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Investigation of selective extraction of copper ions by organic reagents based on dialkylhydrazides of carboxylic acid

Acetic acid dialkylhydrazides were investigated as extractants of copper ions. We found that selective extraction of copper was observed at pH 0.4–1.4. It is found that, depending on the technological conditions of the extraction, the extraction process of copper ions occurs preferably compared with zinc and iron ions at their joint presence in the solution.

Key words: extraction, extractants, hydrazides, alkylhydrazides, selective extraction of ions of copper, iron and zinc, electron-donating substituents.

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The successful application of extraction for the extraction of metals depends largely on the nature of the reagents, so the development of high-performance organic extractants is an important scientific and practical problem.

Earlier we investigated some alkylated derivatives of monoethanolamine vinyl ether as extractants [1] and studied the effect of various factors on their extraction ability. Through a comparative analysis of the extraction ability of reagents proposed, it was found that basicity and length of the hydrocarbon radical affected the extraction capacity of the amines obtained.

It is known from the literature [2] that carboxylic acids hydrazides (CAH) exhibit complexing properties and are proposed for extraction of copper (II) in the presence of metal impurities.

However, hydrazides are compounds poorly compatible with organic solvents. They are insufficiently resistant to hydrolysis and have a small capacity of the organic phase over copper. In our opinion, the introduction of alkyl substituents would improve the extractive properties of the reagent obtained. Synthesis of acetic acid dialkylhydrazides (AA DAH) [1] was carried out by reacting acetic acid hydrazide with twofold molar amount of alkyl bromide under basic conditions (for binding HX). The starting reactant was obtained by keeping the corresponding acid with hydrazine hydrate.

To evaluate the compounds synthesized as extractants there were studied their physico-chemical properties such as solubility in water, in the most important solvents and solutions of mineral acids, hydrolysis resistance, as well as mass capacity. The experimental data showed that acetic acid dialkylhydrazides were practically insoluble in water. Their solubility in 0.1 mol/L solution of hydrochloric acid and 1 mol/L solution of ammonia is negligible. Solubility in organic solvents increases from 0.1 mol/L to 3.8 mol/L with increasing length of the radical from C_2H_5 to C_5H_{11}, and then reduces for the reactants with a radical C_6H_{13} and C_7H_{15}.

To investigate the extraction ability of the acetic acid dialkylhydrazides synthesized solutions of cyanide complexes of gold and silver were used [3]. The solution was basified to pH 8–9. The organic phase was 0.03 molal solution of AA DAH in a solvent consisting of 90 % of kerosene and 10 % of octanol. Extraction was carried out with ratio of organic and aqueous phase 1:2.

The experimental results showed a linear dependence degree of extraction of metalloacids anions on radical lengths. It was found that the extraction ability of the compounds increased with increasing concentration of the latter. The best results were obtained by extraction with 0.32 mol/L solution of AA DAH. There was a tendency for change in the total mass capacity of metal extractants depending on the number of carbon atoms in the molecule. Since the mass capacity of the extractant is the main characteristic of any extractant, it follows that the best extractant has the highest mass capacity. The results of the study of dependence of mass capacity from the hydrocarbon chain length showed that the increase of the number of carbon atoms in the radical caused a reduction in mass capacity.

In this paper acetic acid diamylhydrazide was approved as an extracting agent for the extraction of copper ions and the accompanying ions of iron and zinc. These ions are present universally in the solutions obtained in the leaching of the poor feedstock, in solutions of dump and underground leaching, in sewage and mine waters. Since the salt form of the extractant was used, its pre-treatment was carried out. Kerosene was used as an organic diluent. It has a low content of aromatics and is inert to the ions present in the extraction conditions.

Standard solutions of Cu^{2+}, Zn^{2+} sulfates and Fe^{3+} chloride with a mark «chemically pure» were prepared for research. Temperature of the initial solution was 21 ºC and pH 2.4. Extraction was carried out with constant stirring and pH regulation for 30 minutes. 1 N solutions of NaOH and H_2SO_4 were used as neutralizers. The temperature of the solution during the extraction was 21 ± 3^0C. Figure 1 shows the dependence of the degree of extraction of the above metal ions at their joint presence on the pH value of the solution. Studies showed that selective extraction of copper was observed in the pH range 0.4–1.4. According to the results partition coefficients of the copper-zinc and copper-iron were calculated, which were 33–653 and 98–1378, respectively. Taking into account that the extractant AA DAH has a functional-active group it can be assumed that the complexation with metal ions will occur by similar mechanisms.

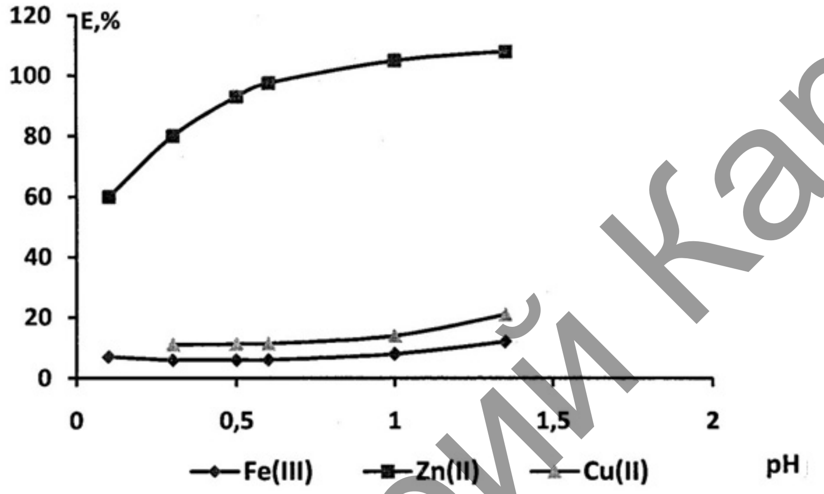

Figure 1. The dependence of the degree of extraction of metals at their joint presence in solution

However, the degree of metal extraction data indicate a weak interaction of the reagent with zinc and iron cations. The stability of the complex particles (ions, molecules) in the solution depends on the nature of the central atom and ligands. The most important characteristics of the central atom that determine the stability of the complex compounds are oxidation state (charge of the central ion in ionic complexes), the size and electronic structure. Bonding strength of ligands and polyatomic ions depends on the nature of atoms, through which the connection to the central atom is implemented and the charge characteristics of the molecule (ion) of ligand. As the literature contains no data on the stability constants of complexes of Cu (II), Zn (II), Fe (III) with AA DAH explanation of possibility of complex formation and sustainability can be found based on the position of the principles of hard and soft acids and bases of F.Basolo and R.Pearson [4].

Based on the concept of hard and soft acids and bases the cations of metals (copper, zinc and iron), possessing electron donors properties and having free orbitals, are acids. AA DAH is a base. According to the proposed classification of Lewis acids, copper cations are soft acids and zinc and iron cations are referred to intermediate ones. It follows that AA DAH acts as a soft base. According to [5] soft bases include donor particles in which the donor atoms have low polarizability and high electronegativity. With regard to the formation of complex compounds it is advisable to refer to the theory of M.I.Usanovich, whereby a cation, which ionization potential is greater, will have most acidic function in the row. Due to the ionization potentials metal cations can be placed in the next row (eV): Cu (20.29)> Zn (17.96)> Fe (16.18). Possibly, a strong acid function of copper cations leads to an increase of the metal's ability to form more stable complexes with the extractant. In this regard, an increase in the degree of extraction of copper ions from solutions is observed.

Since the formation of stable complexes creates difficulties at the transition of metal from the organic phase into water, in this paper the possibility of re-extraction solution of copper ions by sulfuric acid is investigated (Fig. 2).

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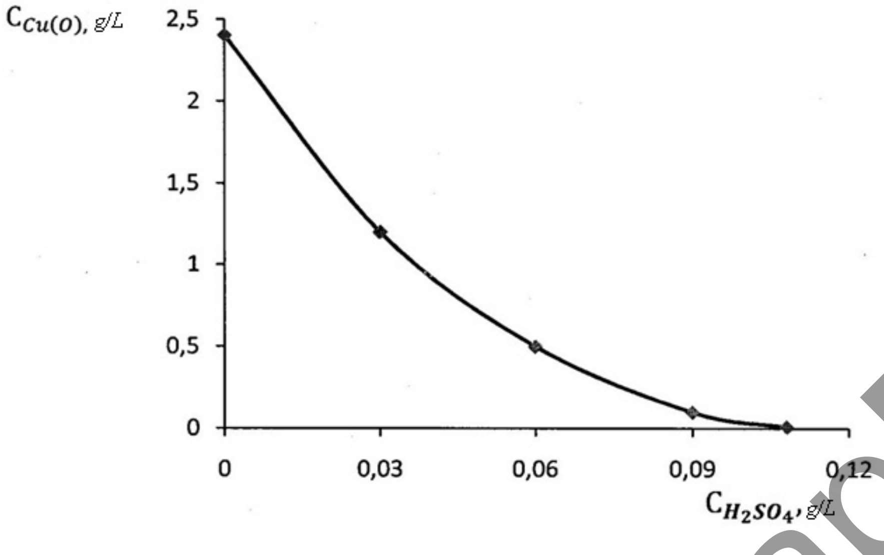

Figure 2. The curve of copper extraction from the organic phase by solutions of sulfuric acid

During the process the formation of emulsions was observed. At the sedimentation of the system separation was very slow. According to the experimental data it was revealed that the introduction of an organic salting out agent ($CuSO_4$) into the system led to a stabilization. The equilibrium was reached for 5 minutes. Effect of a salting out agent typically is carried out through the common ion or by hydrolysis to form, for example, hydrogen ion. At the allocation of non-electrolyte (c) the addition of an electrolyte causes often a change in the distribution ratio in accordance with the rule of Sechenov:

$$lg\frac{m_c^*}{m_c} = kx_s,$$

where m_c — partition coefficient in the absence of salt; m_c^* — partition coefficient in the presence of salt at concentration x_s; k — constant, reflecting the effect of salt concentration.

Reducing k with increasing concentration in the mixture indicates an increase in desalting (dehydrating) ability of $CuSO_4$.

Thus, our studies indicate the prospects of the use of the extractant synthesized for the selective recovery of copper from solutions of complex composition. Note that one of the important factors to ensure the selectivity of the extractant is strict maintenance of a particular pH of aqueous solutions. Preferably the extraction of copper ions, compared to zinc and iron ions at their joint presence in the solution, depends on of the extractant and extraction processing conditions as well.

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Карбон қышқылының алкилгидразидтері негізіндегі органикалық реагенттермен мыс иондарын селективті экстракциялауды зерттеу

Сірке қышқылының алкилгидразидтері мыс иондарының экстрагенттері ретінде зерттелді. Мысты талғамдап бөліп алу рН 0,4–1,4 аумағында байқалатыны табылды. Экстракциялаудың технологиялық жағдайларына байланысты мыс иондарының темір және мырыш иондарына қарағанда басымдылау бөліп алынуы ерітіндіде олар бір мезгілде болғанда жүретіні анықталды.

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Исследование селективной экстракции ионов меди органическими реагентами на основе алкилгидразидов карбоновой кислоты

Алкилгидразиды уксусной кислоты исследованы в качестве экстрагентов ионов меди. Найдено, что избирательное извлечение меди наблюдается в области рН 0,4–1,4. Установлено, что, в зависимости от технологических условий экстрагирования, происходит предпочтительное извлечение ионов меди по сравнению с ионами железа и цинка при их совместном присутствии в растворе.

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