ISSN 1067-8212, Russian Journal of Non-Ferrous Metals, 2014, Vol. 55, No. 3, pp. 219–224. © Allerton Press, Inc., 2014.
Original Russian Text © Sh.K. Amirkhanova, R.M. Shlyapov, A.S. Uali, 2014, published in Izvestiya VUZ. Tsvetnaya Metallurgiya, 2014, No. 2, pp. 14–19.

MINERAL PROCESSING OF NONFERROUS METALS

Thermodynamic Aspects of the Selection of Sulfur-Containing Collectors during Flotation of Sulfide Ores

Sh. K. Amirkhanova*, R. M. Shlyapov, and A. S. Uali**

Karaganda State University, ul. Universitetskaya 28, Karaganda, 100028 Kazakhstan
**e-mail: amerkhanova_sh@mail.ru*
***e-mail: ualieva.84@mail.ru*

Abstract—Investigations into the complexing ability of sulfur-containing collectors relative to metal ions (Cu^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+}) at 298 K and an ion force of 0.075–0.75 mol/L ($NaNO_3$) are carried out. It is established that potassium dibutyl dithiophosphate possesses the largest affinity to metal ions among phosphorus-containing collectors, while the maximal complexing ability is characteristic of the Co^{2+} ion. Series of thermal stability are found; the variations in enthalpy, entropy, and the Gibbs energy, as well as temperature-dependent and temperature-independent contributions of complexes of metal ions with collector anions into ΔG^0, are calculated.

Keywords: sulfur-containing collectors, xanthate, flotation reagent, stability constant, thermodynamic parameters

DOI: 10.3103/S106782121403002X

INTRODUCTION

In recent time, the attention of leading scientists in the branch of coordination chemistry and technologists of the concentration branch of industry is devoted to questions that touch the evaluation of the influence of physicochemical properties of collectors on the complexing ability [1]. However, there are almost no publications devoted to analyzing thermodynamic functions of binding processes of metal ions by various flotation reagents and their interrelation with a practical yield of high-condition concentrates. Therefore, this study is aimed at the flotation activity of xanthates. As objects of investigations, we selected the iron-containing ore, potassium butyl xanthate, and potassium dibutyl thiophosphate.

EXPERIMENTAL

Starting solutions of metal salts, alkali metal and ammonia dibutyl dithiophosphates, and potassium butyl xanthate, which contain 10^{-3} mol/L of $CuSO_4$, $FeSO_4$, $NiCl_2$, and $Co(NO_3)_2$, were prepared by dissolving an exact charge in bidistilled water; working solutions were diluted to concentrations 10^{-4} mol/L.

The pH-metric measurements were performed using a 410-brand pH meter according to procedure [2]. IR spectra of prepared complex compounds were recorded using a Thermo Nicolet Avatar 360 FTIR spectrometer [3]. Binding constants of metals were performed according to procedure [4]. Thermodynamic parameters were determined based on the temperature dependence of stability constants of complexes according to the Ulikh, Gibbs, and Gibbs–Helmholtz equations [5]. The flotation ability of collectors was analyzed according to [6].

RESULTS AND DISCUSSION

To confirm the structures of forming complexes of copper with potassium dibutyl dithiophosphate and potassium butyl xanthate, we recorded their IR spectra (Fig. 1). Their analysis showed that the formation of metal–sulfur bonds of various strengths is characteristic of transition metal ions. The strength is conditioned by the influence of pH of the medium, the structure of the ligand molecule, and hydration processes in the solution. The absence of splitting the band at $\nu = 3400$ cm^{-1} for the coordination compound of Cu^{2+} ions with potassium butyl xanthate reflects the decomposition process of the metal–ligand complex with the composition M : L = 1 : 2 into dixanthogenide and a complex with M : L = 1 : 1. This is indicated by an increase of transmission of bands at 600–500 cm^{-1} and 1700–1600 cm^{-1}, as well as by the disappearance of the band at 2100 cm^{-1} [7].

For other metal ions, no substantial variations in the location of bands and their intensity is observed, which is caused by the formation of similar structures in which the metal ion is bound with the ligand by means of sulfur atoms, donor–acceptor, and ion

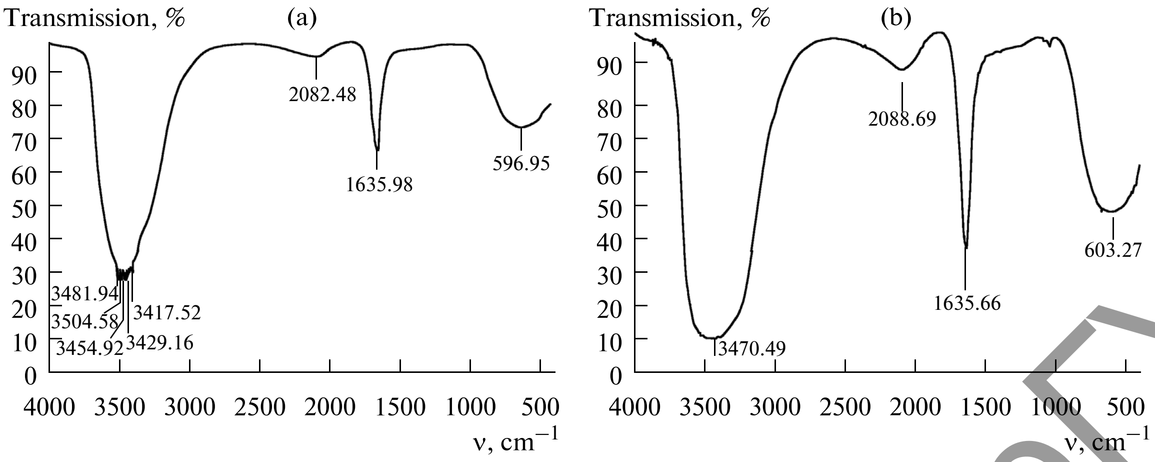

Fig. 1. IR spectra of complexes of Cu^{2+} ions with (a) potassium dibutyl dithiophosphate and (b) potassium butyl xanthate (M : L = 1 : 1).

bonds. The shift of the bands for iron ions is caused by the formation of bonds either with hydroxo groups or with water molecules. The variation of band position for silver ions is caused by exchange processes of water molecules between the first and the second ligand shells. The exchange rate depends on the magnitude of the positive charge of a metal ion in this case; this rate is higher in the case of potassium dibutyl dithiophosphate and, consequently, the exchange rate is lower [8].

Using the results of pH-metric titration at 298 K and different values of the ion force (Table 1), we calculated stability constants of complexes of sulfur-containing collectors with copper ions and the first transition series extrapolated to the zero ion force (Table 2).

Table 1. Results of pH-metric titration of the 10^{-4} M solution of copper sulfate by the 10^{-4} M solution of potassium dibutyl dithiophosphate

V_t, mL	pH				
	0.075 *I*	0.1 *I*	0.25 *I*	0.5 *I*	0.75 *I*
0	0.69	8.11	8.47	7.91	7.28
1	8.57	7.98	8.36	7.75	7.12
2	8.60	7.90	8.17	7.60	7.52
3	8.56	7.79	8.04	7.54	7.47
4	8.52	7.75	7.93	7.45	7.39
5	8.48	7.66	7.81	7.39	7.33
6	8.41	7.75	7.74	7.33	7.26
7	8.36	6.78	7.68	7.29	7.20
8	8.32	6.76	7.12	7.2	7.15
9	7.55	6.81	7.08	6.68	7.10
10	7.49	6.80	7.04	6.65	7.06

It follows from these data that potassium dibutyl dithiophosphate possesses the largest affinity to metal ions for phosphorus-containing collectors. This is caused by a high dissociation constant of dibutyl dithiophosphoric acid and the maximal formation enthalpy of the potassium ion. On the other hand, the substitution of dibutyl dithiophosphate anion by the xanthate anion, which contains the lesser electronegative carbon atom, leads first to an increase in the bond energy with the sulfur atom and second to the appearance of a large negative charge at it. The consequence of this fact is an increased ability of xanthate complexes to dissociation, which is indicated by relatively low stability constants [6]. At the same time, Co^{2+} possesses the maximal complexing ability among metal ions, which agrees with the electron structure of the atom; the exclusion is constituted only by the data referring to ammonium dibutyl dithiophosphate. For other metal ions (Cu^{2+}, Ni^{2+}, Fe^{2+}), the complexing ability varies depending on the ligand type. Square-and-plane complexes stabilized by the solvent are implemented for the Cu^{2+} and Ni^{2+} ions in reactions with dibutyl dithiophosphate anion [8].

Based on the data presented in Table 1, we found series of thermodynamic stability of complexes of metal ions with collector anions. For potassium and sodium dibutyl dithiophosphates, they are as follows: Co > Ni > Fe > Cu. The series reversal is observed for potassium butyl xanthate in the case of the copper subgroup, which is associated with the reduction of Cu^{2+} ions to univalent state because of the manifestation of the catalytic activity relative to the sulfur-containing collector, which coincides with the variation in the ionization potential of cations.

Table 2. Stability constants for complexes of *d* metal ions with sulfur-containing collectors in ratio 1 : 2 for transition metal ions

L	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
$C_4H_9OCS_2K$	9.44	18.01	8.68	28.47
$(C_4H_9O)_2PS_2K$	11.58	12.73	11.93	11.34
$(C_4H_9O)_2PS_2Na$	8.47	10.53	10.53	4.48
$(i\text{-}C_3H_7O)_2PS_2Na$	6.30	6.77	5.33	6.87
$(C_4H_9O)_2PS_2NH_4$	4.14	4.50	4.60	3.99

Table 3. Thermodynamic parameters of interaction of *d* metals with sulfur-containing and phosphorus-containing collectors

L	$-\Delta_r H^0_{298}$, kJ/mol				$-\Delta_r S^0_{298}$, kJ/(mol K)			
	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
$C_4H_9OCS_2K$	56.80	−395.77	−354.23	259.02	9.83	−983.19	−1354.87	324.12
$(C_4H_9O)_2PS_2K$	−16.37	32.66	−21.31	−59.62	276.76	261.85	300.84	−417.26
$(C_4H_9O)_2PS_2Na$	−58.73	−51.63	70.57	−31.98	−359.31	−374.80	35.17	−193.15
$(i\text{-}C_3H_7O)_2PS_2Na$	1.87	549.05	120.30	7.58	−110.34	1712.86	290.23	−73.55
$(C_4H_9O)_2PS_2NH_4$	−84.18	37.25	94.35	16.33	−359.90	38.86	544.95	−21.53

The abovementioned series are in a simbate dependence with the formation entropy of hydrated metal ions in solutions. The series Ni > Co > Fe > Cu occurs for ammonium dibutyl dithiophosphate, which corresponds to the variations in the thermal effect of formation of ions in the solution and the radius of cations. For the cobalt ion, the ligands are arranged as follows: potassium butyl xanthate > potassium dibutyl dithiophosphate > sodium dibutyl dithiophosphate > sodium diisopropyl dithiophosphate > ammonium dibutyl dithiophosphate.

It is seen from the presented data on the reaction ability of sulfur-containing ligands that the coordination compounds of iron(II) ions with potassium dibutyl dithiophosphate are most stable; consequently, they will form a monomolecular layer with hydrophobicity sufficient to fasten the bubble in flotation conditions. At the same time, complexes of potassium dibutyl dithiophosphate with Fe^{2+} ions are not only less stable but also able to oxidize in the solution, which leads to the formation of dixanthogenide; a lower strength of the adsorption bond of the complex with the mineral surface; and, consequently, low ligand selectivity.

We further calculated thermodynamic parameters of the reaction of complexing at 298 K and the zero ionic strength (Table 3).

The above-presented data allow us to judge the character of bonds in complexes: for Co^{2+}, the bond strength is determined by electrostatic or energy components, while for other ions the steric effect plays a dominant role. Potassium dibutyl dithiophosphate and sodium dibutyl dithiophosphate, for which the ligand structure is determining, is an exclusion.

An analysis of Table 3 shows that the complexing of ions of *d* metals, excluding Co^{2+} with potassium dibutyl dithiophosphate, is characterized by positive values of varying the enthalpy (ΔH^0), which points to the prevalent role of the entropy summand [9, 10]. At the same time, for other flotation reagents, reactions of formation of complex compounds proceed with heat liberation. Maximal negative magnitudes of ΔH^0 are characteristic of Co^{2+} ions in the case of sodium diisopropyl dithiophosphate. High positive values of varying the heat effect are observed for complexes of Fe^{2+} ions with ammonium dibutyl dithiophosphate and Cu^{2+} with potassium dibutyl dithiophosphate. Thus, high negative magnitudes of enthalpy allow us to judge

Table 4. Temperature-dependent and temperature-independent characteristics of interaction of metal ions with flotation reagents $Me^{2+} + 2L^- = MeL_2$

L	Me	$-\Delta_r G^0_{\mathrm{TD}}$, kJ/mol	$-\Delta_r H^0_{\mathrm{TD}}$, kJ/mol	$-\Delta G^0_{\mathrm{TI}} = -\Delta_r H^0_{\mathrm{TI}}$, kJ/mol	$-\Delta_r S^0_{\mathrm{TD}}$, kJ/(mol K)
$C_4H_9OCS_2K$	Cu^{2+}	−69.55	24.66	241.93	316.12
	Ni^{2+}	−140.30	49.74	244.82	637.71
	Co^{2+}	219.82	−77.94	−200.02	−999.19
	Fe^{2+}	1.36	0.48	72.41	−6.16
$(C_4H_9O)_2PS_2K$	Cu^{2+}	95.32	−33.79	−10.69	133.26
	Ni^{2+}	−62.66	22.21	150.64	284.84
	Co^{2+}	−25.99	9.22	118.53	118.14
	Fe^{2+}	−57.37	20.34	143.38	260.76
$(C_4H_9O)_2PS_2Na$	Cu^{2+}	46.01	−16.31	0.53	−209.15
	Ni^{2+}	−4.22	1.495	84.21	19.17
	Co^{2+}	85.97	−30.48	−6.01	−390.79
	Fe^{2+}	82.57	−29.27	−14.321	−375.31
$(i\text{-}C_3H_7O)_2PS_2Na$	Cu^{2+}	84.48	−29.95	−25.39	−384.00
	Ni^{2+}	−7.03	2.49	57.313	31.94
	Co^{2+}	−373.309	132.35	431.83	1696.86
	Fe^{2+}	−125.17	44.38	181.038	568.97
$(C_4H_9O)_2PS_2NH_4$	Cu^{2+}	59.09	−20.95	−16.45	−268.61
	Ni^{2+}	−83.13	29.47	129.29	377.88
	Co^{2+}	−1.36	0.481	44.88	6.17
	Fe^{2+}	46.10	−16.35	−1.82	−209.54

on the maximal degree of ionicity of the bonds in the complex, as well as on a considerable strength of compounds.

We further calculated the temperature-dependent (TD) and temperature-independent (TI) characteristics of interaction of metal ions with sulfur-containing collectors (Table 4) [11].

Among the ions of *d* metals, Co^{2+} possesses the maximal complexing ability, which is indicated by a high TD component of the Gibbs energy (ΔG^0) for potassium butyl xanthate and a TI component for sodium diisopropyl dithiophosphate. In the case of copper ions, the formation of electrostatic complexes with potassium dibutyl dithiophosphate, sodium diisopropyl dithiophosphate, and ammonium and sodium dibutyl dithiophosphates occur. However, copper(II) ions form donor–acceptor complexes with potassium butyl xanthate. For other ligands, the fraction of covalence decreases in the series potassium dibutyl dithiophosphate > ammonium dibutyl dithiophosphate > sodium diisopropyl dithiophosphate. In connection with this, the TD and TI components of the variation in the Gibbs energy, along with the degree of hydration of the ion in the solution, can serve as a criterion for the selection of collectors.

Iron(II) ion manifests itself as an intermediate-type complexing agent, for example, its compounds with potassium butyl xanthate are characterized both as donor–acceptor and electrostatic. The above-described effects are associated with the features of the ligand structure, their liability to dissociation, and the degree of delocalization of the electron density at the carbon or phosphorus level. Potassium butyl xanthate possesses the highest complexing properties with respect to copper, nickel, and cobalt ions. Further, sodium diisopropyl phosphate, potassium dibutyl dithiophosphate, ammonium dibutyl dithiophosphate, and sodium dibutyl dithiophosphate are arranged according to degree of complexing ability.

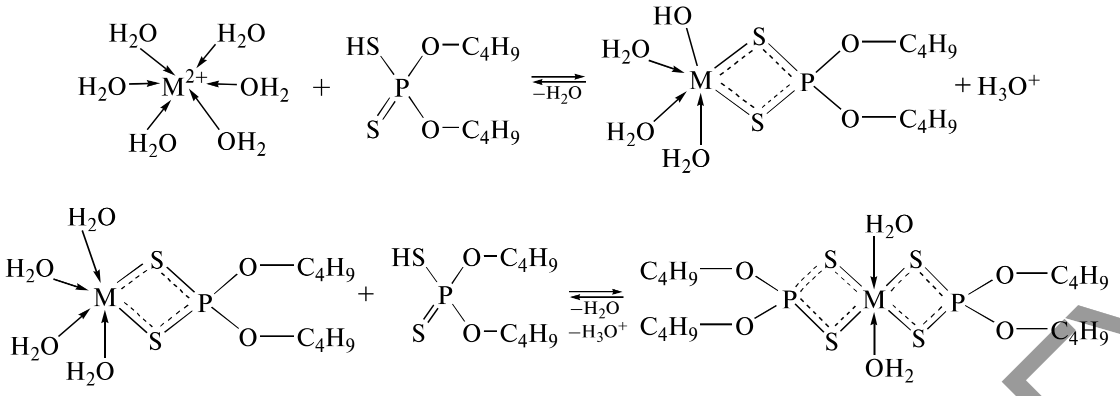

Fig. 2. Mechanism of complexing of transition-metal ions with sulfur-containing ligands (M = Fe^{2+}, Co^{2+}, Ni^{2+}).

Based on the data of Table 4, we proposed a complexing mechanism for metal ions with a phosphorus-containing collector in aqueous solutions (Fig. 2).

In the course of investigations of the thermodynamics of complexing, a high affinity of potassium dibutyl dithiophosphate to ions of transition metals of the iron subgroup is established at collector concentrations used in the flotation practice. To confirm the theoretical notions, we performed laboratory tests of the flotation activity of potassium butyl xanthate and potassium dibutyl dithiophosphate relative to the samples of the iron-containing ore (Table 5), the results of which showed the following.

The higher degree of recovery of metal with the use of potassium dibutyl dithiophosphate determines the application of this reagent as a collector to perform the flotation of pyrite, since it possesses high selectivity relative to iron-containing ores. On the other hand, good characteristics of the yield of the concentration found for potassium butyl xanthate are noticed; consequently, this flotation reagent can be applied for the collective flotation of ores. The data of Table 5 agree completely with theoretical considerations of the authors touching the thermodynamic characteristics of complexing and evaluation of selectivity of collectors.

Table 5. Results of determining the flotation activity of collectors

Reagent	m_{ore}, g	m_{conc}, g	ω_{conc}, %	α, %	β
Potassium dibutyl dithiophosphate	200	33.10	16.55	76.13	9.10
Potassium butyl xanthate		103.90	51.95	19.40	2.30

Flotation conditions: $T = 308$ K, the reagent content is 250 g/t, and the lime content is 10 kg/t. ω_{conc} is the concentrate yield, %; α is the metal recovery, %; and β is the degree of concentration.

CONCLUSIONS

(i) Thermodynamic parameters of binding processes of metal ions by molecules of sulfur-containing collectors are calculated.

(ii) Series of reaction ability of metals and ligands which make it possible to predict the selective interaction between the solution components are found.

(iii) TD and TI components of the variation in the Gibbs energy for complexing reactions of ions of transition metals with a phosphorus-containing collector are calculated.

(iv) The formation mechanism of complexes of metal ions with sulfur-containing ligands is proposed.

(v) Froth flotation of the iron-containing ore is performed and selectivity of potassium dibutyl dithiophosphate relative to iron sulfide is established.

(vi) It is shown that the strength of coordination bonds for complexes of *d* metals with sulfur-containing and phosphorus-containing ligands can be characterized from several points of view: the hydration theory, the principle of strong and weak acids and bases (SWAB) of the analysis of TD and TI contributions to the thermodynamic functions of the complexing theory, and the Debye–Hückel theory. Series of reaction ability found based on the calculation of thermodynamic parameters can serve as criteria for selecting organic ligands to perform the flotation processes of complex ores.

REFERENCES

1. Brylyakov, Yu.E., Gershenkop, A.Sh., and Lygach, V.N., *Prog. Tekhnol. Kompl. Pererab. Miner. Syr'ya*, 2008, vol. 5, no. 5, p. 265.
2. Amerkhanova, Sh.K., *Khal'kogenidy metallov v potentsiometrii. Teoriya, metodika, praktika* (Metal Chalcogenides in Potentiometry. Theory, Methods, and Practice), Karaganda: Profobrazovanie, 2002.
3. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, 2009, 6th ed.
4. Bek, M. and Nadpal, R., *Noveishie metody issledovaniya kompleksoobrazovaniya v rastvorakh* (Investigation of Complexing by Newest Methods), Moscow: Mir, 1989 [Russian Translation].
5. Pyreu, D.F., Khrenova, E.V., and Kozlovkii, E.V., *Koord. Khim.*, 2008, vol. 34, no. 10.
6. Aver'yanov, V.A., *Laboratornyi praktikum po obshchei khimicheskoi tekhnologii* (Laboratory Practicum on General Chemical Technology), Moscow: BINOM, 2010.
7. Shaqidulin, R.R., Vinogradova, A.V., and Mukhametov, F.S., *Organophosphorus Compounds: Interpreted Spectrograms*, Springer, 1991.
8. Bakeev, M.I., *Teoriya gidratatsii i svoistva rastvorov elektrolitov* (Hydration Theory and Properties of Solutions of Electrolytes), Karaganda: Karaganda State Univ., 2007.
9. *Bol'shoi khimicheskii spravochnik* (Large Chemical Reference Book) Volkov, A.I., Zharskii, I.M., Eds., Moscow: Sovremennaya shkola, 2005.
10. Korolev, V.P., *Zh. Strukt. Khim.,* 2006, vol. 47, no. 6, pp. 1094–1101.
11. Vasil'ev, V.P., Volkov, A.V., Gorboletova, G.G., and Kochergina, A.A., *Russ. J. Phys. Chem.,* 2001, vol. 75, no. 4, pp. 512–515.

Translated by N. Korovin