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On the Interaction of Electrochemical and Physicochemical Indicators of *d* Metal Complexes with Sulfur-Containing Ligands

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Abstract—Redox potentials of metal complexes, refraction values, and polarizability indicators of a donor—organic ligand—have been calculated. Correlation dependences between transition constants of outer sphere complexes to inner sphere ones and redox potentials of complexes, taking into account structural and energetic features of ligands and metal ions, have been established.

Keywords: redox potential, stability constants, polarizability, refraction, ionization potential of metal, phosphorus-containing ligands, *d* metals, outer sphere complex, inner sphere complex

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INTRODUCTION

Methods for estimating thermodynamic characteristics of complexations can be classified by two features: the character of theoretic justification and probable results. The first suggests the following methods for calculation: quantum-chemical methods, statistical thermodynamics, semi-empirical models of complexion, and empirical generalizations [1–3]. On the other hand, theoretical calculation methods are primarily based on significant experimental data of isolated compounds of the studied class of substances, allowing us to reveal some of the most important features.

In regards to complexation activity, all organic ligands can be classified by the presence of the functional group, which directly forms a bond with metal ions, as well as by the influence of an atom or group of atoms interrelated with the functional group or groups on the reactivity. Among them, it is worth noting the phosphorus- and sulfur-containing ligands possess the maximal affinity to ions of transition metals, which allows their use in different industrial branches, such as the enrichment industry, the electrochemical field (production of metals), sewage treatment, and others.

This work is aimed at establishing a correlation between physicochemical and electrochemical parameters of the transition-metal ion-complex formation and sulfur-containing ligands.

EXPERIMENTAL

Basic solutions of metal salts, alkali metal, and ammonia dibutyl dithiophosphates, as well as potassium butyl xanthate, which contain 10^{-3} mol/L of $CuSO_4$, $FeSO_4$, $NiCl_2$, $Co(NO_3)_2$, and $AgNO_3$ were prepared by dissolving an exact charge in bidistilled water; working solutions were diluted to concentrations of 10^{-4} mol/L.

The pH-metric measurements were performed using a 410 pH meter with an ESK-10601/7 glass electrode of according to method [4]. IR spectra of prepared complex compounds were recorded using a Thermo Nicolet Avatar 360 FTIR spectrometer. Bidistilled water was used as solvate [5]. The common constants of the complex formation were determined according to technique [6]. Thermodynamic parameters were calculated by methods [1, 7, 8]. The boundary concentration of the ligand, as well as the normal potentials, was determined using [9] and [10], respectively.

RESULTS AND DISCUSSION

The dissociation constants (pK_α) for dibutyl dithiophosphoric, diisopropil dithiophosphoric, and butyl xanthic acids were determined respectively as 1.723, 5.67, and 3.25 using the conductometric method. The dissociation proceeds as follows:

$$(C_4H_9O)_2PS_2H \leftrightarrow (C_4H_9O)_2PS_2^- + H^+, \qquad (1)$$

$$(i\text{-}C_3H_7O)_2PS_2H \leftrightarrow (i\text{-}C_3H_7O)_2PS_2^- + H^+, \qquad (2)$$

$$C_4H_9OCS_2H \leftrightarrow C_4H_9OCS_2^- + H^+. \qquad (3)$$

As follows from the data of dissociation constants, the formation of alkali metal cations and ammonium in the solution decrease acidity, increasing the organic ligand stability. The influence of the positive inductive effect of methyl groups is characteristic of the potassium dibutyl dithiophosphate, resulting a very strong

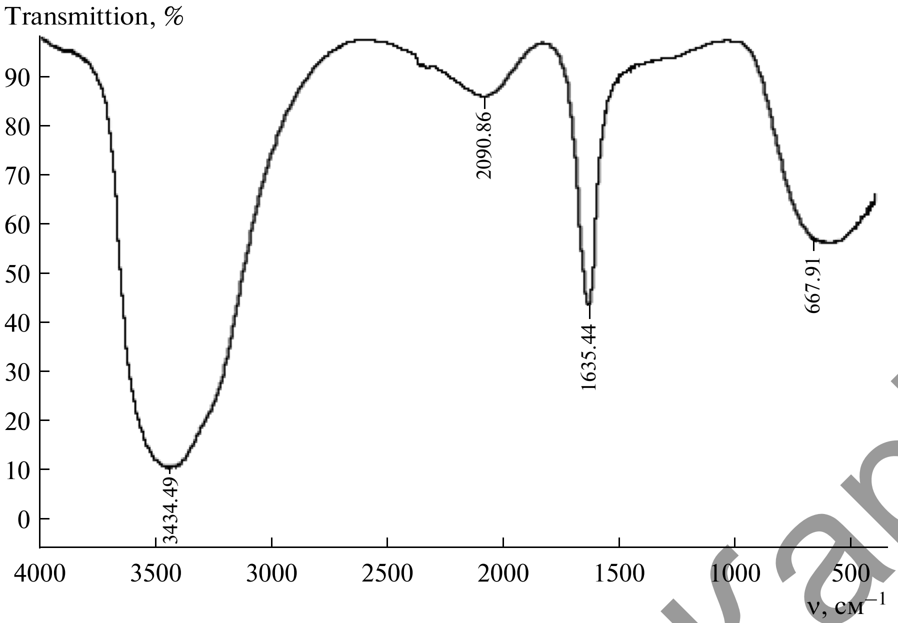

Fig. 1. IR spectrum of silver dibutil dithiophosphate.

bond between the sulfur atom and alkali metal ion or hydrogen ion. IR spectra of complexes of silver and potassium dibutyl dithiophosphates have been recorded (Fig. 1). It is shown that narrowing band in the range of $\nu = 3400–3500\ \text{cm}^{-1}$ reflects the weakening hydrogen bonds with solvent molecules, and the shift of the band intrinsic for P = S bond is responsible for the coordination of silver ions with organic ligand.

Stability constants are determined by potentiometric method and presented in [11]. The complexation of transition metal ions proceeds as follows:

$$(C_4H_9O)_2PS_2H + Cu^{2+} \leftrightarrow ((C_4H_9O)_2PS_2)_2Cu + H^+, \quad (4)$$

$$(C_4H_9O)_2PS_2H + Ag^+ \leftrightarrow (C_4H_9O)_2PS_2Ag + H^+. \quad (5)$$

Based on the stability constants of complexes, the boundary ligand concentrations and normal potentials of the system ML/M were calculated. The results are represented in Tables 1 and 2 [9].

It follows from Table 1 that $C_4H_9OS_2K$ and $(C_4H_9O)_2PS_2K$ are the most effective for most metal complexes; in accordance with the ability for complex formation, the metals for $(C_4H_9O)_2PS_2Na$ can be arranged as $Co^{2+} \approx Ni^{2+} > Fe^{2+} > Ag^+ > Cu^{2+}$. In the case of sodium and ammonium isopropyl ethers of phosphoric acid, the ligand concentration necessary for the formation of a quite simple complex is higher than the basic ligand concentration. This allows one to also conclude that there is not enough of the complex accumulated in the solution; i.e., in this case free metal ions prevail.

As is seen from Table 2, the positive potential is only for silver ions; i.e., silver complexes are oxidants and recover in the easiest manner, while complexes of cobalt ions with ammonium dibutil dithiophosphate possess the maximal recovery. Herewith, the series of recovery for complex metal ions is as follows: $C_4H_9OS_2K > (C_4H_9O)_2PS_2K > (C_4H_9O)_2PS_2Na > (i\text{-}C_3H_7O)_2PS_2Na > (C_4H_9O)_2PS_2NH_4$; for copper (II) ions it is $C_4H_9OS_2K > (C_4H_9O)_2PS_2K > (C_4H_9O)_2PS_2Na > (i\text{-}C_3H_7O)_2PS_2Na \approx (C_4H_9O)_2PS_2NH_4$.

Table 1. Boundary ligand concentrations at p(L) complex formation

L	Fe^{2+}	Co^{2+}	N^{2+}	Cu^{2+}	Ag^+
$C_4H_9OCS_2K$	4.72	9.01	4.34	14.24	4.91
$(C_4H_9O)_2PS_2K$	5.79	6.37	5.97	5.67	7.23
$(C_4H_9O)_2PS_2Na$	4.24	5.27	5.27	2.24	2.68
$(i\text{-}C_3H_7O)_2PS_2Na$	3.15	3.39	2.67	3.44	1.67
$(C_4H_9O)_2PS_2NH_4$	2.07	2.25	2.30	2.00	2.63

Table 2. Normal potentials ($-E$, mV) of reduction of metal ion complexes

L	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Ag^{+}
$C_4H_9OCS_2K$	600.8	694.2	368.4	386.4	–508.7
$(C_4H_9O)_2PS_2K$	824.9	952.3	602.8	603.4	–81.5
$(C_4H_9O)_2PS_2Na$	957.1	1145.0	795.9	617.6	77.0
$(i\text{-}C_3H_7O)_2PS_2Na$	1025.0	1227.0	835.2	702.5	175.4
$(C_4H_9O)_2PS_2NH_4$	1029.0	1242.0	852.9	702.2	330.6

Table 3. Interrelation between RPs of metal ion complexes and RPs of metal ion/metal and ligand ion/dimer pairs

M^{n+}	Dependence $E_{ML_2/M} = aE_{2L^-/L_2} + b$		L	Dependence $E_{ML_2/M} = aE_{M^{2+}/M} + b$	
	a	*b*		*a*	*b*
Fe^{2+}	–2.667	–0.501	$C_4H_9OCS_2^-$	0.819	–0.338
Co^{2+}	–3.344	–0.562			
Ni^{2+}	–2.931	–0.255	$(C_4H_9O)_2PS_2^-$	0.385	–0.680
Cu^{2+}	–2.001	–0.327			
Ag^{+}	–8.640	0.790	$(i\text{-}C_3H_7O)_2PS_2^-$	0.220	–0.938

The series of metals for aforecited ligands are given below:

for potassium butyl xanthate and potassium dibutil dithiophosphate:

$$Ag^+ > Ni^{2+} > Cu^{2+} > Fe^{2+} > Co^{2+};$$

for sodium dibutil dithiophosphate: $Cu^{2+} > Ag^+ > Ni^{2+} > Fe^{2+} > Co^{2+}$;

for sodium diisopropil dithiophosphate: $Cu^{2+} > Ni^{2+} > Ag^+ > Fe^{2+} > Co^{2+}$;

for ammonium dibutil dithiophosphate: $Cu^{2+} > Ni^{2+} > Fe^{2+} > Ag^+ > Co^{2+}$.

As is seen from the results, the metal complexes of copper subgroup recover with higher probability, while the metal complexes of the first transition series recover with lower probability; i.e., in the first case the metal ion recovery proceeds and in the second one the metal ion maintains a degree of oxidation and disulfides are the common product.

The standard oxidation potential of the system dixanthate–xanthate determined by the electrochemical method by different authors varies from 0.037 to 0.081 V [12]. Herewith, ions Cu(II) and Ag(I) that form complexes of the composition 1 : 1 are oxidants relative to this anion. In the case of dialkil dithiophosphates of alkali metals and ammonium, the redox potential (RP) for CH_3, C_2H_5, C_3H_7, $i\text{-}C_3H_7$, C_4H_9, $i\text{-}C_4H_9$, C_5H_{11}, $i\text{-}C_5H_{11}$, and C_6H_{13} takes the following positive values: 0.315, 0.215, 0.187, 0.196, 0.122, 0.155, 0.050, 0.086, and 0.0156 V [13]. As can be seen, the standard potential of the reaction dialkil dithiophosphate–bisulfide is higher than for xanthate; thus, the ability to oxidize is somewhat lower. However, the tendency to oxidize the metal ion complexes of the sulfur subgroup is maintained.

The series above are in the antibate dependence on the RP of the pair xanthate (dialkil dithiophosphate)–bisulfide. The higher the RP of this pair is, the lower the potential of the complex recovery is. The new dependences between RPs of the ligand ion/dimer and metal ion/metal pairs, as well as RPs of the ion metal complexes, are shown in Table 3.

The equations (Table 3) allow calculating the RP from one of the known magnitudes for unstudied objects in this series. The presence of metal ion is shown to enhance the recovery of the complex. Herewith, the binding metals and ligands, which are diametrically opposite in properties, should induce the maximal oxidative and the maximal reductive properties of the complexes.

On the other hand, due to the possibility of hydrogen-bond formation both in metal salt solutions and their complexes with organic ligands, a quantitative account of the interaction of aqua complexes—dibutil dithiophosphate metal complexes with water—based on refraction data becomes necessary [14]. Thus, in metal sulfate hydrates, the refraction reduces in the series $Fe^{2+} > Co^{2+} > Ni^{2+} \approx Cu^{2+}$ from 3.04 to 2.86 cm^3, which indicated the sufficient strength of hydrogen bonds and their reduction. This series completely matches RPs of metal ions; i.e., metal with the maximum recovery possesses a high affinity to hydrogen of the water molecules. The addition of one ligand increases the refraction of salts of dibutil dithiophosphoric acid to 72.97 and 72.61 cm^3, salts of diisopropil dithiophosphoric acid to 65.05 and 64.68 cm^3, and salts of xanthic acid to 55.93 and 55.96 cm^3 for iron(II) and copper(II) ions, respectively. Moreover, the increase in refraction is known to testify to bond strengthening; i.e., the most durable trans-structure complexes will form dibutil dithiophosphate anion and ions of two-valent iron [14]. The strength of hydrogen bonds will reduce during the formation of the complex of 1 : 1 composition.

Based on ligand refraction, the transition constants of outer sphere complexes to inner sphere ones for different ions of transition metals and organic ligands were calculated.

As is seen from Fig. 2, nickel ion possesses a minimal ability to form inner sphere complexes, while maximal ability is characteristic of two-valent iron and silver ion in the case of dibutyl dithiophosphate anion and copper ion in the case of diisopropil dithiophosphate and xanthate anions.

In the first case it is due to the high polarizability of nickel ion, the strength of the bond with water molecules, and the hydration Gibbs energy. Iron, copper, and silver ions are characterized by low polarizability; high mobility of water molecules in the inner hydrate sphere; low hydration Gibbs energy; and, as follows, high complexation ability [15].

According to increase in softness (decrease in charge density), the cations are arranged as follows: $Ni^{2+} > Cu^{2+} > Co^{2+} > Fe^{2+} > Ag^+$; i.e., the softest cation forms the most durable inner sphere complex, while the hardest cation forms the outer sphere complex. Among the ligands, the dibutil dithiophosphate anion has more ability to form outer sphere complexes, while the diisopropil dithiophosphate anion possesses the lowest ability in this property due to the ligand structure and ability to dissociate. On the other hand, the polarizability of the donor changes in the series $C_4H_9OCS_2^- > (C_4H_9O)_2PS_2^- > (i\text{-}C_3H_7O)_2PS_2^-$. RPs of ligands change to it simbatly; i.e., the most polarizable donor possesses the maximum thermodynamic stability.

The practical significance of the results is the possibility of the selective flotation of nickel-containing ores in the presence of pyrite with potassium dibutil dithiophosphate and iron-containing ores with sodium diisopropil dithiophosphate, which does not undergo oxidation on the pyrite surface and forms a solid monomolecular hydrophobic layer. Using potassium butyl xanthate in the individual state is unprofitable because of its high reactivity relative to transition metal ions and the subsequent separation of the collective concentrate has to be done.

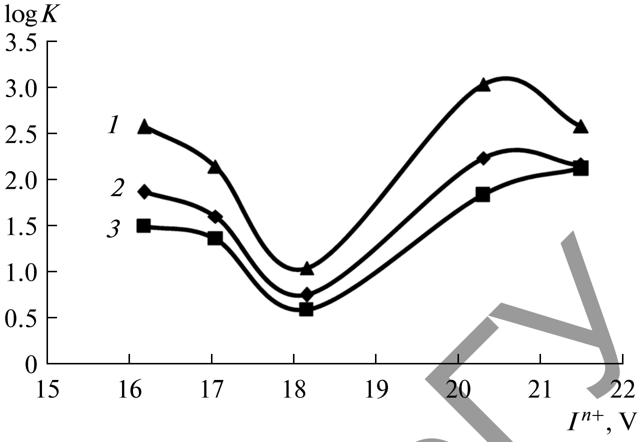

Fig. 2. Dependence of transition constant from an outer sphere complex to an inner sphere one on the ionization potential of metal ions. (*1*) $(i\text{-}C_3H_7O)_2PS_2^-$; (*2*) $C_4H_9OCS_2^-$; and (*3*) $(C_4H_9O)_2PS_2^-$.

The rectilinear dependence takes place between the transition constants of outer sphere complexes to inner sphere ones for metal ions being intermediate in accordance with the rigidity–softness scale based on electronegativity and ionization potentials [16], as well as for ions of maximal and minimal rigidity. With the increasing RP of the complex, the ability to form inner sphere complexes increases; i.e., the complex possessing of the maximal reduction is formed accordingly to the outer sphere mechanism, where the ligand oxidizes in the first place. Simultaneously, the formation of a more durable bond between the metal and sulfur atom compared to the oxygen atom leads to an increase in the covalence share and induces the transition to the zero-valent state.

Taking into account all the above, we note that the copper (II) ion complexes that formed at the first state according to the outer sphere mechanism transfer to the inner sphere mechanism at the second state with subsequent ligand oxidation. The nickel complexes undergo no changes. Thus, copper sulfides float in the first place, while nickel sulfides float in the second place; i.e., metal ions forming in the individual state the inner-sphere complexes possess more reactivity in the solutions in the composition of mineral crystalline lattice than those forming outer-sphere complexes. This fact is also a rational for using flotoreagents with a higher RP in the enrichment industry.

CONCLUSIONS

Boundary ligand concentrations allowing an estimation of the ability to form and accumulate the complex, as well as redox potentials of metals with phosphorus-containing ligands, were calculated based on the stability constants of complexes.

The redox series of *d* metal complexes that are in the linear dependence on standard potentials of a metal ion/metal pair are obtained. They allow calculations from one of the known magnitudes.

Based on the refraction data of metal complexes with organic ligands, the transition constants from outer sphere complexes to inner sphere ones are determined.

Correlation dependences of the transition constants from outer sphere complexes to inner sphere ones with redox potentials of complexes are established by taking into account structural and energetic features of ligands and metal ions.

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