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The Selection of Reagents for Ionic Flotation of Non-Ferrous Metals in the Series of N-Acyl-N'-Mezylhydrazines

A series of new ligands — N-acyl-N'-mesylhydrazines (MSH) — of the general formula $RC(O)NHNHSO_2CH_3$ has been obtained and considered as reagents for ionic flotation (IF) of non-ferrous metals (M(II). Reagents with a radical length of C_6H_{13} and above form hardly soluble complexes with M(II) so it is possible to implement a kind of the ionic flotation techniques — "precipitate flotation". The ranges of pH values of the most complete precipitation of cations from solutions have been determined. Precipitates of the metal complexes were isolated; their composition was confirmed by IR spectroscopy and elemental analysis. The conditional values of the solubility product (SP) of the complexes $[M(HL)_2]$ were calculated. The dependence $–\lg SP = 11.8 + 0.61N$ is fulfilled for the MSH series and Cu(II) ions. The surface-active properties of compounds with $R > C_6H_{13}$ were established. The reagents with optimal radical length for ionic flotation were selected. The ionic flotation of non-ferrous metals with N-nonanoyl-N'-mesylhydrazine was carried out. The up to 95–99 % recovery of metal ions, separation of copper and associated metal ions in diapason of pH 5–6.5 was shown to be possible.

Keywords: ionic flotation, precipitate flotation, sulfonylhydrazines, non-ferrous metals, physico-chemical properties, surface-active substances.

Introduction

Ion flotation (IF) is a simple and effective method for concentrating and separating metals from solutions containing fewer 500 mg/l of metal ions. Versatility, high performance and efficiency of this technique [1; 9] are of interest for purifying and deep post-treating waste waters and recycled waters, as well as for recovering valuable metals in industrial productions and in hydrometallurgy [2–5]. Improving the efficiency of IF is largely related to the efficiency of the reagents used [6]. At present, alkyl carboxylates [7], alkyl sulfonates, alkyl sulfates, alkylamines, quaternary ammonium salts [8–12], and xanthates [13] have been practically employed. As for the development of ion flotation, it would seem as appropriate to develop and improve a methodology for selecting an optimal collector. The traditional way of selecting a flotation reagent-collector is using compounds with a functional group capable of forming a chemical bond to a metal cation. Today the calculation of quantum-chemical characteristics of potential collectors (nucleophilic hardness, molecular electric moments, energy of complexation, etc.) has widely been used. It greatly facilitates the search for reagents, narrowing the range of ligands suitable for further studies [14]. However, as a rule, these calculations do not take into account the influence of solvents, salt composition, and competing complexation reactions in polycationic systems. In addition, the most important factor of the synthesis direction at developing potential collectors is the presence of a set of properties in the reagent that meet the basic requirements for flotation reagents [6]. One approach in the development of collectors for nonferrous metal ions is the directed synthesis method based on the choice of a suitable functionally active atom group (FAG) capable of forming compounds with metal ions and the organic radical (R). The optimal composition and structure of the radical are selected on the basis of "composition-property" dependences derived by semi-empirical methods as a result of a comprehensive study of the physic-chemical properties of a homologous series of ligands. Polydentate compounds, which form sparingly soluble metal complexes, are known to be of interest for the IF [6]. From this viewpoint, noteworthy are acylsulfonylhydrazines containing in their composition a hydrazide group capable of forming chelate complexes with non-ferrous metal ions [15; 34–50], and sulfonyl, which enhances acidic properties of the compounds. Previously, the physic-chemical properties of some N-acyl-N'-(aryl-, naphthyl)sulfonylhydrazines were studied, with a fundamental possibility of using them in flotation processes shown [16, 17].

This work is devoted to the study of the physic-chemical properties and patterns of recovery of Cu(II), Co(II), Ni(II), Zn(II), Cd(II) ions in the series of N-acyl-N'-mesylhydrazines in order to determine the possibility of their application as collectors in ion flotation and to select a reagent with optimal properties.

Experimental

N-acyl-N-'mesylhydrazines (MSH) of the general formula $RC(O)NHNHSO_2R^1$ (1), where R = C_4H_9 (**I**), C_6H_{13}(**II**), C_8H_{17}(**III**), $C_4H_9CH(C_2H_5)$(**IV**), $C_{10}H_{21}$(**V**), $C_{12}H_{25}$(**VI**), $C_{14}H_{29}$(**VII**); R^1=CH_3, was obtained by the interaction of equimolar amounts of hydrazides of the corresponding acids with methanesulfonylchloride at t = 0 ÷ 5 °C in a dry pyridine medium [18; 128]. The compounds obtained are white crystalline substances. The individuality and purity of the reagents were confirmed by IR and ^{1}H NMR spectroscopy and elemental analysis. IR spectra in the range 400–4000 cm^{-1} were recorded on a Fourier spectrometer Vertex 80V (Bruker) (suspension in vaseline oil); ^{1}H NMR spectra were recorded on a Bruker Avance Neo spectrometer (400 MHz; in $CDCl_3$, internal standard hexamethyldisilazane (0.055 ppm)). Elemental analysis was performed on a Vario EL cube CHNS analyzer (Elementar); thermal analysis of complex compounds — on a TGA/DSC1 thermogravimetric analyzer (Mettler Toledo).

The solubility of the reagents was determined by gravimetric (in EtOH) and spectrophotometric (in 0.1 mol/L KOH) methods. The spectrophotometric method was used to explore protolytic equilibria [19; 144–161]. UV-spectra were recorded on spectrophotometer SF-2000; pH values were measured on ionometer I-160M equipped glass and silver chloride electrodes. The surface tension at the interface between an AMH solution and the air was determined by the Dew Nui ring method [20] on a processor tensiometer K100 (KRÜSS). The measurements were performed at 25 °C in a 0.1 mol/L solution of KOH, as the reagents under study are insoluble in water, but moderately soluble in alkaline solutions. The choice of the concentration range was related to the solubility limitations of the reagents. The surface activity (G, mN·m^2/mol) was calculated as the value of the slope tangent of the straight line tangent to the isotherm of the surface tension of reagent solutions in the range of low concentrations according to the formula:

$$G = \lim\left(-\frac{d\sigma}{dc}\right) = \frac{\Delta\sigma}{C_{\Delta\sigma}}, \tag{1}$$

where C is the concentration of the reagent solution (mol/L); σ is the surface tension of the solution (mN/m); $C_{\Delta\sigma}$ is the concentration of the reagent, causing a decrease in surface tension by the value Δσ.

The values of critical micelle formation concentrations (CMC) were determined graphically at the inflection point of the curve mirroring the dependence of surface tension on solution concentrations (surface tension isotherm) when it reaches an area parallel to the abscissa axis [20; 152].

The complexation of metal ions with MSH was studied by the precipitation technique. To this end, a reagent solution was added to an aqueous solution of the metal salt, therewith adjusting the ratio of [M(II)]:[AMH] = 1:2. Ammonia solutions were used to regulate the pH values. 10–30 Minutes later, with the equilibrium time determined experimentally for each metal, the formed precipitate was filtered off. The ionic flotation experiments were carried out on a laboratory pneumatic flotation cell according to the procedure described in [21]. The residual concentration of metals in the filtrate was determined on an atomic-absorption spectrometer with flame atomization iCE 3500 (Thermo Scientific). The degree of precipitation (flotation) (S(E), %) was calculated using the formula:

$$S(E) = \frac{(C_0 - C_i)}{C_0} \cdot 100\,\%, \tag{2}$$

where C_0 is the initial metal concentration in the aqueous phase, mg/l; C_i is the metal concentration in the aqueous phase after precipitation (flotation), mg/l.

The conditional solubility product (SP) of the complexes was calculated by the method described in [15; 114–118], without taking into account the ionic states of the metals in solution, according to the formula:

$$SP_{\left[\mathrm{M(HL)_2}\right]} = \left(\frac{K_{a_1}\cdot(C_{\mathrm{H_2L}} - 2C_{\mathrm{M(II)}}\cdot\frac{S_i}{100}}{\left[\mathrm{H^+}\right]}\right)^2 \cdot \left[\mathrm{M(II)}\right]_{equil}, \tag{3}$$

where K_{a1} is the ionization constant of ligands (H_2L) at I stage; M(II) and C_{H_2L} are the initial concentrations of M(II) and ligand, respectively, mol/L; S_i is the degree of M(II) deposition, %; [H+] is the equilibrium concentration of H^+, mol/L; $[M^{2+}]_{equil}$ is the equilibrium concentration of M(II) in the solution after precipitation, determined experimentally, mol/L.

The following reagents were used in the work: $CuSO_4{\cdot}5H_2O$ (pure, 98.5 %), $NiSO_4{\cdot}7H_2O$ (chemically pure, 99.0 %), $ZnSO_4{\cdot}7H_2O$ (pure, 98.0 %), $3CdSO_4{\cdot}8H_2O$ (chemically pure, 99.5 %), $CoSO_4{\cdot}7H_2O$ (pure, 99.0 %); NH_3 (aqueous), (analytical grade, 25 %), HCl (chemically pure, 35 %), HNO_3 (chemically pure, 65 %), H_2SO_4 (chemically pure, 93.5–95.6 %).

Results and Discussion

The main requirements for IF collectors are as follows: sufficient solubility in aqueous solutions, availability of surface activity and foam-forming properties, ability to form insoluble compounds with metal ions, selectivity. The studied reagents were found as being moderately soluble in aqueous solutions of alkalis and EtOH; they exhibited themselves as weak dibasic acids (H_2L) [16]. The diagrams demonstrating distribution of the protolytic equilibrium forms of the reagents as a function of the pH were constructed (Fig. 1, an example for reagent III). They make it possible to predict the ranges of pH values for the formation of compounds of reagents with metal ions. The reagents' solubility was determined as being decreasing with lengthening the hydrocarbon radical chain; at this point, acid properties weaken (Table 1).

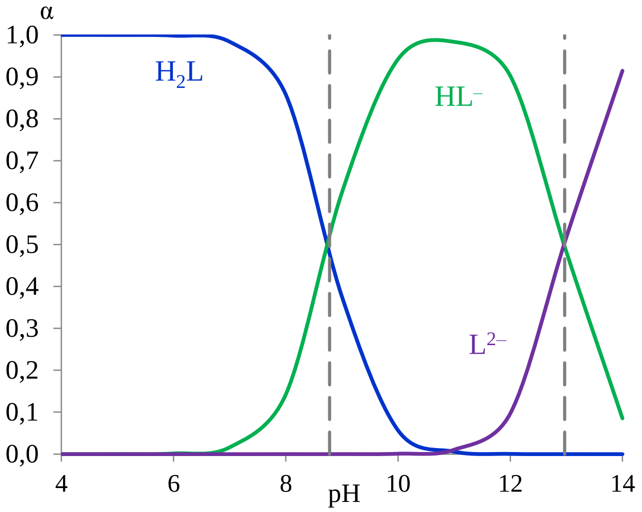


Figure 1. Distribution diagram of molecular ionic forms of reagents (H_2L) for N-nonanoyl-N'-mesylhydrazine (III) as a function of solution pH

Surface-active substances are commonly used as collectors for ionic flotation. The surface tension isotherms of MSH compounds are shown in Figure 2, the results of their processing are summarized in Table 2. As follows from the data obtained, all the reagents of the series with R = C_6H_{13} exhibit surfactant properties, while those with R = $C_{10}H_{21}$ and $C_{12}H_{25}$ are strong surfactants decreasing surface tension at solvent-air interface in 1.5–2 times as compared to pure solvent (0.1 mol/l KOH). A decrease in CMC in the homologous series with increasing the number of carbon atoms in a radical, indicates an enhancing micelle-forming ability. The increment of the adsorption potential (ΔW) as a contribution to the adsorption work of the methylene unit of the alkyl chain at the phase boundary was calculated. For this, a graph of dependence "ln C–N" (with C is a substance concentration causing a decrease in the surface tension by a value $\Delta\sigma$, and N is the number of methylene groups) was plotted. The graph is constructed as a line with the slope angle tangent (where W — increment of adsorption potential). For the MSH series, the equation of linear dependence looks as follows: $-\ln C = 0.75N - 5.87$ ($R^2 = 0.9633$); $W = 1.86$ kJ/mol.

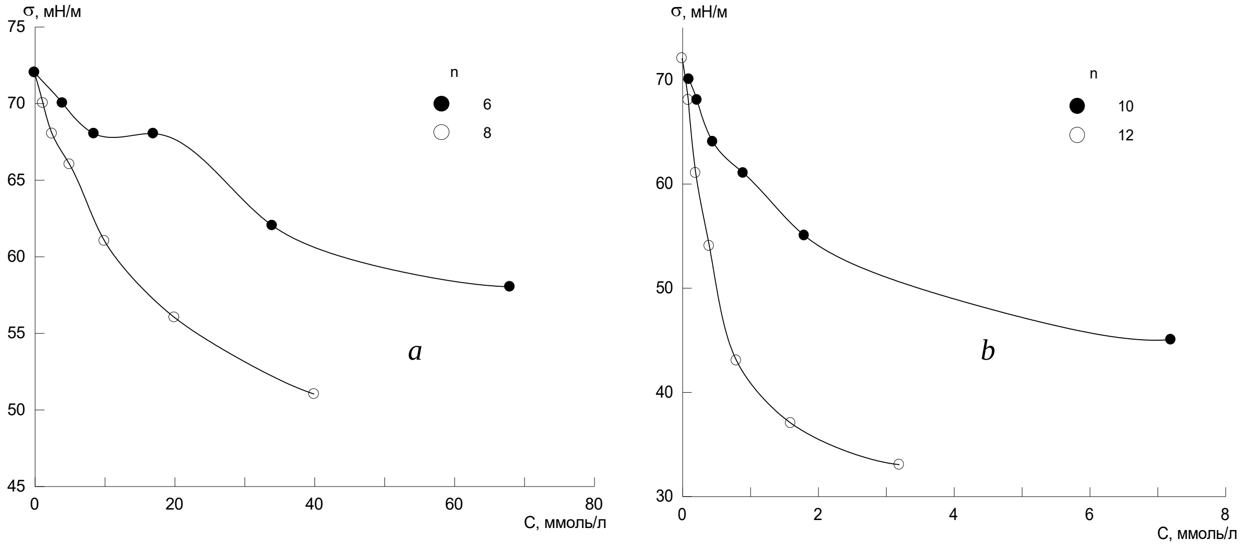
Table 1

Physico-chemical properties of the compounds $RC(O)NHNHSO_2(CH_3)$

R	$T_{m.}$, °C	Solubility, mol/l (g/l)		pK_{a_1}** pK_{a_2}	R_f*
		EtOH	0.1 mol/l KOH		
C_5H_{11} **(I)**	81–82	$7.8 \cdot 10^{-1}$ (162,2)	$9.2 \cdot 10^{-2}$ (19.14)	8.5±0.06 –	–
C_6H_{13} **(II)**	82–84	$7.3 \cdot 10^{-1}$ (161.0)	$8.0 \cdot 10^{-2}$ (17.7)	8.68±0.05 –	0.74
C_8H_{17} **(III)**	89–91	$3.2 \cdot 10^{-1}$ (79.8)	$4.5 \cdot 10^{-2}$ (11.3)	8.84±0.09 12.71±0.02	0.70
$C_4H_9CH(C_2H_5)$ **(IV)**	91–93	1.2 (282.6)	$1.18 \cdot 10^{-2}$ (2.8)	8.78±0.08	0.77
$C_{10}H_{21}$ **(V)**	95–96	$9.4 \cdot 10^{-2}$ (26.0)	$7.5 \cdot 10^{-3}$ (2.1)	9.19±0.04 –	0.72
$C_{12}H_{23}$**(VI)**	96–98	$1.0 \cdot 10^{-2}$ (3.1)	$3.6 \cdot 10^{-3}$ (1.1)	9.27±0.20 12.91±0.12	–
$C_{14}H_{29}$ **(VII)**	102–103	$2.3 \cdot 10^{-3}$ (0.74)	$2.5 \cdot 10^{-3}$ (0.84)	9.67±0.19 –	0.32

Note. *Thin-layer chromatography was carried out for compounds II–V in the solvent system benzene : ethyl acetate, 1:1; for VII — benzene : ether — 3:2.

** pKa_1 and pKa_2 are constants characterizing the process of ionization of reagents. The process of ionization of compounds at the first stage is attributed to detaching a proton of the $NHSO_2$ fragment due to a greater acceptor action of the sulfonyl group as compared with the carbonyl group [22].



R: (*a*) 6 — C_6H_{13}, 8 — C_8H_{17}; (*b*) 10 — $C_{10}H_{21}$, 12 — $C_{12}H_{25}$

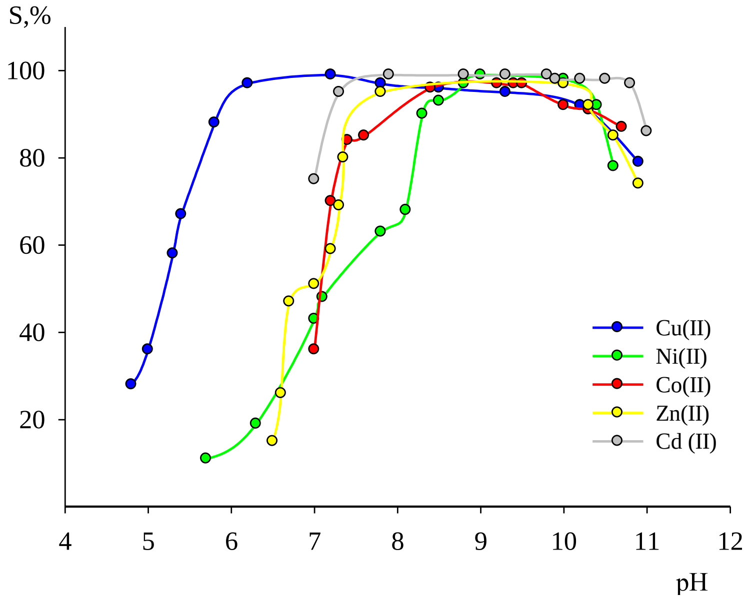
Figure 2. Surface tension isotherms of $RC(O)NHNHSO_2CH_3$ at t = 25 °C in 0.1 mol/L KOH

The dependence of the degree of recovery of non-ferrous metals(II) with N-pentadecanoyl-N'-mesylhydrazine on pH_{equil} is shown in Figure 3. Equilibrium in the formation process of copper, nickel, and cobalt complexes is attained for 10 min, with this time for zinc and cadmium equaling 30 min. The most complete precipitation of cations was ascertained in the following pH ranges: Cu(II) — 5.5–10.0; Zn — 7.5–10.5; Co — 8.0–9.5; Ni — 8.0–10.0; Cd — 7.8–11.0. At this point, maximal degree of recovery (%) and residual metal concentration in the solution after precipitation (mg/l) equaled, respectively: Cu(II) — 99.9 (0.06); Co(II) — 97.7 (1.31); Ni(II) — 99.5 (0.37); Zn(II) — 99.8 (0.14); Cd(II) — 99.4 (0.29).

Table 2

Minimum values of surface tension, CMC, surface activity of $RC(O)NHNHSO_2CH_3$

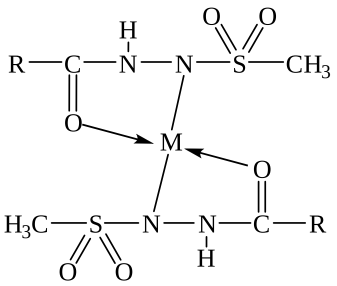
Reagent	R	CMC, mmol/l (g/l)	σ_{min}, mH/m ($C_{Reag.ent}$, mmol/l)	*G*, mH·m^2/mol
II	C_6H_{13}	2,80 (0,622)	58,0 (69,0)	0,49
III	C_8H_{17}	1,70 (0,425)	51,0 (40,0)	1,56
IV	$C_4H_9CH(C_2H_5)$	1,80 (0,255)	50,2 (40,0)	1,22
V	$C_{10}H_{21}$	0,80 (0,224)	46,0 (7,3)	18,6
VI	$C_{12}H_{25}$	0,10 (0,306)	33,0 (3,2)	59,2



$C_{M(II)}$, mg/l: Cu = 60.0; Ni = 74.6; Co = 56.9; Zn = 72.8; Cd = 47.7; [M(II)]:[Reagent] = 1:2

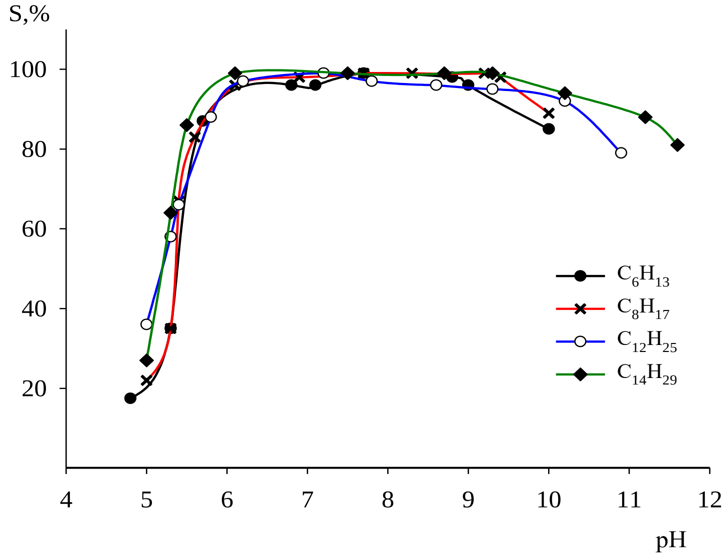
Figure 3. Dependence of the degree of recovery of non-ferrous metals (II) (*S*, %) with N-pentadecanoyl-N-' mesylhydrazine by precipitation method on pH_{equil}.

Using copper(II) ions as an example, it was found that the pH_{equal} interval, within which the degree of recovery is maximal, slightly extends with increasing radical length in the AMH series (Fig. 4). Metal compounds with N-tridecanoyl-N'-mesylhydrazine (selected as a sample) were isolated preparatively at a ratio of $[M(II)]:[H_2L] = 1:2$ The precipitates obtained are sparingly soluble in water and partially soluble in ethanol. The data of IR spectroscopy and elemental analysis (Table 3) provide evidence for the formation of complexes of the composition $[M(HL)_2]$, which can be represented by the structural formula:



(3)

The structure of the Cu(II) complex compound was previously confirmed by X-ray diffraction study of the grown single crystal [23].

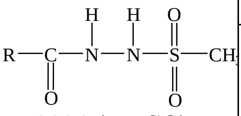


$C_{M(II)}$ = Cu = 60.0 mg/l; $C_{reagent} = 2 \cdot 10^{-3}$ mol/l

Figure 4. Dependence degree of copper (II) recovery (S, %) with N-acyl-N-'mesylhydrazines by precipitation method on pH_{equil}

Table 3

Characteristics of M(II) Complex with N-pentadecanoyl-N-mesylhydrazine

Complex*	Element composition					Stretching vibrations frequencies (ν, cm^{-1})	
	Theoretical./Prakt., %						
	C	H	N	S	M	Reagent	Complex
$[Cu(HL)_2]$ green M.м. = 729.5	52.64 51.74	9.05 8.38	7.68 7.28	8.77 8.21	8.70 7.78	 $R-\underset{\underset{O}{\Vert}}{C}-\overset{H}{N}-\overset{H}{N}-\underset{\underset{O}{\Vert}}{\overset{\overset{O}{\Vert}}{S}}-CH$ 3326 (NHCO), 3247 ($NHSO_2$); 1687, 1675 (C=O); 1322, 1157 (SO_2)	3319 (NHCO); 1543 (C=O); 1324, 1167 (SO_2); 721–741 (Cu–L)
$[Ni(HL)_2]\cdot 2H_2O$** dark blue M.м. = 760.7	50.48 50.25	9.20 8.75	7.36 7.21	8.41 7.98	7.72 6.98		3305 (NHCO); 1604 (C=O); 1281, 1131 (SO_2); 3419 (H_2O)
$[Co(HL)_2]\cdot 2H_2O$ dark pink M.м. = 760.9	50.47 51.89	9.20 9.73	7.36 7.39	8.41 8.05	7.74 7.05		3299 (NHCO); 1582 (C=O); 1281, 1123 (SO_2); 3395 (H_2O)
$[Cd(HL)_2]$ white M.м. = 778.4	49.33 49.37	8.48 9.34	7.19 6.92	8.22 7.88	14.44 13.65		3287 (NHCO); 1599 (C=O); 1304, 1125 (SO_2); 668 (Cd–L)
$[Zn(HL)_2]\cdot 2H_2O$ white M.м. = 767.4	50.03 48.97	9.12 8.45	7.30 6.78	8.34 7.79	8.52 7.89		3320(NHCO); 1608 (C=O); 1321, 1145 (SO_2); 3434 (H_2O)

Note. *HL- — ionized form of the reagent by I stage; ** Presence of crystallization water in Ni, Co, and Zn complexes was confirmed by thermal analysis.

The calculated SP values (Table 4) confirm the complex compounds of all the metals under study as being sparingly soluble substances; therefore, implementation of one variant of ionic flotation — “precipitate flotation” — appears to be possible [24]. The data of Table 4 evince copper and zinc complexes to have the lowest solubility, with cobalt having the highest.

I.A. Kakovsky showed that the PR values of compounds formed by the extracted ion in the homologous series of ionogenic collectors are related to the number of carbon atoms (N) in the radical: $-\lg PP = \alpha + \beta N$. The calculated coefficients of the equation for the series of xanthates, dithiophosphates, etc. correlate well with the experimental data and enable the optimal N values in the series of the compounds under study to be determined [1; 55–62]. The conditional SP values of the reagent complexes with Cu(II) ions were calculated (Table 5).

Table 4

Data for calculations and -lg *SP* values of N-pentadecanoyl-N'-mesylhydrazine (H_2L) complexes

Complex	$pH_{equil.}$	S_i	$[M(II)]_{equil}$, mol/l $\times 10^{-6}$	$[HL^-]$, mol/l	–lgSP
$[Cu(HL)_2]$	7.0	99.9	0.90	$1.03 \cdot 10^{-7}$	19.99
$[Ni(HL)_2]$	8.3	99.5	6.30	$2.27 \cdot 10^{-7}$	17.94
$[Co(HL)_2]$	8.5	97.7	22.2	$7.61 \cdot 10^{-6}$	14.89
$[Cd(HL)_2]$	7.8	99.4	2.58	$1.56 \cdot 10^{-5}$	15.20
$[Zn(HL)_2]$	8.5	99.8	2.14	$2.70 \cdot 10^{-7}$	18.81

Note. *PS* is the conditional PS of complexes; S_i is the degree of M(II) precipitation, %; $[M(II)]_{equil}$ is the equilibrium concentration of M(II) in the solution after precipitation; $[HL^-]$ is the equilibrium concentration of HL^- ions

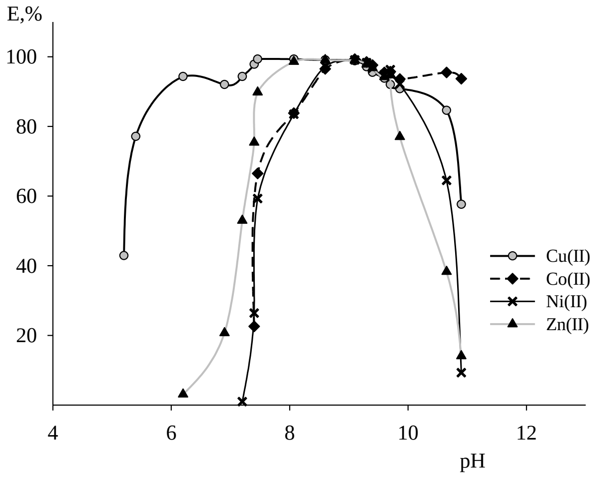
Table 5

Data for calculations, –lg*SP* values of $[Cu(HL)_2]$ complexes for $RC(O)NHNHSO_2(CH_3)$ ligands

Reagent	R	$pH_{equil.}$	S_i	$[M(II)]_{equil}$, mol/l $\times 10^{-6}$	$[HL^-]$ mol/l $\times 10^{-6}$	–lg*SP*
II	C_6H_{13}	7.7	98.2	17.6	8.29	14.92
III	C_8H_{17}	7.7	99.2	7.12	1.57	16.75
IV	$C_4H_9CH(C_2H_5)$	6.8	99.2	7.34	0.34	18.07
V	$C_{10}H_{21}$	7.0	99.4	5.87	0.33	18.20
VI	$C_{12}H_{23}$	6.9	99.7	2.91	0.19	18.99
VII	$C_{14}H_{29}$	7.0	99.9	0.90	0.10	19.99

When calculating, the composition of the complexes for all the reagents was assumed to be the same and analogous to that established for N-tridecanoyl-N'-mesylhydrazine $[Cu(HL)_2]$. It is determined that the dependence: $-\log SP = 11.8 + 0.61N$ ($R^2 = 0.9601$) is fulfilled in the series MSH with linear radicals. As follows from the equation obtained, in the series of ligands, minimal residual concentration of copper from solution during precipitation is possible when reagent VII is used. However, with lengthening the alkyl radical chain, the solubility of the reagents in aqueous and alcoholic solutions sharply decreases (Table 1), therewith hindering their practical use. The reagents III and IV appear to be the most promising ligands of the series.

The experiments on individual and collective flotation of M(II) ions with N-nonanoyl-N'-mesylhydrazine (III) were carried out (Fig. 5). Recovering metal ions up to 95-99 % in their conjoint presence (residual concentrations, mg/l: Cu — 0.21 (pH 7.0–7.5); Co — 1.4 (pH 8.5–8.8); Ni — 0.89 (pH 8.5–9.0); Zn — 1.1 (pH 8.5–8.9)), as well as separation of copper and associated metal ions at pH 5–6.5 was shown to be possible.



$C_{M(II)}$, mg/l: Cu = 29.9; Co = 24.7; Ni = 24.0; Zn(II) — 21.0; [Cu(II)]:[Reagent] = 1:1; τ = 5 min

Figure 5. Dependence of the recovery degree of metals by ionic flotation on $pH_{equil.}$

Conclusions

The exploratory research of physic-chemical properties of N-acyl-N'-mesylhydrazines gave rise to ligands characterized by optimal length of hydrocarbon radical chain and suitable for ionic flotation processes: N-nonanoyl- and 2-ethylhexanoyl-N'-mesylhydrazines. The reagents, being moderately soluble in aqueous alkali solutions, are medium-strong surfactants and form hardly soluble complexes with non-ferrous metals. This trait enables using them as collectors for “precipitate flotation”. The experiments aimed at exploring individual and collective flotation processes of M(II) ions with N-nonanoyl-N'-mesylhydrazine had evinced the possibility of recovering metal ions up to 95–99 %, separating copper and associated metal ions in the range of pH 5–6.5.

Acknowledgments

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N-ацил-N'-мезилгидразиндер қатарындағы түсті металдардың иондық флотациясына арналған реагенттерді таңдау

Бірқатар жаңа лигандтар, $RC(O)NHNHSO_2CH_3$ жалпы формуласының N-ацил-N'-мезилгидразиндері (МСГ) алынды және түсті металдардың (ТМ) иондық флотациясының (ИФ) реагенттері ретінде қарастырылды. Радикалды ұзындығы C_6H_{13} және одан жоғары МСГ ТМ иондарымен азеритін комплекстер түзетіні анықталды, сондықтан иондық флотацияның нұсқаларының бірі — преципиациялық флотацияны жүзеге асыруға болады. Ерітінділерден катиондардың ең толық тұнбаға түсуі болатын pH мәндерінің диапазондары нақтыланды. ТМ кешендерінің шөгінділері айқындалды; олардың құрамы ИҚ-спектроскопия және элементтік талдау арқылы расталды. Кешендердің ПР шартты мәндері $[M(HL)_2]$. Cu(II) иондарын мысал ретінде қолданып, МСГ қатарында тәуелділік орындалатыны көрсетілді: $–\log ПР = 11{,}8 + 0{,}61N$, оны қолдану лигандтардың жиынтық қасиеттерін олар түзетін қосылыстардың ерігіштігі бойынша болжауға мүмкіндік береді. $R > C_6H_{13}$ бар қосылыстарда беттік-белсенді қасиеттердің болуы анықталды, бұл қосымша көбік түзетін агенттерді қолданбай-ақ МСГ-ді ИФ пайдалануға мүмкіндік жасайды. МСГ физика-химиялық қасиеттерін зерттеу нәтижелері бойынша оптималды радикал ұзындығы бар ИФ үшін реагенттер таңдалды: BuCH(Et), C_8H_{17}. N-нонаноил-N'-мезилгидразинмен ТМ(II) иондарын жеке және ұжымдық флотациялау үшін эксперименттер жүргізілді. Металл иондарын 95–99 %-ға дейін бөліп алуға, pH 5–6,5 диапазонында мыс пен онымен бірге жүретін ТМ иондарын бөлуге болатыны көрсетілген.

Кілт сөздер: иондық флотация, шөгінді флотациясы, ацилсульфонилгидразиндер, түсті металдар, тұндыру, физика-химиялық қасиеттері, беттік белсенді заттар.

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Выбор реагентов для ионной флотации цветных металлов в ряду N-ацил-N'-мезилгидразинов

Получен и рассмотрен в качестве реагентов для ионной флотации (ИФ) цветных металлов (ЦМ) ряд новых лигандов — N-ацил-N'-мезилгидразинов (МСГ) общей формулы $RC(O)NHNHSO_2CH_3$. Установлено, что МСГ с длиной радикала C_6H_{13} и выше образуют труднорастворимые комплексы с ионами ЦМ, поэтому возможна реализация одного из вариантов ионной флотации — флотация осадков. Определены области значений pH, при которых происходит наиболее полное осаждение катионов из растворов. Выделены осадки комплексов ЦМ; их состав подтвержден данными ИК-спектроскопии и элементного анализа. Рассчитаны условные значения ПР комплексов $[M(HL)_2]$. На примере ионов Cu (II) показано, что в ряду МСГ выполняется зависимость: $–\lg ПР = 11{,}8 + 0{,}61N$, использование которой позволяет прогнозировать собирательные свойства лигандов по растворимости образуемых ими соединений. Установлено наличие поверхностно-активных свойств у соединений с $R > C_6H_{13}$, что позволяет использовать МСГ в ИФ без применения дополнительных пенообразователей. На основе результатов исследования физико-химических свойств МСГ выбраны реагенты для ИФ с оптимальной длиной радикала: BuCH(Et), C_8H_{17}. Проведены опыты индивидуальной и коллективной флотации ионов ЦМ(II) с N-нонаноил-N'-мезилгидразином. Показано, что возможно извлечение ионов металлов до 95–99 %, отделение меди и сопутствующих ионов ЦМ в области рН 5–6,5.

Ключевые слова: ионная флотация, флотация осадков, ацилсульфонилгидразины, цветные металлы, осаждение, физико-химические свойства, поверхностно-активные вещества.

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