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Kinetics of Liquid-Phase Prosess Extraction of Transition Metals from Ammonia Solutions With 2-Hydroxy-5-Alkyl Benzylethylenediamine

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ABSTRACT

The possibilities of extracting the separation of transition metals with similar physicochemical properties from ammoniasolutions by liquid extraction using 2-hydroxy-5-alkyl (C_8-C_9) benzylethylenediaminehavebeenstudied. It was found that the extraction of iron and zinc is strongly reduced in the presence of carbonate or sulfate ions in the system. It is shown that the turbulent boundary layer model describes the mass transfer between a fixed solvent droplet boundary and a turbulent fluid flow containing metal ions with a complex profile of the turbulent diffusion coefficient. According to this model, the substance concentration is constant in the flow, in the turbulent sublayer it gradually decreases when approaching the buffer sublayer, where the turbulence gradually fades turning into a laminar regime. The process of extraction of metals 2-hydroxy-5-alkyl (C_8–C_9) benzylethylenediamine in hexane from ammonia solutions is characterized by unsteady behavior, and therefore, mass transfer models significantly differ depending on the nature of the hydrodynamic flow around the particle.

Keywords: Liquid-phase extraction, Turbulent diffusion, Laminar flow, Re-extraction, Kinetics, Ionic composition, Ammonium salts, Metal separation.

INTRODUCTION

The extraction method of inorganic transition metal compounds from ammonia solutions and their separation is a relevant and important issue of hydrometallurgy[1–8]. The properties of the initial solution and the metals being extracted limit the number of extractants that can used. It should be taken into account that primary amines usually extract anionic sulfate complexes best, while tertiary amines and quaternary ammonium compounds extract anionic chloro complexes best. Taking into account such properties of extractants allows saving a lot of time and money when developing a technological process. After selecting the most suitable extractant, the technological parameters of the extraction process are determined: specificity of the selected extractant with respect to the metal being extracted; characteristics of saturation of the organic solution and metal reextraction, dependence of the extraction degree on pH, requirements for the type of diluent and modifier; kinetics of extraction, washing and reextraction, concentration of the extractant and the required phase ratio, solubility of the extractant in an aqueous solution and physical characteristics of the system. But for the successful solution of this issue, the choice and creation of available, highly effective, selective and cheap extractants is mainly required.

The process of ammonia leaching has a number of advantages compared to acid processing methods[7]. These solutions have high selectivity in relation to valuable components, the ability to form well-soluble compounds of non-ferrous metals, low aggressiveness, simple regeneration, etc. When processing the raw material with ammonia solutions, cobalt, nickel, copper, zinc and other non-ferrous metals form well-soluble complex compounds, which allows them to be transferred into solution, separated from iron and rock-forming components[8–12].

Recently, scientists of some countries show great interest in deep-water manganese nodules, which in the future can become a raw material source of copper, nickel and cobalt.

The purpose of the work is the study and development of extraction and separation of zinc(II), cobalt(II), copper(II) and iron(III) with a hexane solution of 2-oxy-5-alkyl (C_8–C_9) benzylethylenediamine from ammonia solutions and the influence of individual kinetic factors for extraction with their joint presence.

It should be noted that higher temperatures usually increase the extraction rate, but can also affect the stability of metal-ammonia complexes.

When researching to develop an extraction process for a particular metal and its isolation from a particular aqueous solution, certain limitations inevitably arise. Parameters such as temperature and solution flow rate are sometimes essentially given, and the extraction process being developed must certainly meet them. To improve the efficiency of extraction methods, new extractants are being developed, fundamental research is being conducted to determine the distribution patterns and quantitative characteristics of extraction processes, which is necessary for creating modern process flow charts. Along with the synthesis of new selective extractants, much attention is paid to the study of extractant mixtures.

Consequently, the development of fundamental and applied work on the study of element distribution patterns in systems with various extractants, as well as the possibilities of using them to extract, separate and purify substances is very important. These systems can also be effective for obtaining valuable products from man-made and secondary raw materials[13-14].

After selecting the most suitable extractant, the technological parameters of the extraction process are determined: specificity of the selected extractant with respect to the metal being extracted; characteristics of organic solution saturation and metal re-extraction, dependence of the extraction degree on pH, requirements for the type of diluent and modifier; kinetics of extraction, washing and re-extraction, concentration of the extractant and the required phase ratio, solubility of the extractant in an aqueous solution and physical characteristics of the system.

Thus, kinetics plays an important role in comparing and evaluating the performance of extractors.

The economics of separating two metals with similar properties are difficult to evaluate due to the difficulties in choosing the type of multi-stage extractor and the importance of choosing the right extractant. In addition to the price of extractants, factors such as solubility, selectivity, capacity and kinetics should be taken into account for a complete economic assessment. The kinetics of liquid-phase extraction of transition metals from ammonia solutions involves understanding how transition metals (such as nickel, cobalt, and copper) are transferred from the aqueous phase to the organic phase in the presence of ammonia. This process is important in various fields, including hydrometallurgy and chemical engineering[15].

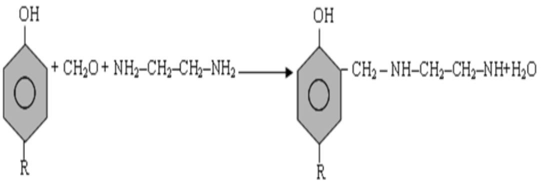
In work[16] discusses the extraction of nickel and cobalt, including using ammonia solutions, and the kinetics of these processes, while[17] studies in detail the kinetics of copper extraction from ammonia solutions using using sterically hindered β-diketone. It has been demonstrated in works[18-20] that the extraction of nickel from ammonium sulfate solutions using Versatic 10 is controlled by both reaction kinetics and mass transfer processes, and when using Cyanex 272 as the cobalt extractant from ammonia solutions, involves a rate-limiting step associated with the formation of a cobalt-extractant complex. The study showed that the kinetics can be improved by increasing the extractant concentration and operating at higher temperatures. The authors[20] stated that the kinetics of copper extraction using LIX 84-I involves a rapid initial extraction followed by a slower approach to equilibrium. This behavior was explained by the formation of intermediate copper-ammonia-extractant complexes. In summary, many studies have now found that 1. Increasing temperature generally increases the extraction rate of transition metals, indicating that the processes are endothermic and controlled by chemical reaction kinetics. 2. ammonia concentration and solution pH are critical parameters affecting the extraction efficiency. The studies by Biswas and Eksteen[14] and Salgueiro and Correia[18] highlight the need to optimize these parameters to achieve efficient recovery. 3. both mass transfer and interfacial chemical reactions play an important role in determining the overall kinetics of the extraction process. The rate determining step may vary depending on the specific system and conditions used.

Identifying and studying the above liquid phase extraction process of transition metals from ammonia solutions with 2-hydroxy-5-alkyl benzyl ethylenediamine are the objectives of this study.

The copper concentrate used in the work was obtained from Filizthay polymetallic ore by flotation.

MATERIALS AND METHODS

Extraction was carried out in separatory funnels with a capacity of 50 mL at room temperature. The work mainly used a 0.2 M hexane solution of 2-oxy-5-alkyl (C_8-C_9) benzylethylenediamine, which was synthesized by us by the Mannich reaction, respectively, with ethylenediamine and with the industrial fraction of alkylphenol in the presence of formaldehyde:



The reaction takes place at a temperature of 75–80⁰C without a catalyst. 2-oxy-5-alkyl (C_8–C_9) benzylethylenediamine is a substance of amber color, odorless and not carcinogenic. The solubility in water is quite low – 0.02 g/L. It is not toxic, it dissolves well in organic solvents (benzene, hexane, heptane, carbon tetrachloride) and kerosene. The obtained product was first subjected to purification and then used as a solution in organic solvents.

Solutions of the salts of the investigated metals with a concentration of 10-3 mol/L were prepared from their salts $CuSO_4$•$5H_2O$, $ZnSO_4$, $CoSO_4$, $Fe_2(SO_4)_3$ of the of chemically pure grade. The ratio of the organic and aqueous phases was taken V_o:$V_{aq.}$=1:2.

The equilibrium concentration of metals in phases was determined by colorimetric methods: copper-sodium diethyldithiocarbamate;[2]; cobalt-nitrosa-R-salt[22]; iron-by titrometric method using Trilon-B[15], and zinc by polarographic method[23]. The concentration of ammonia in the initial solution was taken into account when calculating its consumption for the formation of ammonia complexes of the corresponding ions. The pH of the medium was measured on a device of the ionomer brand "EV-74".

Figure 1 shows experimental data on the extraction of metals depending on the time of phase contact.

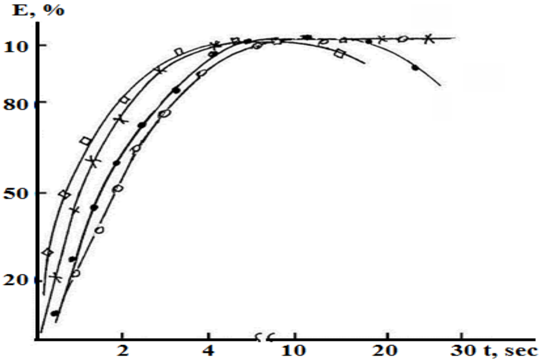


Fig. 1. Dependence of the degree of extraction of metals during extraction with a solution of 2-hydroxy-5-alkyl (C_8–C_9) benzylethylenediamine on the contact time of the phases: –Cu, x–Co, •–Fe, o–Zn

As can be seen from Fig. 1, equilibrium in the system is established when the phases are mixed for 3–5 minute. Further mixing of the system does not affect the completeness of the extraction. The phases separate quickly and clearly.

Table 1: Dependence of extraction of Co, Co, Fe and Zn with 0.2 M kerosene solution of reagent on the concentration of ammonia.[Me] = 0.5 g/L; τ = 5 minute

Ammonia concentration in the initial solution, g/L	Copper		Cobalt		Iron		Zinc	
	$[Cu]_E$, g/L	E, %	$[Co]_E$, g/L	E, %	$[Fe]_E$, g/L	E, %	$[Zn]_E$, g/L	E, %
0.81	not found	100	0.019	96.2	0.005	99	notfound	100
4.20	not found	100	0.008	96.8	0.003	99.4	notfound	100
6.40	not found	100	0.004	99.2	0.003	99.4	0.01	97.5
10.10	0.011	97.8	0.003	99.4	0.0025	99.5	0.021	93.6
15.00	0.015	97	0.001	96	0.0023	99.54	0.029	91.7
20.0	0.022	93.8	0.0012	97.7	0.002	99.6	0.03	90.9
25.3	0.028	92	0.0018	96.7	0.002	99.6	0.03	90.9

During extraction, it turned out that 0.1–0.5M solutions of 2-hydroxy-5-alkyl (C_8–C_9) benzylethylenediamine in organic solvents do not extract the studied metals from solutions of their salts. However, when aqueous ammonia is added to the system, with the transition of these elements into ammonia complexes, their intensive extraction into the organic phase is observed. The data obtained during the extraction of copper, cobalt, iron and zinc from aqueous solutions depending on the concentration of free ammonia are shown in Table 1.

Kinetics of liquid-phase extraction

The kinetics of liquid-phase extraction of transition metals from ammonia solutions involves understanding how transition metals (such as nickel, cobalt, and copper) are transferred from the aqueous phase to the organic phase in the presence of ammonia. This process is important in a variety of fields, including hydrometallurgy and chemical engineering.

The most common model of the kinetics of extraction of metal ions is the film model, according to which, in each phase, stationary or moving laminar boundary layers adjoin directly to the boundary of solvent droplets, in which the transfer is carried out by molecular diffusion[24,25]. Thus, for an immobile single solvent drop, the scheme corresponds when the entire boundary layer is an area where there is no mixing by turbulent pulsations and the change in the concentration of the dissolved substance is characterized by a linear dependence. With intensive mixing in the apparatus, due to the occurrence of developed isotropic turbulence, the kinetic curves may differ from a linear dependence due to the complex distribution profile of the turbulent diffusion coefficient and flow velocity in the boundary layer[26–28]. The turbulent boundary layer model describes the mass transfer between a fixed solvent droplet boundary and a turbulent fluid flow containing metal ions with a complex turbulent diffusion coefficient profile. According to this model, the substance concentration is constant in the flow, in the turbulent sublayer it gradually decreases when approaching the buffer sublayer, where the turbulence gradually fades, turning into a laminar regime. The process of extraction of metals 2-hydroxy-5-alkyl (C_8–C_9) benzylethylenediamine in hexane from ammonia solutions is characterized by unsteady behavior, and therefore, mass transfer models differ significantly depending on the nature of the hydrodynamic flow around the particle. It should be noted that the main condition for the dissolution of metal ions in a solvent is the condition that diffusion and convective fluxes are equal on the surface of the boundary layer.

$$-D_E \frac{\partial C}{\partial r}\Big|_{r=\delta} = \beta(C - C^*) \qquad (1)$$

Where *r*–is the coordinate along the thickness of the interfacial layer, *C*–the concentration of the absorbed substance,δ– the thickness of the interfacial layer, which is proportional to $\delta \sim (\alpha D/V_0)^{1/2}$, V_0– is the flow velocity on the particle surface, D_E– is the mass transfer coefficient, D_E– is the effective diffusion coefficient. According to the statistical theory ofturbulent diffusion, the mean square displacement of the particles of the dissolved medium from the initial position in the radial direction is determined by the dependence.

$$r^2 = 2D_T \Delta t \qquad (2)$$

Using condition (1), introducing a change of variables from expression dr = $(2D_E)^{1/2}$ $t^{-1/2}$ *dt*, we write expression (1) as:

$$\frac{\partial C}{\partial t} = -K(C - C^*) \qquad (3)$$

$$C(t)\big|_{t=0} = C_0$$

Here $K = \left(\frac{2}{D_E t}\right)^{1.2} \beta$ -is the mass transfer coefficient forthe dissolution process, C_0– is the initial concentration of substances in hexane, *C(t)* – is the equilibrium concentration of substances in the organic phase. Expression (3) is the equation of the kinetics of the mass transfer diffusion process of extraction. For a non-stationary extraction process, if the value of the coefficient K depends on time, then the solution of equation (3) will be represented as:

$$C(t) = C^* - (C^* - C_0)\exp(-\int_0^t K(t)dt) \qquad (4)$$

For a pure solvent $C_0 = 0$, this equation simplifies to the form

$$C(t) = C^*\left(1 - \exp\left(-\int_0^t K(t)dt\right)\right) \qquad (5)$$

Using experimental data you can put :$K(t) = K_0 t^{-1/2}$, $K_0 = \left(2/D_E\right)^{1/2} \beta$ and $C^*(T) = 57.33 + 0.7T$°C. For extraction with a single drop, using these expressions, from equation (5) we finally obtain the equation for the extraction of metals from a solution in the form:

$$C(t) = C^* (1-\exp(-\alpha t^{1/2})) \qquad (6)$$

Where $\alpha = 2K_0$. For the "collective" dissolution of many particles, one should use the effective time-average value of the mass transfer coefficient.

$$\beta_E = \frac{\int_0^{T_P} \beta dt}{T_P} = \beta \frac{t}{T_P} \qquad (7)$$

Where T_p– is the time of complete dissolution of particles. Given expression[7], solution (7) will be presented as:

$$C(t) = C^*(1-\exp(-\alpha t^{3/2})) \qquad (8)$$

Where $\alpha = 2K_0/3T_P$. The results of experimental studies and calculated values according to formula (8) for the extraction of various metals (Cu, Co, Fe, Zn) with a solution of 2-hydroxy-5-alkyl (C_8–C_9) benzylethylenediamine in hexane from ammonia solutions depending on the phase shaking time are shown in Fig. 2. From the experimental data it is clear (Tables 2, 3) that the coefficients α for each extracted metal are as follows: α = 0.65 (Cu), α = 0.52 (Co), α = 0.38 (Fe), α = 0.25 (Zn). This graph determines the degree of extraction of each metal from the solution.

Table 2: Dependence of extraction of Co, Co, Fe and Zn with 0.2 M kerosene solution of reagent onthe concentration of of ammonium salts $[NH_3]$ = 8.60 g/L, C_{Meref}. = 0.35 g/L; τ = 5 minute

$(NH_4)_2CO_3$ Concentration of in the initial solution, g/L	Copper		Cobalt		Iron		Zinc	
	$[Cu]_E$, g/L	EE, %	$[Co]_E$, g/L	EE, %	$[Fe]_E$, g/L	EE, %	$[Zn]_E$, g/L	EE, %
9.85	0	100	0.02	94.4	0.11	70	0.008	97.7
24.7	–	100	0.019	94.5	0.132	62.15	0.005	98.6
30.65	–	100	0.0017	95	0.208	40.4	0.001	99.7
49.6	–	100	0.011	96.9	0.28	20	not found not found	100
60.15	–	100	0.01	97.3	0.314	10.2	not found not found	100
75	–	100	0.007	97.92	0.35	-	not found	100
100	–	100	0.005	98.4	0.35	-		100
120.1	0.006	98.3	0.004	98.9	0.35	-		100

$(NH_4)_2SO_4$ Concentration of in the initial solution g/L	Copper		Cobalt		Iron		Zinc	
	$[Cu]_E$, g/L	E, %	$[Co]_E$, g/L	EE, %	$[Fe]_E$, g/L	EE,%	$[Zn]_E$, g/L	EE, %
12.8	0	100	0.015	95.8	0.0175	5	0.012	96.5
30.2	0.07	99.8	0.013	96.2	0.01	3.1	0.0074	97.88
50.6	0.0017	99.5	0.012	96.7	0.35	notfound	notfound	100
60.15	0.0049	98.6	0.009	97.4	0.35	–	–	100
70	0.0056	98.4	0.0073	97.9	0.35	–	–	100
90.5	0.0073	97.9	0.0063	98.2	0.35	–	–	100
100	0.0094	97.3	0.0049	98.6	0.35	–	–	100
120.15	0.0011	97	0.0052	98.5	0.35	–	–	100

From ammonia solutions containing both $NH_4)_2SO_4$, $(NH_4)_2CO_3$ and Na_2CO_3 or $NaHCO_3$, iron is not extracted with benzylethylenediamine even at low concentrations of 2-hydroxy-5-alkyl (C_8–C_9).

During the extraction of copper, cobalt, iron, and zinc with the indicated extractant, the stability of the extracted metal compounds in the organic phase decreases in the series Fe, Co, Zn, Cu.

The re-extraction of these metals has also been studied. It has been established that copper is easily and quantitatively reextracted from the organic phase by 0.1-0.2 N. mineral acid solution (H_2SO_4, HCl) at V_o:V_β = 1:2 and stirring for 10 minute. (Table 3).

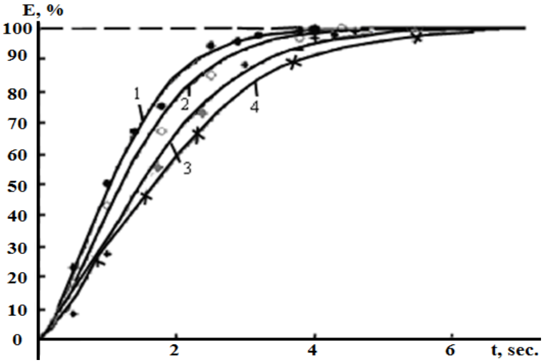


Fig. 2. Kinetic curves for the extraction of metals with a hex solution of 2-hydroxy-5-alkyl (C_8–C_9) benzylethylenediamine depending on the contact time of the phases from ammonia solutions; 1–Cu; 2–Co; 3–Fe; 4–Zn

Table 3: Re-extraction of Cu, Co, Fe and Zn from the organic phase with mineral acids $Cu^{2+}] = [Co^{2+}] = 5.0$ g/L $[Fe^{3+}] = 5.05$ g/L $[Zn^{2+}] = 5.03$ g/L; V_o:$V_{aq.}$ = 1:2; τ = 10 minute

	Copper			Cobalt	
H_2SO_4 N	Copper content in organic phase, g/L	Reextraction,%	H_2SO_4 N	Cobaltcontent in organic phase, g/L	Re-extraction, %
0.1	4.0	80	0.1	3.5	70
0.2	4.8	96	0.2	4	80
0.3	5.0	100	0.5	4.65	93
0.4	5.0	100	1	5	100
0.5	5.0	100	1.5	5	100
1.0	5.0	100	2	5	100
1.2	5.0	100	2.2	5	100

	Iron			Zinc	
H_2SO_4 N	Iron content in the organic phase, g/L	Re-extraction. %	H_2SO_4 N	Zinc content in the organic phase, g/L	Re-extraction, %
0.1	1.8	35.4	0.1	1.11	22.6
0.2	2.55	50.4	0.2	1.81	35.9
0.5	3.36	66.5	0.5	3.3	65.6
1.0	3.94	78.2	1	3.9	77.5
1.5	4.58	90.7	1.5	4.55	90.45
2.0	5.05	100	2	4.98	99.01
2.2	5.05	100	2.2	5.03	100
2.25	5.05	100	2.25	5.03	100

The re-extraction of zinc, cobalt and iron under identical conditions occurs only when the extract is treated with 0.5-1.0 N mineral acid solution (H_2SO_4, HCl).

Such a difference in the extractability of copper, cobalt, zinc and iron (III) with a solution of 2-hydroxy-5-alkyl (C_8-C_9) benzylethylenediamine during extraction, as well as the behavior of the extracted compounds during re-extraction with mineral acids, make it possible to extract and selectively separate these metals from ammonia solutions obtained by ammonia leaching of intermediate products and various substandard concentrates.

It has been shown that the new 2-hydroxy-5-alkyl (C_8–C_9) benzylethylenediamine is an effective and selective extractant for the extraction and separation of divalent transition elements cobalt, copper, zinc, and iron from ammonia solutions.

RESULTS AND DISCUSSION

As can be seen, all the studied elements within the range of ammonia concentration in the initial solution of 0.81–25.3 g/L with a single extraction almost completely pass into the organic phase. A slight decrease in copper extraction is observed only at low ammonia concentrations.

When these metals are extracted with a 0.5 M kerosene solution of 2-hydroxy-5-alkyl (C_8–C_9) benzylethylenediamine, the phase is saturated (g/L): copper-36, cobalt-23, iron-21, zinc-20. Such limiting values of the capacity of the extractant in relation to the listed metals do not change from their initial concentration in an aqueous solution.

Some differences in the extractability of these elements appear in the presence of ammonium salts in the initial solution. Under the same conditions ([NH_3] = cont.), the presence of large amounts of carbonate ions in the system has almost no effect on the recoverability of copper, cobalt and zinc, but significantly reduces the extraction of iron (Table 2).

Copper is also quantitatively extracted from an aqueous solution containing up to 90-100 g/L of ammonium sulfate. As can be seen from the data in (Table 2), cobalt and zinc at low concentrations of sulfate ions are not completely extracted, but with an increase in their content in solution, the transition of metals into the organic phase increases. Unlike copper, cobalt, and zinc, the extraction of iron is strongly suppressed and, at a concentration of $(NH_4)_2SO_4$ = 50-60 g/L, it completely remains in the aqueous solution. All necessary calculations were performed using the software package "Optim Me"[29,30].

CONCLUSION

Thus, as a result of the research, an extraction method was developed for the selective extraction of zinc, copper, cobalt and iron from ammonia solutions, the kinetics of the extraction process was studied, and a kinetic model was proposed.

Based on a film model, the kinetics of the process of liquid-phase extraction of metals with a solution of 2-hydroxy-5-alkyl (C_8–C_9) benzylethylenediamine was studied and a kinetic model was proposed. A difference was found in the extractability of zinc, copper, cobalt, and iron depending on the ionic composition of the aqueous solution. It was found that in the presence of carbonate or sulfate ions in the system, the extraction of iron and zinc is strongly suppressed. Some aspects of the kinetics of the extraction process and the re-extraction of metals have been studied. Copper from the organic phase is easily and quantitatively re-extracted 0.1–0.2 n, and zinc, cobalt and iron 2.0 n mineral (H_2SO_4, HCl) acid solution.

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Conflict of interest

The author declare that we have no conflict of interest.

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