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THE ROLE OF SURFACTANTS IN PRECIPITATE FLOTATION AS SEPARATION ANALYTICAL METHOD

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Abstract: Sodium dodecylsulfate (NaDDS) is selected as the most appropriate tenside for effective flotation of Ag and Cd as an analytical procedure for metal trace preconcentration from water matrix. Atomic absorption spectrometry (AAS) is used as an instrumental method for determination of the concentrations of simultaneously preconcentrated analyts without any previous chemical conversion. The electrokinetic (ζ) potential of the collector particles, which is a relevant parameter for the selection a surfactant suitable for flotation, was determined electrophoretically. At pH 6, ionic strength 0.02 mol/L, Ag and Cd can be separated quantitatively (97.3 % Ag, 100.0 % Cd) by addition of 1 mL 0.5 % alcoholic solution of NaDDS, 10 mg Fe and 3 mL 0.1 mol/L hexamethylenedithiocarbamate (HMDTC$^-$) to 1 L of water sample.

Key words: preconcentration, metal traces, surfactants, flotation, atomic absorption spectrometry

1. Introduction

Surface active agents (surfactants or tensides) are potassium or sodium salts of long-chain organic acids, known as soaps and detergents. They are able to decrease the surface tension of the solvent in which it is dissolved or the tension at the interface between two immiscible liquids. Tensides are substances whose molecules consist of two well-defined regions: one which is oil-soluble (hydrophobic) and one which is water-soluble (hydrophilic). The hydrophobic part is non-polar and usually consists of aliphatic and aromatic hydrocarbon residues. The hydrophilic part consists of polar groups which can interact strongly with water (especially hydroxyl, carboxyl and ionic groups). Surfactants have many applications in industry, as well as in medicine, pharmacology, agriculture, etc. One of their first applications was in the mining industry, during the process of flotation concentration of valuable minerals in ores.

The role of a surfactant in a mineral flotation (so called *macroflotation*) is to transform the hydrophilic substances of interest in hydrophobic, to make possible the attaching of the gas bubbles to them and their separation from the impurities. When the flotation began to be applied as an analytical preconcentration method for trace elements (*microflotation*), the use of suitable tensides, helpful for this kind of separation, began to be investigated [1-6]. To perform microflotation, the tenside or system of tensides has to form a stable froth layer on the top of the liquid phase. If the foam layer is fixed well at the gas/liquid interface, it is less exposed on the reflux in the cell. Consequently, this facilitates the separation of the solid phase from the processed water phase of the system.

The aim of this work is to find the appropriate tenside or a combination of tensides, which would be the best for flotation separation of sublates of Ag and Cd as colligends and hydrated iron(III) oxide, $Fe_2O_3{\cdot}xH_2O$, and iron(III) hexamethylenedithiocarbamate, $Fe(HMDTC)_3$, as precipitate collectors. The type of tenside and pH were established by a series of flotations with previously optimized mass of collectors and ionic strength (I_c) The determination of Ag and Cd was performed by atomic absorption spectrometry (AAS).

2. Experimental

2.1. Apparatus

A Perkin-Elmer 11 00B spectrophotometer with Ag and Cd hollow cathode lamps was used (Table 1). For pH readings a digital Iskra pH-meter MA 5705 with a combined glass electrode was used. The flotation cell used to carry out the preconcentration was a glass cylinder (4 x 105 cm) with a sintered glass disc (porosity No. 4) at the bottom to generate air bubbling. The equipment for the electrophoretic determination of the electrokinetic (ζ) potential of the collector particle surfaces was a device analogous to Chaikovskii's equipment [7].

Table 1. Optimal AAS instrumental parameters

Parameter	Ag	Cd
Wavelength	328.1 nm	228.8 nm
Spectral slit	0.7 nm	0.7 nm
Lamp current	10 mA	4 mA

2.2. Reagents and standards

All chemicals used were of an analytical-reagent grade except for tensides sodium dodecylsulfate (NaDDS), sodium oleate (NaOL), sodium palmitate (NaPL), sodium stearate (NaST), benzethonium chloride (BTC), cetyltrimethylammonium bromide (CTAB) and triton X-100 (TX100). Dissolving an appropriate amount of surfactant in water (TX–100), in 95 % ethanol (NaDDS, NaOL, BTC, CTAB) and in 99.7 % propan-2-ol (NaPL, NaST) the solutions of tensides were made as 0.5 %. Stock solutions of colligends (1 g/L) were prepared by dissolving Ag and Cd nitrate in redistilled water. Iron(III) stock solution was made as 30 g/L solution of $Fe(NO_3)_3$. Before each investigation standard solutions were freshly prepared by diluting these stock solutions. HMA-HMDTC was made as 0.1 mol/L in 96 % ethanol. The pH was regulated by HNO_3 (0.1 mol/L) and of KOH (10%) solutions and I_c by a saturated solution of KNO_3.

The preconcentration procedure employed in this work has consisted of coprecipitation and flotation. The details are reported in the previous papers [5, 6].

3. Results and discussion

3.1. ζ potential of the collector particle surfaces

A series of electrophoretic measurements of ζ potential of two collector used were carried out within pH range, where the system is in the colloid state. At the moment when the system reaches pH at which its coagulation begins (c.a. 5.5), all further measurements using a device analogous to Chaikovskii's equipment are impossible. So the ζ potential values of the collector flocs was obtained only for the pH's of 3.5 to 5.44. The ζ potential of the first collector $Fe_2O_3 \cdot xH_2O$ particles at pH's from 3.5 to 5.44 have values of 25.0 to 28.0 mV, while the second collector $Fe(HMDTC)_3$ flocs have also positive but higher values of ζ potentials 68.4 - 69.0 mV. The positive sign of the ζ potential of two collectors used suggested that anionic surfactants should be necessary during the flotation.

3.2. Selection of surfactant

The choice of the most appropriate foaming agent was performed by a series of flotations of 1 L solutions containing 25 μg the colligends with 10 mg Fe, $3.0 \cdot 10^{-4}$ mol $HMDTC^-$, at

Applicability of diverse foaming reagents for colloid precipitate flotation of Ag and Cd with $Fe_2O_3 \cdot xH_2O$ and $Fe(TMDTC)_3$ as collectors (pH = 6.0, I_c = 0.02 mol/L, γ(Fe) = 10 mg/L, $c(HMDTC^-) = 3 \cdot 10^{-4}$ mol/L)

Ag	*R* / %						
pH	3.5	4.0	4.5	5.0	5.5	6.0	6.5
BTC	foam, no flotation						
CTAB	foam, no flotation						
NaDDS	no foam	no foam	30.1	71.5	83.6	97.3	96.9
NaOL	no foam	no foam	27.4	68.9	87.7	96.5	95.6
NaPL	no foam	no foam	no foam	32.7	83.3	83.3	78.1
NaST	no foam	no foam	no foam	77.3	89.6	89.6	59.1
TX–100	foam, no flotation						
NaDDS/NaOL	no foam	no foam	41.3	70.5	83.9	96.2	96.0
NaST/NaOL	no foam	no foam	62.1	65.0	65.0	69.8	71.3
NaPL/NaOL	no foam	no foam	26.8	29.3	83.5	89.5	89.5
Cd	*R* / %						
pH	3.5	4.0	4.5	5.0	5.5	6.0	6.5
BTC	foam, no flotation						
CTAB	foam, no flotation						
NaDDS	no foam	no foam	59.3	84.6	98.8	98.8	100.0
NaOL	no foam	no foam	19.8	44.2	81.8	79.9	93.9
NaPL	no foam	no foam	no foam	35.3	49.6	53.3	81.8
NaST	no foam	no foam	no foam	35.3	47.8	64.5	79.9
TX–100	foam, no flotation						
NaDDS/NaOL	no foam	no foam	4.8	51.4	70.2	81.8	95.2
NaST/NaOL	no foam	no foam	3.2	37.1	44.2	58.2	64.5
NaPL/NaOL	no foam	no foam	14.7	51.4	58.8	72.1	79.8

constant I_c (0.02 mol/L) within the pH interval of 3.5-6.5. To each solution 1 mL of 0.5 % solution of surfactant was added. The investigations with the cationic surfactants (BTC, CTAB) affirmed the suggestion of the previous investigation of ζ potential.

They foamed very well over the whole pH range investigated, a copious white scum was formed at the top of the liquid phase in the flotation cell, but the black precipitate of coagulated $Fe(HMDTC)_3$ remained in the water. The non-ionic surfactant (TX-100) was completely ineffective, too.

The anionic surfactants were shown to be more effective. They were investigated singly and in pairs (NaDDS/NaOL, NaPL/NaOL and NaST/NaOL) (Table 2). Within pH range of 3.0 to 5.0 their effectiveness was poor due to their protonation in acidic media. The data show that NaOL, NaST and NaPL singly, as well as in a pair of NaST/NaOL or NaPL/NaOL were less effective than NaDDS and the pair NaDDS/NaOL. Among all surfactant, NaDDS was the most effective and was selected as the most appropriate reagent for the proposed flotation procedure. The pair NaDDS/NaOL was shown also to be very good, but it gave an unnecessarily copious scum, which was very difficult to destroy. If NaDDS is used singly the destroying needs less acid which is one advantage of procedure.

4. Conclusion

The present paper proved that flotation separation of Ag and Cd with a collector mixture of $Fe_2O_3 \cdot xH_2O$ and $Fe(HMDTC)_3$ can be successfully performed using NaDDS as the most effective tenside at pH 6. NaDDS is the detergent, which provides good foaming in hard water because of its soluble calcium and magnesium salts. The use of this surfactant has facilitated the flotation separation from the processed water phase helping the preconcentration of colligends and, consequently, extending the range of conventional AAS determination for Ag and Cd.

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Апстракт. Натриум додецилсулфатот (NaDDS), е избран како најпогоден тензид за флотација на Ag и Cd во траги како аналитичка постапка за концентрирање. ААС употребена е како најпогодна инструментална метода, која овозможува определување на групно концентрирани аналити од водени матрикси без никакво претходно хемиско одвојување. Електрокинетичкиот (ζ) потенцијал на колекторските честички, од кој зависи видот на тензидот кој може да биде употребен за дадена флотација, определен е електрофоретски. При pH=6 и јонска јачина 0,02 mol/L, Ag и Cd можат квантитативно да се сепарираат (97,3 % Ag, 97,8 % Cd) со додавање на 1 mL 0,5 % раствор од NaDDS, 10 mg Fe и 3 mL 0,1 mol/L хексаметилен дитиокарбамат ($HMDTC^-$) на 1 L раствор.