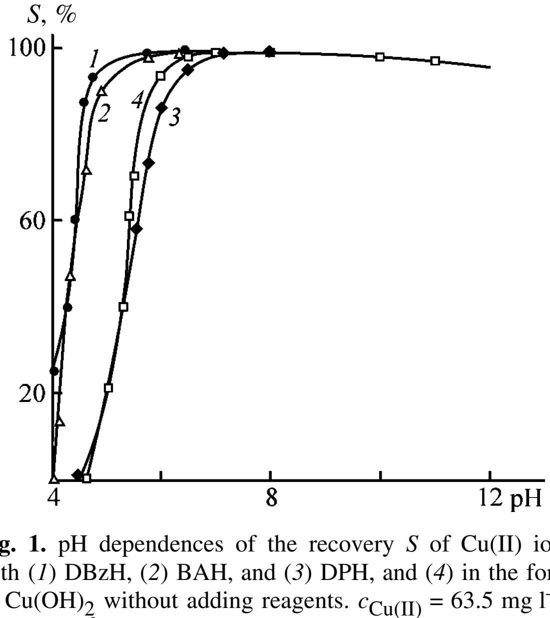


Fig. 1. pH dependences of the recovery *S* of Cu(II) ions with (*1*) DBzH, (*2*) BAH, and (*3*) DPH, and (*4*) in the form of $Cu(OH)_2$ without adding reagents. $c_{Cu(II)} = 63.5$ mg l^{-1}, $c_{H_2L} = 10^{-2}$ M in EtOH; [Cu(II)] : [H_2L] = 1 : 1, $\tau = 5$ min.

degree of precipitation of Cu(II) in the form of $Cu(OH)_2$ under the action of alkali is 99.8% in the pH range 7.0–10.0. The 99.9% precipitation of Cu(II) in the presence of DBzH was observed at pH 5.5 (curve *1*); in the presence of BAH, at pH 6.3 (curve *2*); and in the presence of dipropionylhydrazine (DPH), at pH 7 (curve *3*). These differences can be accounted for by considering the dissociation of 1,2-diacylhydrazines:

$$H_2L \overset{pK_{a_1}}{\rightleftarrows} HL^- \overset{pK_{a_2}}{\rightleftarrows} L^{2-}. \tag{1}$$

The acid properties of the reagents under consideration increase in the order DPH (pK_{a_1} 11.21±0.04, pK_{a_2} 12.5±0.3 [7]) < BAH (pK_{a_1} 9.37±0.03, pK_{a_2} 10.9±0.2) < DBzH (pK_{a_1} 9.22±0.04, pK_{a_2} 10.8±0.3 [3]). Therefore, the complexation of Cu(II) with DPH occurs in neutral and weakly alkaline solutions, whereas BAH and DBzH form complexes with Cu(II) even at pH 4.5–5.

We calculated the amount of H^+ (moles) released in complexation of DBzH and BAH with Cu(II) at varied pH_{eq} and constant concentration ratio Cu(II) : H_2L = 1 : 1 by slope analysis in the coordinates $\log\varepsilon$–pH_{eq}, where ε is the sorption ratio [$\varepsilon = S_i/(1 - S_i)$]. Equations (2) and (3) wre obtained by the least-squares method for BAH and DBzH, respectively:

$$\log\varepsilon = 1.8 \pm 0.1 \quad (r = 0.9995,\ n = 4,\ P = 0.95), \tag{2}$$

$$\log\varepsilon = 1.7 \pm 0.1 \quad (r = 0.9995,\ n = 4,\ P = 0.95). \tag{3}$$

Hence, Cu(II) ions form with DBzH and BAH the complexes CuL in which the ligand is double-deprotonated.

The composition of the complexes was confirmed by potentiometric titration. For this purpose, a 100-ml beaker was charged with 5.0 ml of a 0.9×10^{-3} M solution of $CuSO_4$ and 60 ml of a 1 : 1 EtOH–H_2O mixture. The resulting solution was titrated with 1×10^{-3} M solutions of potassium salts of the reagents. The complexation with DBzH and BAH occurred in steps; the bends in the curve were observed at Cu(II) : H_2L concentration ratios of 2 : 1, 1 : 1, and 1 : 2 (Fig. 2).

Then we isolated complexes at the Cu(II) : H_2L concentration ratios of 1 : 1 and 2 : 1 in alkaline solutions. A 250-ml beaker was charged with 50 ml of a 1×10^{-2} or 2×10^{-2} M solution of $CuSO_4$, 1.6 ml of a 1×10^{-1} M KOH solution was added, and 50 ml of a 1×10^{-2} M solution of DBzH or BAH in ethanol was added with stirring. The mixture was allowed to stand for 20 min. The precipitates were filtered off, washed on the filter with ethanol and hot water, and dried in air.

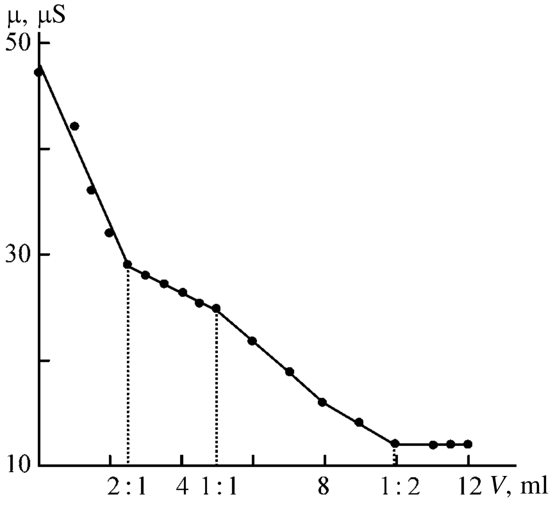


Fig. 2. Electrical conductivity μ of a $CuSO_4$ solution as a function of the precipitant (BAH) solution volume *V* (alkaline medium). $c_{Cu(II)} = 0.9 \times 10^{-3}$ M, $c_{BAH} = 10^{-3}$ M.

With DBzH and BAH at a Cu(II) : H_2L concentration ratio of 2 : 1 we obtained green precipitates, and at the 1 : 1 ratio, brown precipitates insoluble in water and common organic solvents, which is characteristic of polymeric compounds.

Analysis of the precipitates for Cu(II) gave the following results, wt %: [Cu(II)] : [DBzH] = 1 : 1, 20.75 and 2 : 1, 28.82; [Cu(II)] : [BAH] = 1 : 1, 25.9 and 2 : 1, 33.87. The composition of the complexes corresponds to the following formulas [calculated Cu(II), wt %]: $[Cu(C_6H_5OCNNCOC_6H_5)]$, 21.06; $[(CuOH)_2 \cdot (C_6H_5OCNNCOC_6H_5) \cdot 2H_2O]$, 29.20; $[Cu(C_6H_5O \cdot CNNCOCH_3)]$, 26.51; and $[(CuOH)_2(C_6H_5OCNN \cdot COCH_3) \cdot 2H_2O]$, 34.05.

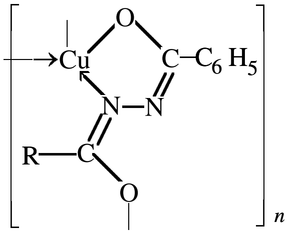
To determine the structure of the complexes, we recorded their IR spectra. As compared to the starting DBzH and BAH, the IR spectra of the complexes do not contain stretching vibration bands of the C=O and N–H bonds, but contain bands at 1395–1404 cm^{-1} corresponding to stretching vibrations of C–O single bonds. The bands at 1520–1535 cm^{-1}, absent in the spectra of the starting diacylhydrazines, can be assigned to stretching vibrations of the C=N bonds [8]. Thus, the IR spectra confirm that Cu(II) ions form complexes with the reagent molecules in the double-deprotonated enol form. The spectra of the 2 : 1 complexes, in contrast to those of the 1 : 1 complexes, Calculated solubility products SP and molar solubilities S of the complexes CuL with reagents $C_6H_5C(O)NHNHC(O)R$ in alkaline solutions

R	$c_{Cu} \times 10^4$	$c_{H_2L} \times 10^4$	S_i, %	$[Cu]^b_{eq} \times 10^6$, M	pH_{eq}	$c_{L^{2-}} \times 10^{12}$	$c_{Cu^{2+}} \times 10^6$	–log SP	$S \times 10^9$, M
	M					M			
CH_3	8.9	8.9	99.8	1.57	7.0	1.8	1.57	17.6	1.70
C_6H_5	10.0	10.0	99.9	1.26	6.5	0.1	1.26	18.9	0.35

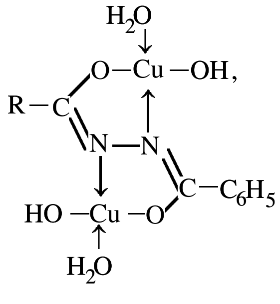
also contain absorption bands in the range 3350–3520 cm^{-1} corresponding to stretching vibrations of hydroxy groups and water of crystallization. The presence of water of crystallization is also confirmed by thermal analysis of the complexes. The DTA curve exhibits endothermic peaks in the interval 170–210°C with maxima at 180°C for the Cu–BAH (2 : 1) complex and at 190°C for the Cu–DBzH (2 : 1) complex, assignable to the loss of water of crystallization.

On the basis of the above facts, the suggested structures of the 2 : 1 and 1 : 1 complexes can be presented by formulas (4) and (5), where R = CH_3 or C_6H_5.

The complexation of DBzH and BAH with Cu(II) ions in alkaline solution at a component ratio of 1 : 1 can be described by Eq. (6).



(4)



(5)

$$Cu^{2+} + H_2L + 2OH^- \rightleftarrows CuL\downarrow + 2H_2O. \quad (6)$$

To calculate the equilibrium concentrations of Cu^{2+} and L^{2-}, we used data from [9].

The solubility products SP and molar solubilities S of the complexes, calculated from data in Fig. 1, are given in the table. It is seen that the molar solubilities of the precipitates of the complexes are lower than that of $Cu(OH)_2$ (1.8×10^{-7} M [10]) by two orders of magnitude. Therefore, Cu(II) ions are recovered from alkaline solutions in the form of complexes with the ligands in question more completely than in the form of $Cu(OH)_2$.

We found that, at the initial Cu(II) concentration of 57 mg l^{-1}, precipitation of the complexes at the 1 : 1 component ratio reduces the residual Cu(II) concentration to 0.08 mg l^{-1} with DBzH and 0.1 mg l^{-1} with BAH. However, to precipitate Cu(II), large amounts of the reagent should be added [2.8 mg of BAH per milligram of Cu(II)], and the reagent is not regenerated. Therefore, it was interesting to examine the possibility of additional recovery of Cu(II) ions from solutions with their low content [after precipitation of Cu(II) in the form of $Cu(OH)_2$] by pneumatic flotation with BAH.

To a solution containing 3 mg l^{-1} of Cu(II) [after precipitation of $Cu(OH)_2$ with NaOH], we added BAH in 0.1 M KOH or in ethanol at the [Cu(II)] : [BAH] ratio of 1 : 1 or 1 : 2; the mixture was stirred for 1–2 min. The precipitates, Cu(II) complexes with the reagents, passed into the foam and were removed from the solution. The flotation installation and the experimental conditions were similar to those described in [11]. The experiments were performed at 20±2°C. The sample of the purified solution was taken through a sampler and analyzed for the residual Cu(II) content by the extraction-photometric method [6]. The degree of additional recovery of Cu(II) at pH 9 was 83.8 and 95%; the residual concentration of Cu(II) ions was 0.5 and 0.15 mg l^{-1}, respectively, which is below MPC for household water [12].

CONCLUSIONS

(1) Conditions for complexation of Cu(II) with 1,2-dibenzoyl- and 1-benzoyl-2-acetylhydrazines in the course of precipitation were optimized. The 1 : 1 and 2 : 1 complexes of Cu(II) with H_2L were isolated from alkaline solutions (pH ~9) and identified.

(2) Replacement of one phenyl radical in 1,2-dibenzoylhydrazine by the acetyl radical increases the solubility of the complex and decreases the degree of recovery of Cu(II) ions.

(3) 1-Acetyl-1-benzoylhydrazine is suitable for afterpurification of wastewater by pneumatic flotation after precipitation of Cu(II) with alkali in the form of $Cu(OH)_2$.

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