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VARIOUS TECHNOLOGICAL PROCESSES

Azo Derivatives of Pyrocatechol, Resorcinol, and Salicylic Acid as Collectors for Sulfide Ore Flotation

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Abstract—Heterocyclic and aromatic azo derivatives of pyrocatechol, resorcinol, and salicylic acid have been investigated as collectors for the flotation of sulfide ores. The acid-base properties of the compounds were studied, their solubility in an alkaline solution was determined. It was established that the fixing of reagents on the surface of the ore occurs mainly by the chemical mechanism. Adsorption constants were calculated. It was found that most of the studied reagents exhibit collective properties with respect to sulfide copper–nickel ore. The use of mixtures of azo compounds with potassium butyl xanthogenate leads to an increase in the degree of extraction of nickel and copper, as well as the quality of the concentrates, in comparison with one butyl xanthogenate.

Keywords: azo derivatives of pyrocatechol, resorcinol, and salicylic acid; sulfide ores; flotation

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Flotation is one of the main technological processes of the ore beneficiation. The depletion of deposits rich in raw materials and the involvement of poorer ores with a poor composition and similar technological characteristics of minerals in the processing require developing ways to increase its efficiency. One of the possible approaches to solving this problem is the use of new flotation reagents, in particular reagent-collectors. Xanthogenates and several types of dialkyldithiophosphates (aeroflot reagents) and their mixtures with various collectors are used as the main types of collectors for flotation of sulfide ores [1–4]. Dialkyldithiophosphates and their modifications are more selective than xanthates and provide high-quality concentrates of non-ferrous, rare and precious metals. For selective flotation of sulfides of copper–zinc ores, a phenylpyrazole-type collector, 1-phenyl-2,3-dimethyl-4-dimethylaminopyrazolone-5, is recommended [5]. Collectors for flotation of sulfide copper–molybdenum and copper–nickel ores based on aliphatic acid hydrazides pronounced collective properties and selectivity for non-ferrous metal sulfide minerals, provide a higher yield of target metals in comparison with potassium butyl xanthogenate, are less toxic and stable during long-term storage [6]. Of recent developments, new carbamate class collectors should be noted for the selective separation of chalcopyrite from galena and arsenopyrite [7, 8]. It was found that the degrees of extraction of chalcopyrite and galena by *O*-isopropyl-*N*-ethylthiocarbamate differ with about 20%. In [9, 10], the reagents of the thioamide class were studied. They showed good selectivity for chalcopyrite and are proposed as collectors for its separation from pyrite and galena. The authors investigated 1-hydroxyethylidene-1,1-diphosphonic acid used in water treatment as a collector [11]. It was found that the reagent has better selectivity for chalcopyrite in comparison with ethylxanthogenate and is considered as its potential substitute.

Potassium butyl xanthogenate (PBX), which is the main type of collector for sulfide ores in our country, in addition to low selectivity, which complicates the technological schemes and losses of metals in numerous operations of cleaning concentrates, is unstable during long-term storage and decomposes with the release of toxic carbon disulfide. Therefore, an important task is the development of more selective and less toxic collectors.

Azo compounds are one of the classes of reagents that have shown collective properties. Azo compounds are low toxic; they are the most numerous class of synthetic dyes. They are sustainable, their production technology has proven itself in the industry. Given these circumstances, it was of interest to study these compounds as collectors for flotation of sulfide ores. However, there is only a few information about their use as collectors for flotation. Handbook[1] lists several aromatic azo compounds used for flotation of oxidized non-ferrous metals ores. The authors of [12] studied aromatic and heterocyclic azo derivatives of phenol and 1-naphthol. It was established that they have high flotation properties in relation to sulfide copper–nickel ores. In a number of cases, a higher degree of enrichment and extraction of metals was achieved compared to PBX. The use of a mixture of azo compounds with PBX (1 : 1) significantly improves flotation performance. Their adsorption on the surface of the ore occurs due to physical interaction.

According to modern concepts, the fixation of reagents on the surface of the ore is considered as the formation of coordination compounds [13]. This allows application of existing patterns of interaction of reagents with metal cations in solution to predict their interaction with minerals containing the same cations. Therefore, for further studies, azo compounds containing several functional groups with a mobile hydrogen atom, in particular, OH and COOH groups, were of interest in the azo component. Such compounds form complexes with transition metal ions in solution [14–16]. It could be assumed that they will also form complexes with the ions of these metals located on the surface of the ore. Changing the mechanism of fixing reagents from physical to chemical can affect their flotation properties.

The aim of the work was to establish the effect of an azo component containing two functional groups (COOH and OH) on the physicochemical and flotation properties of azo compounds. The studies were carried out with heterocyclic and aromatic azo derivatives of pyrocatechol, resorcinol, and salicylic acid.

EXPERIMENTAL

Reagents were synthesized by preparing a diazosalt by reacting the corresponding amine with sodium nitrite in an acidic medium and its subsequent azo coupling with a hydroxyl-containing aromatic compound. Since pyrocatechol is easily oxidized by diazocompounds, to obtain its azo derivatives a method, which consisted in azo coupling with its Al salt was used. Applied in the form of a cyclic Al salt, pyrocatechol reacts well with diazo compounds in an acidic mmedium. At the same time, the oxidizing effect of diazocompounds is suppressed. After the reaction, the Al salt is decomposed by excess acid with the release of azo dye [17]. Using this method, all the pyrocatechol azo derivatives were synthesized. The resulting compounds and their designations are given in Table 1.

The individuality and purity of the reagents are confirmed by ^{1}H NMR, IR spectroscopy, and thin layer chromatography.

IR spectra were recorded on a Vertex80V Fourier spectrometer (Bruker, Germany), ^{1}H NMR spectra were recorded on an Avance Neo 400 spectrometer (Bruker, Germany) in DMSO-d_6 and $CDCl_3$. Protolytic equilibria, solubility, and complexation of the studied compounds with Ni(II) and Cu(II) were studied by spectrophotometric method.[2] Electronic spectra and optical density were recorded on an SP-2000 spectrophotometer (OKB Spectr, Russia), and pH values of solutions were recorded on an I-160M ionomer (ANTEKh, Belarus) with glass indicator and silver cloride reference electrodes.

The measurement of surface tension at the interface between an aqueous solution of a reagent and air was studied by the stalagmometric method. Solutions of 0.1 M KOH were used as the standard liquid, since these compounds are poorly soluble in water. A study of the adsorption of compounds was carried out by shaking a sample of ore (0.5000 g) in a shaker-incubator KS 4000 i control (IKA, Germany) with an alkaline solution of azo compounds. After reaching equilibrium (the time to reach adsorption equilibrium was 3–5 min with a flask shaking frequency of 500 min^{-1}), an aliquot was taken from the solution, filtered, and the residual reagent content was determined photometrically using a calibration curve. The desorption study was carried out with the same ore sample. An alkali solution of the same concentration containing no reagent was added to the flask. Its volume was equal to the volume of an aliquot taken to determine the adsorption. Thus, a solution of a reagent of a lower concentration was obtained in the flask, into which part

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[1] Shubov, L.Ya., Ivankov, S.I., Shcheglova, N.K., *Flotation Reagents in the Processes of Mineral Processing. Handbook*, Kondratieva, L.V., Ed., Moscow: Nedra, 1990, p. 136.

[2] Bernshtein, I.Ya. and Kaminskii, Yu.L., *Spektrofotometricheskii analiz v organicheskoi khimii* (Spectrophotometric Analysis in Organic Chemistry), Leningrad: Chemistry, 2010, pp. 130–170.

Table 1. Investigated reagents

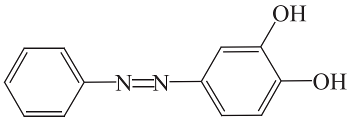
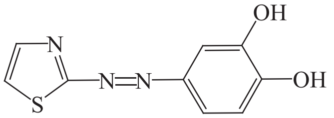
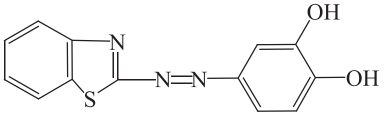
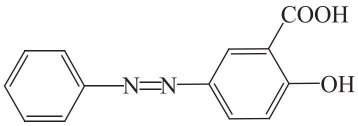
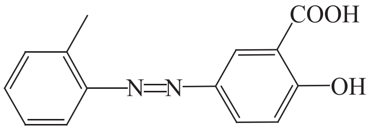
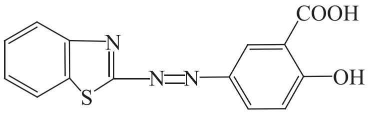
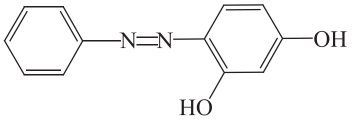
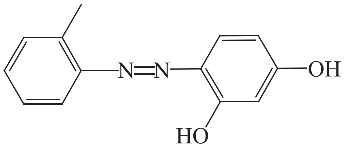
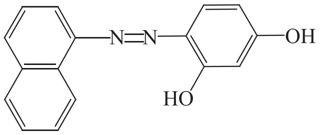
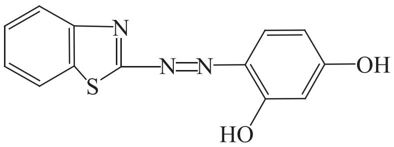
Reagent	Formula	Signification
4-(Phenylazo)pyrocatechol		PAP
4-(2-Thiazolylazo)pyrocatechol		TAP
4-(2-Benzthiazolylazo)pyrocatechol		BeTAP
5-(Phenylazo)salicylic acid		PASA
5-(*o*-Tolylazo)salicylic acid		TolASA
5-(2-Benzthiazolylazo)salicylic acid		BeTASA
4-(Phenylazo)resorcinol		PAR
4-(*o*-Tolylazo)resorcinol		TolAR
4-(1-Naphthylazo)resorcinol		NAR
4-(2-Benzthiazolylazo)resorcinol		BeTAR

Table 2. Reagent solubility in 0.1 M NaOH

Reagent	4-(Phenylazo)-resorcinol	4-(1-Naphthylazo)-resorcinol	4-(*o*-Tolylazo)-resorcinol	5-(Phenylazo)-salicylic acid	5-(*o*-Tolylazo)-salicylic acid	5-(2-Benzthiazolylazo)salicylic acid	4-(Phenylazo)-pyrocatechol	4-(2-Thiazolylazo)-pyrocatechol	4-(2-Benzthiazolylazo)pyrocatechol
Solubility, M (g L^{-1})	8.64×10^{-2} (18.51)	7.17×10^{-2} (18.95)	9.14×10^{-2} (20.87)	8.78×10^{-2} (21.26)	6.98×10^{-2} (17.89)	2.74×10^{-2} (7.76)	1.76×10^{-2} (3.78)	3.54×10^{-2} (7.83)	1.25×10^{-2} (3.39)

Table 3. Acid-base properties of compounds

Reagent	4-(Phenylazo)-resorcinol	5-(Phenylazo)-salicylic acid	5-(2-Benzthiazolylazo)-salicylic acid	4-(2-Thiazolylazo)-pyrocatechol	4-(2-Benzthiazolylazo)-pyrocatechol
pK_{a_1}[a]	6.38 ± 0.03	2.41 ± 0.08	3.94 ± 0.09	7.12 ± 0.08	7.23 ± 0.07
pK_{a_2}[a]	12.10 ± 0.08	11.85 ± 0.05	10.32 ± 0.07	11.23 ± 0.09	12.40 ± 0.05

[a] $P = 0.95$, $n = 4–5$.

of the reagent from ore was transferred to establish a new equilibrium, if it was fixed on it by a physical mechanism. In the case of a chemical fixing mechanism, the reagent remained on the ore. After shaking, its content in the solution was determined by a similar technique. Determination of the adsorption of azo compounds was carried out with the same samples of ore at each experimental point.

The flotation activity of the reagents was studied on sulfide copper–nickel ore with a Cu content of 0.210%, Ni 0.390%, Co 0.014%, and fineness of about 3 mm. An ore sample together with soda taken from the calculation of 3 kg ton^{-1} was ground in a ball mill to a fraction of the class –0.063 mm (the content of this fraction is not less than 75%). Flotation was carried out in a 237FL laboratory flotation machine (chamber volume 0.5 L, impeller rotation speed 2760 rpm; Mechanobr-Technika, St. Petersburg) according to the collective scheme, which included the main (10 min) and control (15 min) flotations. Sodium butyl aeroflot reagent was used as a foaming agent, and the studied azo compounds or their mixtures with PBX were used as collectors. The collector was introduced as a 1% solution in 0.1 M KOH. The products obtained after the experiments were dried, weighed, and abraded. After that, samples were taken for analysis. The samples were decomposed by dissolving them in a HCl : HNO_3 mixture (3 : 1) in a MARS 6 microwave oven (CEMCorporation, USA). The content of copper, nickel, cobalt was determined by atomic absorption spectroscopy on an iCE 3500 spectrometer (ThermoScientific, USA) with flame atomization. The results were compared with the enrichment indices obtained when using one PBX as a collector.

The following reagents were used in the work: 2-aminobenzothiazole (97%), 2-aminothiazole (97%), 1-naphthylamine of analytical pure grade, *o*-toluidine (1-methylaniline) of reagent purity, aniline 99.8%, resorcinol 99%, salicylic acid of reagent purity, pyrocatechol of reagent purity, $NaNO_2$, KOH, NaOH, Na_2CO_3, HCl, H_2SO_4 of highest grade, $CuSO_4·5H_2O$, $CoSO_4·7H_2O$, $NiSO_4·7H_2O$ of analytical pure grade.

RESULTS AND DISCUSSION

The solubility of the compounds in alkaline solutions was sufficient for the preparation of solutions of the required concentration used in flotation (Table 2). The constants of acid dissociation of azo compounds (Table 3) were determined in aqueous solutions by adding to them a minimal aliquot of the reagent in alcohol. The obtained values of pK_{a1} were in the range 2.41–7.23, pK_{a2}, 10.32–12.40. Thus, under flotation conditions occurring in aqueous solutions at pH ~ 10, all reagents are in a single ionized form. It should also be noted that additives of the studied compounds practically do not reduce the surface tension of the alkali solution (Table 4).

The absorption spectra of aqueous solutions of TAP (Fig. 1a*, 1*) and PASA (Fig. 1b*, 1*) and their mixtures with Ni(II) (Fig. 1a*, 2*) and Cu(II) (Fig. 1a*, 2*) do not coincide. The spectra of mixtures are characterized by a shift in the light absorption maxima relative to the spectra of the reactants, which indicates the chemical interaction proceeding in them. Thus, the azo derivatives of pyrocatechol and salicylic acid form complexes with metal cations in an aqueous solution, and it could be expected that chemisorption will be observed for these compounds.

To determine the nature of the interaction of the reactants with the ore surface, their adsorption and desorption were studied. Since the adsorption process is reversible during physical interaction, the degree of absorption of the reagent depends on its concentration in the solution, regardless of how it was obtained–by moving from low to higher concentrations or vice versa. In this case, the adsorption and desorption isotherms coincide. In the case of chemisorption, when a surface compound is formed due to the reagent–metal bond, the adsorption process is not reversible, the adsorbed substance remains on the surface of the ore, and the isotherms will not

Table 4. Surface tension σ of 0.1 M KOH solutions in the presence of the reagents and without them at $T = 20°C$

Reagent (R)	c_R, M	σ, J m^{-2}
4-(Phenylazo)pyrocatechol	0	75.72
	1.5×10^{-2}	66.81
	1.2×10^{-3}	73.26
5-(Phenylazo)salicylic acid	0	75.72
	2.3×10^{-2}	72.59
	1.8×10^{-3}	74.65
4-(2-Benzthiazolylazo)-pyrocatechol	0	75.72
	1.1×10^{-2}	74.80
	9.1×10^{-4}	76.65

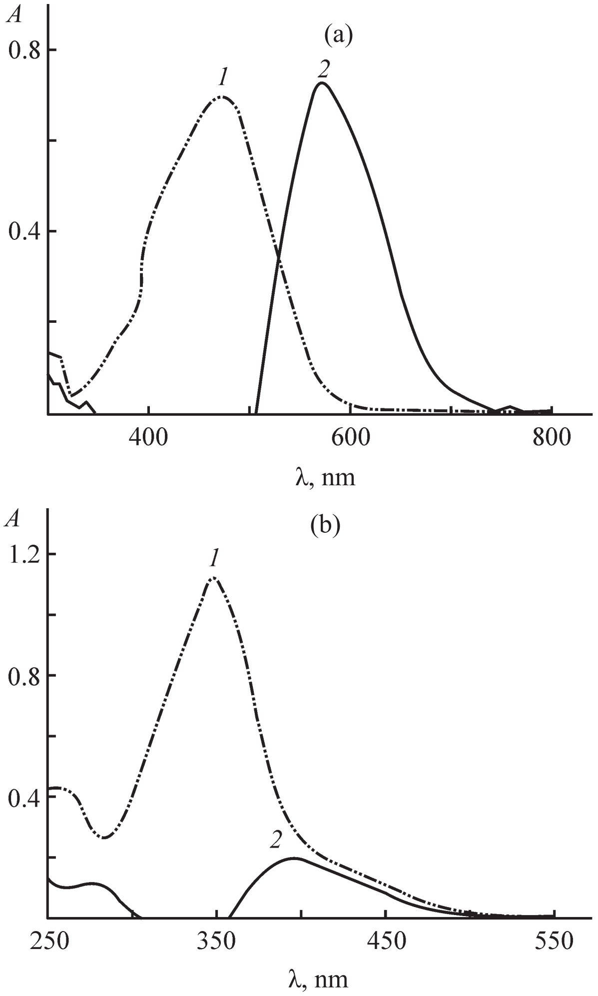


Fig. 1. Spectra of solutions of (a, *1*) 4-(2-thiazolylazo) pyrocatechol (R_1) and (b, *1*) 5-(phenylazo)salicylic acid (R_2), and their mixtures with (a, *2*) Ni(II) and (b, *2*) Cu(II). l = 1 cm; (a) $[R_1]_{in} = [Ni(II)]_{in} = 3 \times 10^{-5}$ M, pH 8.6; (b) $[R_2]_{in} = [Cu(II)]_{in} = 5 \times 10^{-5}$ M, pH 10.1.

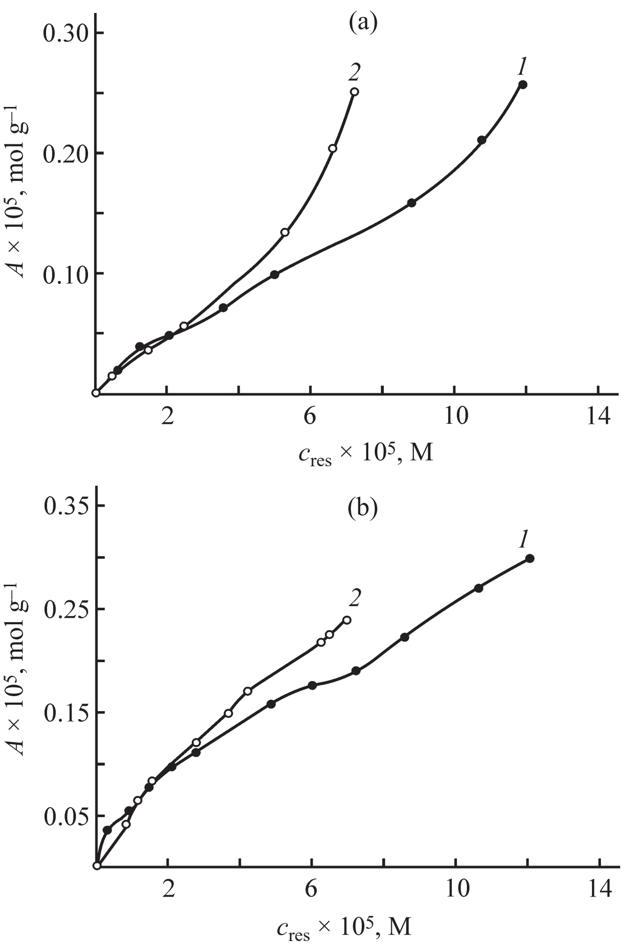


Fig. 2. Adsorption (*1*) and desorption (*2*) isotherms of (a) 4-(2-thiazolylazo)pyrocatechol and (b) 4-(2-benzthiazolylazo) pyrocatechol.

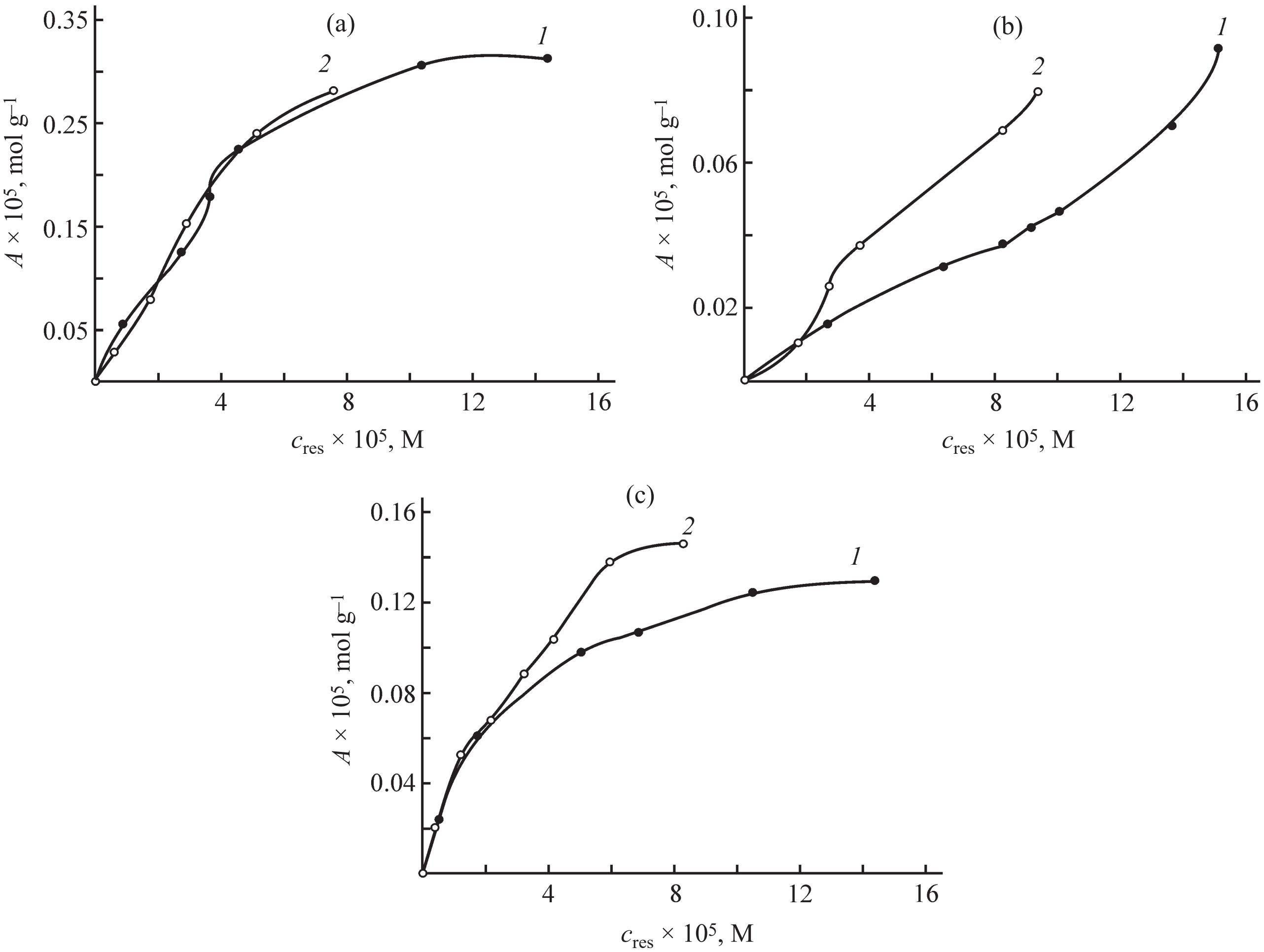


Fig. 3. Adsorption (*1*) and desorption (*2*) isotherms of (a) 5-(phenylazo)salicylic acid, (b) 5-(*o*-tolylazo)salicylic acid, and (c) 5-(2-benzthiazolylazo)salicylic acid.

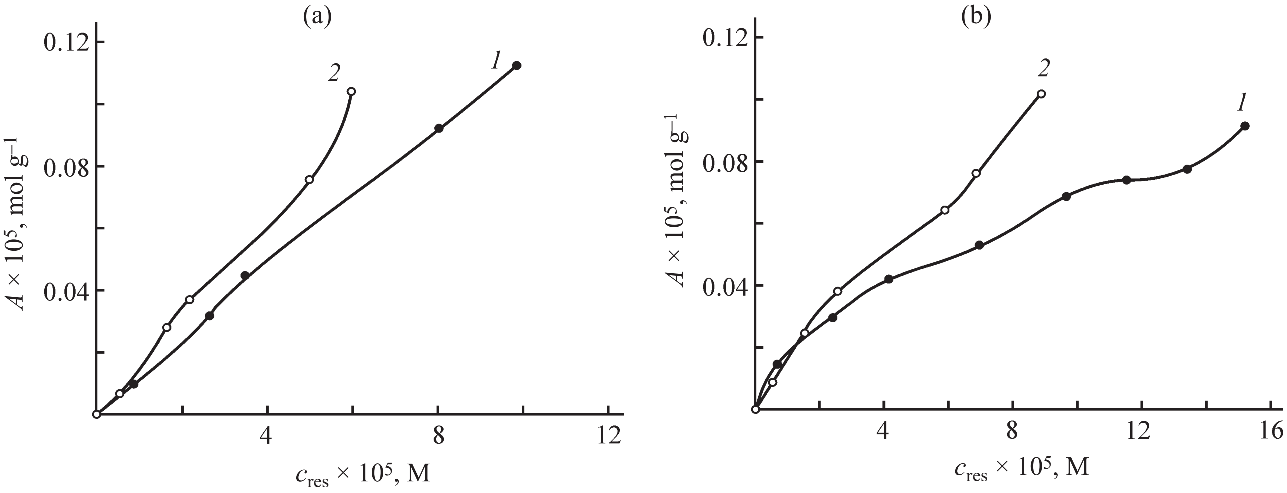


Fig. 4. Adsorption (*1*) and desorption (*2*) isotherms (a) 4-(*o*-tolylazo)resorcinol and (b) 4-(1-naphthylazo)resorcinol.

Table 5. The parameters of the Langmuir isotherms (k_1, a), Henry (k_2), the values of the Langmuir adsorption constants (K_L), Henry (K_H) and the limiting adsorption (A_∞)

Reagent	$k_1 \times 10^5$ $(k_1 = \frac{1}{A_\infty})$	a $(a = \frac{1}{K_L A_\infty})$	k_2 ($k_2 = K_H$)	A_∞, mol g^{-1}	K_L, M^{-1}	K_H, L g^{-1}
4-(*o*-Tolylazo)resorcinol	–	–	0.0057	–	–	0.0057
4-(1-Naphthylazo)resorcinol	14.748	39.724	–	6.78×10^{-7}	3.71×10^4	0.0252
5-(Phenylazo)salicylic acid	21.698	131.420	–	4.61×10^{-7}	1.65×10^4	0.0076
5-(*o*-Tolylazo)salicylic acid	–	–	0.0051	–	–	0.0051
5-(2-Benzthiazolylazo)salicylic acid	6.525	18.981	–	1.53×10^{-6}	3.44×10^4	0.0527
4-(2-Thiazolylazo)pyrocatechol	–	–	0.0182	–	–	0.0182
4-(2-Benzthiazolylazo)pyrocatechol	3.349	14.297	–	2.99×10^{-6}	2.34×10^4	0.0699

coincide. The adsorption and desorption isotherms of TAP, BeTAP, TolASA, BeTASA, TolAR, NAR do not coincide (Figs. 2–4). Thus, the adsorption of these compounds has a chemical nature, which is due to the presence in their structure of OH and COOH groups capable of reacting with metal cations located on the surface of the ore. In PASA, the adsorption and desorption isotherms coincide. In this case, physical adsorption takes place.

For the reagents PASA, NAR, BeTASA, and BeTAP the linear dependences of the adsorption isotherms in the Langmuir coordinates were obtained (Fig. 5). This makes it possible to apply the Langmuir theory and calculate the limiting adsorption (A_∞) and the adsorption constant (K_L). Adsorption of TAP, TolASA, and TolAR is not described by a linear isotherm in Langmuir coordinates. At low concentrations, the amount of adsorbed reagent is proportional to its concentration; therefore, the calculation of the adsorption constants in this case can be performed using the Henry equation for the adsorption isotherm. For these compounds, the linear dependences of their adsorption on the residual concentration were obtained (Fig. 6), which allows calculating the values of the Henry and Langmuir adsorption constants (Table 5).

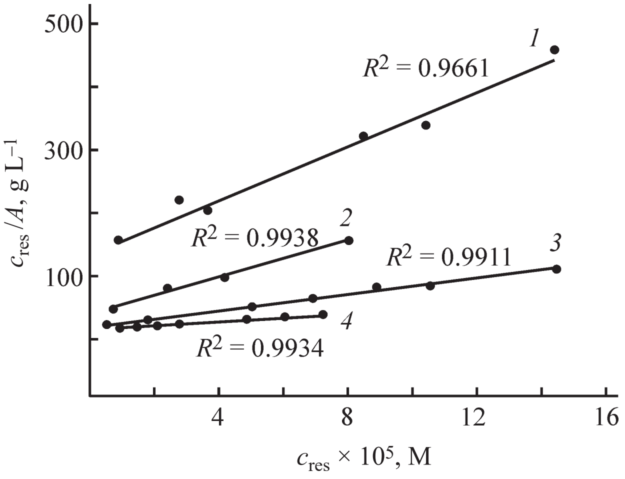


Fig. 5. Adsorption isotherms in Langmuir coordinates: (*1*) 5-(Phenylazo)salicylic acid, (*2*) 4-(1-naphthylazo)-resorcinol, (*3*) 5-(2-benzthiazolylazo)salicylic acid, (*4*) 4-(2-benzthiazolylazo)pyrocatechol.

Adsorption decreases in the series of BeTAP > BeTASA > NAR > TAP > PASA > TolAR > TolASA compounds. Obviously, the degree of adsorption is determined primarily by the presence of aromatic and heterocyclic rings in the diazocomponent. In the first four compounds, it is much higher. BeTAP and BetASA are adsorbed significantly better than TAP due to the presence of an additional benzene ring in their molecules. NAR occupies an intermediate position. Compounds having an aromatic and heterocyclic ring in the diazocomponent are adsorbed better than a compound having two aromatic rings, and it, in turn, is adsorbed better than a compound having one heterocyclic ring.

Table 6 shows the flotation results of sulfide copper-nickel ore with the studied reagents in comparison with PBX. Since the yield of the foam product is different for different compounds, it is difficult to judge their enrichment properties by the degree of metal extraction. A high degree of extraction may be due to a large

Table 6. The results of collective flotation of copper–nickel ore in a rough concentrate with butyl xanthogenate and studied collectors. Reagent consumption: main flotation—reagent 100 g t^{-1}, $CuSO_4$ 15 g t^{-1}, aeroflot 60 g t^{-1}; control flotation—reagent 35 gt^{-1}, $CuSO_4$ 15 g t^{-1}, aeroflot 35 g t^{-1}, sample of ore 200 g; grinding of ore with soda (3 kg t^{-1}) 50 min

Collector	Comparison options	Ni	Cu	Co
Butyl xanthogenate	Foam yield, % 48.60			
	Extraction, %	82.83	92.61	82.35
	Concentrate quality, %	0.744	0.348	0.029
	Tail quality, %	0.146	0.026	0.006
4-(Phenylazo)resorcinol	Foam yield, % 57.41			
	Extraction, %	88.71	93.35	84.13
	Concentrate quality, %	0.718	0.282	0.032
	Tail quality, %	0.123	0.027	0.008
4-(1-Naphthylazo)resorcinol	Foam yield, % 54.25			
	Extraction, %	85.42	90.77	81.02
	Concentrate quality, %	0.724	0.278	0.032
	Tail quality, %	0.146	0.034	0.009
4-(*o*-Tolylazo)resorcinol	Foam yield, % 58.77			
	Extraction, %	88.12	93.22	84.22
	Concentrate quality, %	0.680	0.265	0.032
	Tail quality, %	0.131	0.027	0.008
5-(2-Benzthiazolylazo)salicylic acid	Foam yield, % 55.52			
	Extraction, %	83.96	90.87	81.30
	Concentrate quality, %	0.665	0.267	0.034
	Tail quality, %	0.159	0.033	0.010
4-(2-Benzthiazolylazo)resorcinol	Foam yield, % 56.74			
	Extraction, %	59.92	81.11	57.19
	Concentrate quality, %	0.476	0.230	0.020
	Tail quality, %	0.417	0.070	0.019
4-(2-Benzthiazolylazo)pyrocatechol	Foam yield, % 47.77			
	Extraction, %	82.09	92.36	77.22
	Concentrate quality, %	0.721	0.408	0.027
	Tail quality, %	0.144	0.031	0.007
4-(2-Thiazolylazo)pyrocatechol	Foam yield, % 61.28			
	Extraction, %	87.20	92.93	86.94
	Concentrate quality, %	0.631	0.233	0.025
	Tail quality, %	0.147	0.028	0.006
4-(Phenylazo)pyrocatechol	Foam yield, % 45.65			
	Extraction, %	84.14	90.49	82.79
	Concentrate quality, %	0.855	0.337	0.036
	Tail quality, %	0.135	0.030	0.006
5-(Phenylazo)salicylic acid	Foam yield, % 51.16			
	Extraction, %	86.99	92.19	82.98
	Concentrate quality, %	0.857	0.308	0.039
	Tail quality, %	0.134	0.027	0.008

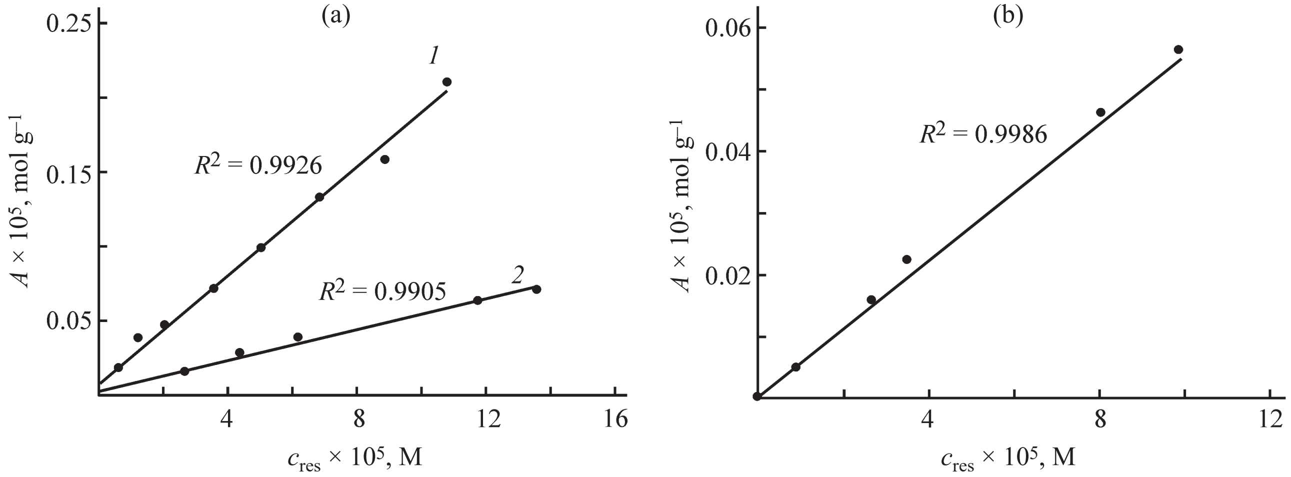


Fig. 6. Adsorption of reagents vs. their residual concentration. (a) (*1*) 4-(2-thiazolylazo)pyrocatechol, (*2*) 5-(*o*-tolylazo)salicylic acid, (b) 4-(*o*-tolylazo)resorcinol.

yield of foam product, rather than enrichment of raw materials. Therefore, to characterize the concentration, the ratio of the metal content in the concentrate to its initial content in the ore (degree of concentration) was selected. The initial content is calculated as the sum of the products of the metal content in the concentrate and in the tailings to their yields in percent divided by 100. The results of the basic experiment with one PBX are the averaged values of two experiments. The degree of concentration in PBX is: 1.70 for Ni, 1.91 for Cu, 1.70 for Co. Among the studied compounds, PAP has the best collective properties. Its indices are higher than that of PBX, especially for Ni and Co: the degree of concentration for Ni, Cu, Co are 1.84, 1.98, 1.83, respectively. BeTAP is not inferior to PBX in terms of flotation of nickel and copper (1.72 and 1.93, respectively), for cobalt this indicator is slightly lower (1.63). TAP has markedly worse enrichment results compared to other reagents studied, with the exception of BeTAR. A higher degree of metal recovery in this case is achieved due to the greater amount of foam product. Derivatives of salicylic acid, especially BeTASA, have a higher foam mass. Despite this, the degree of metal recovery is lower due to the worse quality of the concentrate. PASA has enrichment properties higher than other salicylic acid derivatives, and they are close to the PBX values (degree of concentration for Ni, Cu, Co is 1.70, 1.80, 1.63, respectively). For BeTASA, they are lower by 0.15–0.20. PAR, NAR, TolAR have approximately the same flotation properties. Azo derivatives of resorcinol are characterized by a noticeably greater yield of foam product. Due to this, in some cases, a higher degree of metal recovery is achieved, but the degree of concentration in them is worse than that of PBX, and is in the range of 1.45–1.67. In the case of BeTAR, nickel and cobalt enrichment is practically not observed. Correlations between the adsorption of reagents and their flotation properties could not be found.

Table 7 shows the flotation results of sulfide copper-nickel ore with mixtures of reagents with PBX in a ratio of 1 : 1.

The use of these mixtures significantly increases the flotation properties of the reagents. In many mixtures, the yield of foam product is either at the level of or less than that of PBX. This with similar or higher degrees of metal recovery provides a higher quality concentrate. In some cases, an increase in enrichment is achieved compared to one PBX. The enrichment properties of TAP increased most significantly. Its mixture surpasses PBX: for Ni, degree of concentration is 1.87, for Cu 2.02, for Co 1.85. PAP has the same degree of concentration of Ni and Co at close to PBX for Cu. BeTAP showed slightly worse properties: the degree of metal concentration is in the range of 1.63–1.85. The mixture with BeTASA has lower enrichment characteristics for all the metals under study, and the mixture with PASA has a higher rate for Ni (1.81), for Cu and Co they are similar to the base experiment 1.94 and 1.74, respectively. The enrichment properties of resorcinol derivatives have increased significantly. In NAR, PAR, and TolAR, the degree of concentration of Ni, Cu, and Co is in the ranges 1.61–1.80, 1.93–2.05, and 1.68–1.91,

Table 7. The results of collective flotation of copper–nickel ore in rough concentrate with mixtures of butyl xanthogenate : reagent (1 : 1). Reagent consumption: main flotation—reagent 100 g t^{-1}, $CuSO_4$ 15 g t^{-1}, aeroflot 60 g t^{-1}; control flotation—reagent 35 g t^{-1}, $CuSO_4$ 15 g t^{-1}, aeroflot 35 g t^{-1}, sample of ore 200 g, grinding of ore with soda (3 g t^{-1}) 50 min

Collector	Comparison options	Ni	Cu	Co
Butyl xanthogenate	Foam yield, % 48.60			
	Extraction, %	82.83	92.61	82.35
	Concentrate quality, %	0.744	0.348	0.029
	Tail quality, %	0.146	0.026	0.006
Butyl xanthogenate : 4-(phenylazo)resorcinol	Foam yield, % 44.69			
	Extraction, %	80.67	91.47	84.72
	Concentrate quality, %	0.673	0.389	0.022
	Tail quality, %	0.130	0.029	0.003
Butyl xanthogenate : 4-(1-naphthylazo)resorcinol	Foam yield, % 48.40			
	Extraction, %	85.36	93.33	83.26
	Concentrate quality, %	0.798	0.393	0.026
	Tail quality, %	0.128	0.026	0.005
Butyl xanthogenate : 4-(*o*-tolylazo)resorcinol	Foam yield, % 48.24			
	Extraction, %	84.44	93.81	81.03
	Concentrate quality, %	0.738	0.413	0.023
	Tail quality, %	0.127	0.025	0.005
Butyl xanthogenate : 5-(2-benzthiazolylazo)salicylic acid	Foam yield, % 52.57			
	Extraction, %	84.77	94.50	85.72
	Concentrate quality, %	0.722	0.391	0.023
	Tail quality, %	0.144	0.028	0.007
Butyl xanthogenate : 4-(2-benzthiazolylazo)resorcinol	Foam yield, % 58.18			
	Extraction, %	82.61	92.01	81.78
	Concentrate quality, %	0.619	0.265	0.027
	Tail quality, %	0.181	0.032	0.008
Butyl xanthogenate : 4-(2-benzthiazolylazo)pyrocatechol	Foam yield, % 50.42			
	Extraction, %	84.21	93.44	81.00
	Concentrate quality, %	0.671	0.376	0.027
	Tail quality, %	0.128	0.027	0.006
Butyl xanthogenate : 4-(2-thiazolylazo)pyrocatechol	Foam yield, % 45.76			
	Extraction, %	85.66	92.54	85.46
	Concentrate quality, %	0.898	0.363	0.033
	Tail quality, %	0.127	0.025	0.005
Butyl xanthogenate : 4-(phenylazo)pyrocatechol	Foam yield, % 50.21			
	Extraction, %	86.30	91.97	86.26
	Concentrate quality, %	0.792	0.311	0.034
	Tail quality, %	0.127	0.027	0.005
Butyl xanthogenate : 5-(phenylazo)salicylic acid	Foam yield, % 47.54			
	Extraction, %	85.95	91.99	82.20
	Concentrate quality, %	0.914	0.331	0.042
	Tail quality, %	0.135	0.026	0.008

respectively. They are either at the level of PBX, or in the case of NAR surpass it. A mixture of PBX with BeTAR has weaker enrichment properties compared to one PBX.

CONCLUSIONS

It was established that under flotation conditions the reagents are in a single ionized form. They do not alter the surface tension of aqueous alkali solutions, which indicates the absence of activity at the reagent–air interface. The adsorption of reagents on the ore surface is mainly chemical in nature, and the degree of adsorption is determined by the number of aromatic and heterocyclic rings in the diazocomponent. Of the individual azo compounds studied, only 4-(phenylazo)pyrocatechol, 4-(2-benzthiazolylazo)pyrocatechol, and 5-(phenylazo) salicylic acid have enriching properties that are higher or close to those of potassium butyl xanthogenate. Other reagents, especially azo derivatives of resorcinol, turned out to be worse. The use of mixtures of azo compounds with potassium butyl xanthogenate in a ratio of 1 : 1 significantly increases their flotation properties. In some cases, they surpass it both in enrichment of Ni, Cu, Co, and in the degree of extraction of Ni and Co. Therefore, the studied reagents can be considered as potential modifiers for flotation.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest requiring disclosure in this article.

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