STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLV, 1-2, 2000

REAGENTS WITH CHELATANT ACTION FOR Zn (II) AND THE POSSIBILITY OF USING THEM IN FLOTATION

GABRIELA OPREA and CRISTINA MIHALI

Universitatea de Nord Baia Mare

ABSTRACT. In this paper we followed up the data correlation of analytical chemistry of complexation for Zn (II) with chelatants in aqueous solution and the collector power of these reagents in the flotation of the minerals smithsonite and blende that contains this ion.

INTRODUCTION

The problem of scientific base creation for the research and the synthesis of new flotation reagents with some established before properties has constitued the subject of many works [1-3], in which it was proposed a chemical way of approach for solvating this problem. So, the selectivity of the flotation reagents action is considered from the point of view of the chemical nature of the reagent and the electronic structure of the cation that enters in the crystalline network of the floated mineral. For the reagents synthesis the active functional group contained by the reagents is important to be known because its fixation on the mineral must be selective.

It is considered that the fixation of flotation reagents on the mineral surface takes place, in many cases, through chemical bonds, when formed chelat compounds between superficial adsorption center and the reagent atoms. The reagent, which had proved that it is specific to a metallic ions group in solution probably, keeps its selectivity in certain conditions, even in the case of the adsorption at mineral's surface, which contains these metallic ions [3-16].

Unlike the specific action of organic reagents with the metallic ions in solution, in case of minerals, because of the unhomogenity of surface and of the different unsaturation of the superficial adsorption centers, the quantitative appreciation of adsorption requires experiments. The most results are realized in Hallimond minicells using pure minerals or in laboratory cells using artificial mixtures.

Among the reagents with chelatant action that form in solution chelat compounds with Zn(II), have been studied: 1-(2'-hydroxy-5-'sodiumsulfonate fenylazo) 2 naphtol (Violet solochrome R), 8-hydroxyquinoline (oxyne), 2-hydroxy-benzaldehide oxime (salicylaldoxime), o-aminobenzoic acid (antranilic acid), 2-quinoline carboxilic acid (quinaldinic acid) and trimetildiaminotetraacetic acid [17].

We followed the collecting action of the mentioned reagent over blende (ZnS) and smithsonite ($ZnCO_3$) to check how both the mineralogic form and the nature of the anion, influence the action of the collectors. The calcite and the magnesite that usually accompanies the utile minerals also in ores should float very little with these reagents. To check this, the reagents with chelatant action were tested in parallel with calcite and magnesite.

The stability of the complex formed between the cations Zn(II), Mg(II) and Ca(II) and the ligands depend on the pH, the modifications resulting from the variation of pH being characterized by the apparent constant of formation, K'.

We have taken in consideration the curves of variation log K' depending on pH for the following systems: chelatant-Zn(II), chelatant-Ca(II) and chelatant-Mg(II) [3].

EXPERIMENTAL

For the experimental determination we used a microflotation instrument named Hallimond cell [16].

The minerals used smithsonite, blende, calcite and magnezite had the grading between 100-250 μm. One gram of mineral is introduced in the cell and the collector sollution with known concentration and pH. The work conditions, kept constant were: the conditioning time (180 seconds), the flotation time (30 seconds), the debit of air (10 l/hour). The floated product is filtrated, dried in the drying stove at 80°C and weighted. The percent of recuperation, %R, for the studied minerals at different pH values and reactant concentrates was calculated. The experiments were orientated towards the determination of the optimum conditions necessary for a good recovery, the concentration of the reagent and the pH domain.

In table 1 are presented for each reagent the amount of the substances weighed (m), the solvent used and the molar concentration(c) of the obtained solution.

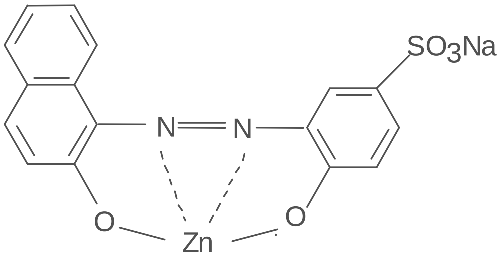
Table 1

The solutions of the reagents prepared in 1l marked balloon.

Nr.	Reagent	m (g)	Solvent	c, mol / l
1.	Violet solochrome R	0,366	water	10^{-3}
2.	Oxyne	0,145	acetone and water	10^{-3}
3.	Salicylaldoxime	0,41	water	$3x10^{-3}$
4.	Antranilic acid	0,137	water	10^{-3}
5.	Quinaldinic acid	0,173	water	10^{-3}
6.	Trimetildiaminotetraacetic acid	0,0306	NaOH solution	10^{-4}

RESULTS AND DISCUSSIONS

1-(2’-hydroxy-5’-sodiumsulfonate fenylazo)-2 naphtol *(Violet solochrome R)*



Structure I

This reagent forms with Zn (II) in solution a chelat compound with the structure I [17], which has a maximum stability for the pH between 7,5 – 10, as indicated in figure 1. It can be noticed that the Mg compound has also great stability for pH 11,5-13,5.

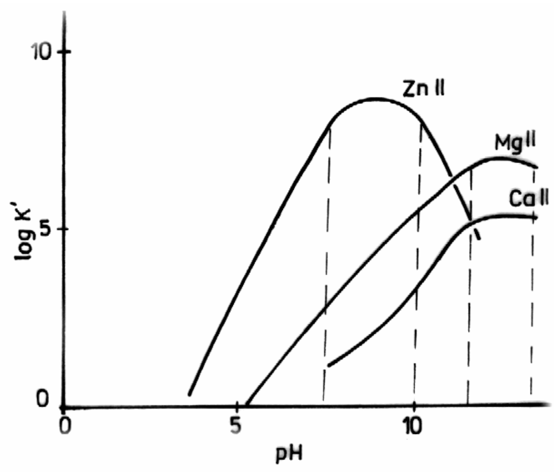


Figure 1
The variation of log K' with the pH for the compounds formed by Violet solochrome R with Zn (II), Ca (II) and Mg (II)

The reagent was utilised also for malachite and cerusite recovery using flotation [3].

For flotation we utilised 10^{-3} mol/l solution in the presence of 0,1 g/l isooctane at pH between 5,5 and 10,5. The results are presented in Figure 2 which shows that the maximum recuperations of 85% are obtained for blende at pH 8,5 and 84% for smithsonite at pH 10,5. Calcite floats little, 14%, and magnesite 20%.

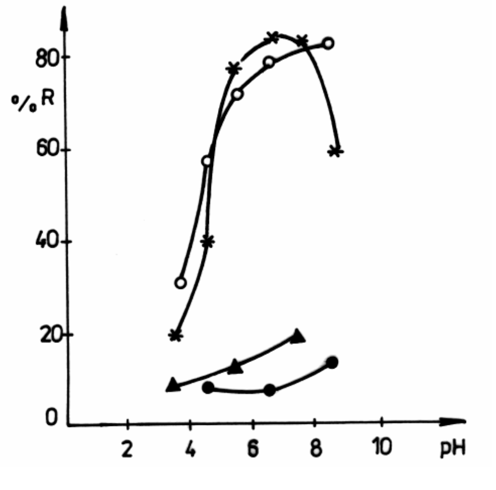
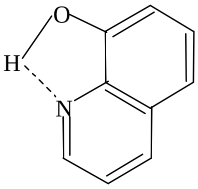


Figure 2
The variation of %R depending on the pH with 0,366 g/l Violet solochrome R and 0,1 g/l isooctane for: ✱ blende
○ smithsonite
● calcite
Δ magnesite

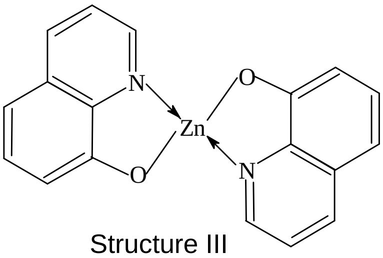
The results are in good concordance with the foresights deduced from the data of analytical chemistry.

8 – Hydroxiquinoline (oxyne)

This reagent presents the structure II and forms with Zn (II) a chelat compound with structure III.



Structure II



Structure III

If the precipitation takes place in solution, the Zn oxynate presents the maximum stability for the pH between 4 and 11,5 as indicated in figure 3. The Mg (II) and the Ca (II) oxynate have inferior stability.

In a series of reviews summarized the application of the oxyne is as collector in the flotation of the of zinc and lead oxydes and sulphures [5,12], silicates [8], blende, smithsonite, cerusite galene and copper oxidised ore [3, 14, 16].

During the determinations in the Halimond cell we have maintained constant the concentration of the oxyne, 10^{-3}mol/l, in the presence of 0,1g diesel oil and we have change the pH from 2 to 12.

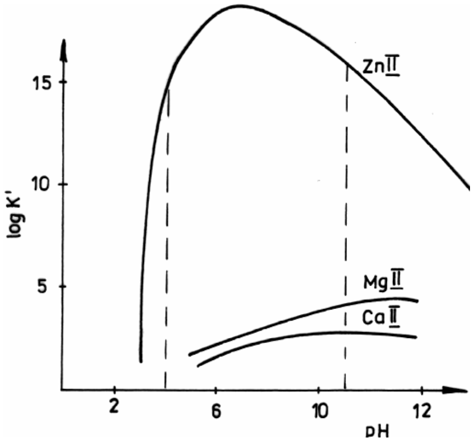


Figure 3
The variation of log K' with the pH for the Zn(II) oxynate, Ca(II) oxynate and Mg(II) oxynate

Figure 4 shows the variation of the recovery percent, %R depending on pH for blende, smithsonite, calcite and magnesite. The maximum recovery of 98% and 100% was obtained for blende with the pH between 5 and 10 and for smithsonite with the pH between 4 and 10. The magnesite and the calcite float little, the maximum recovery being 18%. The blende and the smithsonite float well in a pH-domain where the stability of the chelat compounds formed in the solution is maxim.

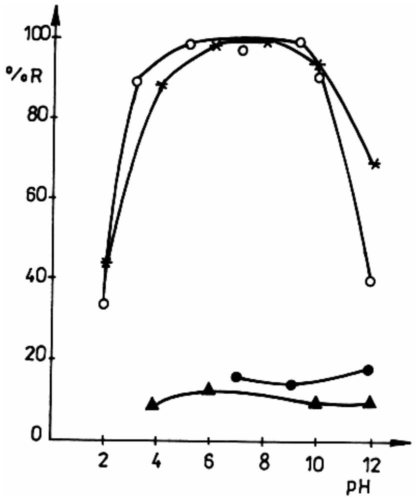


Figure 4

The variation of the recovery percent (%R) depending on the pH with 0,145g/l oxyne and 0,1g/l diesel oil for:

✷ blende
○ smithsonite
● calcite
Δ magnesite

For smithsonite at pH 7 we have followed the variation %R depending on the concentration of the oxyne solution in the presence and in the absence of diesel oil. The data are presented in Table 2 and in figure 5.

The maximum recovery (100%) is obtained only in the presence of diesel oil and at the minimum concentration of 10^{-3} g/l oxyne. The alone oxyne is only partly effective. We obtained maximum 38% recoveries for smithsonite.

Table 2.

The variation %R of smithsonit with the concentration of oxyne

The concentration oxyne, mol/l x10^{-3}		0,2	0,5	1	2	3	6	8
%R smithsonite	with 0,1g/l diesel oil	6	90	100	100	98	100	98
	without diesel oil	4	12	18	20	25	38	12

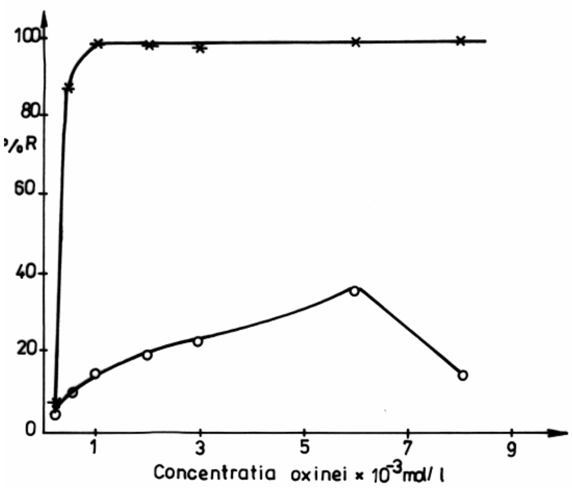


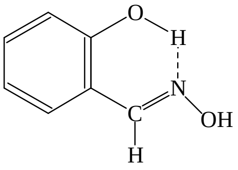
Figure 5

The variation of the recovery percent (%R) depending on the oxyne concentration on pH=7:

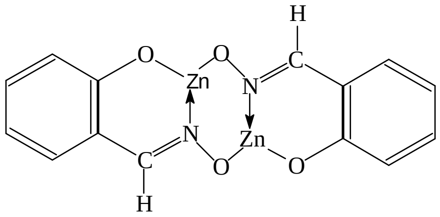
✷ with diesel oil
○ without diesel oil

Salicylaldoxime

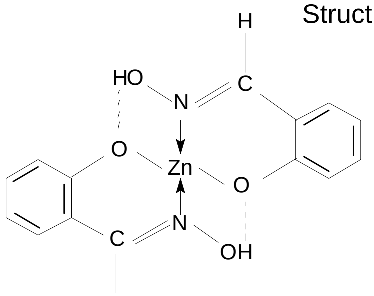
This reagent presents the structure IV and forms chelat compounds having structure V and VI for Zn (II) [9, 11].



Structure IV



Structure V



Structure VI

Salicylaldoxime was utilised as collector for the flotaton of the malachite, cerusite, smithsonite [3], casiterite [4], zinc and lead oxydes and sulphures [5].

We worked with $3x10^{-3}$ mol/l solution (0,41 g/l salicylaldoxyme) and 0,1 g/l isooctane at pH between 5 and 10. The obtained recoveries for blende and smithsonite are little as it is illustrated on Table 3. Calcite and magnesite float little, with recoveries of maxim 15% and 18%.

Table 3

The determination with 0,41 g/l salicylaldoxyme solution and 0,1g/l isooctane

%R	pH					
	5	6	7	8	9	10
Blende	24	28	15	16	7	10
Smithsonite	20	26	10	10	14	10
Calcite	-	-	12	14	15	10
Magnesite	-	8	10	18	14	10

Antranilic acid

In the analytical chemistry the antranilic acid is indicated as precipitation reagent for Zn (II) with which forms a chelatic compound.

The antranilic acid was tested for smithsonite and blende, minerals that contains Zn (II). To check the selectivity we used also calcite and magnesite, minerals that forms the barren gangue in the flotation.

The tested solution contains 0,137 g/l (10^{-3} mol/l) antranilic acid and 0,1 g/l light oil. We worked at pH between 3 and 11. The experimentals results are represented in Figure 6.

It was noticed that the maximum recuperations of 76% for blende and of 70% for smithsonite were obtained at pH 8.

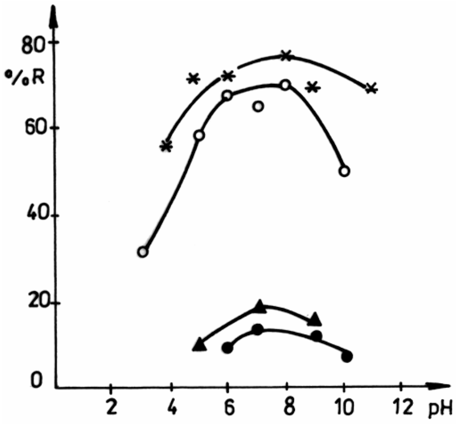


Figure 6
The variation of the recovery percent (%R) depending on pH with 0,137 g/l antranilic acid and 0,1 g/l light oil for:

✷ blende
○ smithsonite
● calcite
Δ magnesite

Quinaldinic acid

The reagent have chelating action for Zn (II) in solution.

The flotation tested solution have the following composition: 10^{-3} mol/l (0,173 g/l) chinaldinic acid and 0,1 light oil. We worked at pH between 3 and 11. As it is shown in Figure 7, both blende (with recovery of maximum 79%) and smithsonite (76% recovery) float well at pH 8. Calcite floats very little, 12% (at pH 10) and magnesite 18% at pH 9.

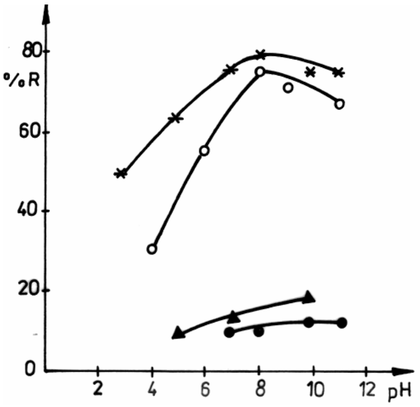
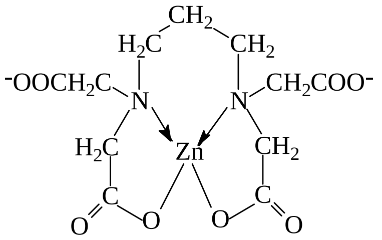


Figure 7
The variation of the recovery percent (%R) depending on pH with 0,173 g/l quinaldinic acid and 0,1 g/l isooctan for:

✷ blende
○ smithsonite
● calcite
Δ magnesite

Trimetilendiaminotetraacetic acid

The reagent forms stable chelats with Zn (II) having the structure VII, at pH between 6,5 and 10,3 as it is shown in Figure 8.



Structure VII

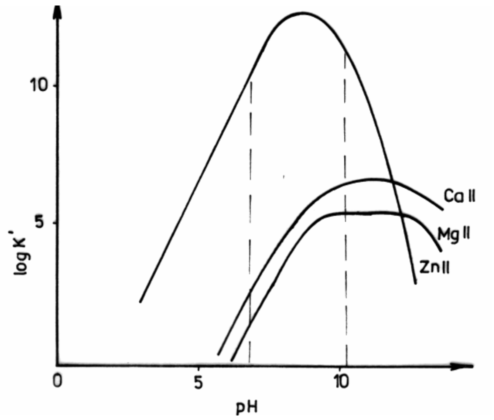


Figure 8
The variation of log K' depending on the pH for the chelatic compounds formed between the trimetilendiamino-tetraacetic acid and Zn(II), Ca(II) and Mg(II)

This solution don't float the smithsonite and the blende in contradiction with the enough great stability of the Zn (II) chelats in solution.

CONCLUSION

1-(2'-hydroxy-5'-sodiumsulfonate fenylazo)-2 naphtol (Violet solochrome R) in the presence of isooctanol floats well blende and smithsonite, realising maxim 85% separations. The results are in concordance with the foresight deducted from the analytical chemistry data regarding the apparent constant of complexation and the pH domain for the Zn (II) chelats formed in solution.

8 – Hydroxiquinoline (oxyne) floats well blende and smithsonite with maxim recoveries of 100% in a pH domain where the stability of chelatic compounds formed with Zn (II) in solution is maxim. The collector system must contain oxyne and also diesel oil because the oxyne forms with Zn (II) from the mineral's surface insoluble chelats at which, the diesel oil adheres by physical adsorption, realising the mineral's hydrofobisation.

Salicylaldoxime and trimetildiaminotetraacetic acid form stable chelatic compounds with Zn (II) in solution but they don't float the studied minerals.

The quantity of the utilised oxyne is greather than those of salicylaldoxime, but it can be reduced by recovery and recirculation or a better emulsification.

Antranilic acid and quinaldinic acid**,** in the presence of light oil floats well blende and smithsonite realising recoveries of maximum 76% and 79%, but in solution forms stable complexes with Zn(II).

Calcite and magnesite floats very little with the mentioned reagents and in a different pH domain by the one corresponding of the maxim recovery for blende and smithsonite that permits the separation of the barren gangue from the useful mineral.

For the reagents violet solochrome R, oxyne, antranilic acid and quinaldinic acid the realised recoveries for smithsonite (oxydated mineral of Zn) are comparable with the ones realised for blende (ZnS). This means that choosing a corresponding reagent with chelating action floats both the oxidised and the sulphuric minerals of Zn (II), which have not an identical action as a conventional collector.

The experimental results presented in this paper for smithsonite and blende recovery by flotation are comparable with those reported in the mentioned litterature.

REFERENCES

1. A. V. Glemboßki, Þvetnîie Metallî, vol. 9, p. 117-121, 1977;
2. V. I. Riaboi, Obogascenie Rud, vol. 6, p. 78-84, 1969;
3. J. L. Cecile, Thèse pour obtenir le grand Docteur de specialité, Univ. Orleans, 1978;
4. G. Rinelli, A. M. Marabini, V. Aless, In symposium A. M. Gaudin flotation AIME New-York, N. Y.,Vol. 1, p. 549-600, 1976;
5. G. Rinelli, A. M. Marabini, Intern. Min. Process. Congress, London, Vol. 20, p.29 1973;
6. S. Raghavan, D. W., Fuerstenau, J. Coll. & Interf. Sci., Vol. 50, p. 319-330, 1975;
7. H. D. Peterson, M. C. Fuerstenau, J. D. Miller, Trans. of AIME, Vol. 232, p. 388-392 1965;
8. M. Marabini, G. Rinelli, Trans. IMM C 82 Vol. 805, p. 225-228, 1973;
9. M. A. Jarski, E. C. Lingafelter, Acta. Cryst. Vol. 17, p. 1109-1112, 1964;
10. M. C. Fuerstenau, R. W. Harper, J. D. Miller, Trans of AIME, Vol. 247, p. 69-73, 1970;
11. J. L. Cecile, Rapport BRGM nr. 80 SGN 407 MIN, p. 232-235, 1980;
12. L. Usoni, G. Rinelli, A. Marabini, AIME annual meeting, vol. 71 B, p. 10-21, 1971;
13. S. I. Gorlovski, Z. I. Yeropkin, E. M. Kovalov, 8-th Intern. Min. Process. Congress Leningrad, Vol. B3 p. 8,1968;
14. J. L. Cecile, G. Barberi, Mineraux et minerais, Nancy, p. 26-29, 1978;
15. G. Oprea, Scientific Symposium with International Participation: Technologies for processing of refractory raw materials and for environment protection in areas with extractive industry, vol. I, p. 127-135, Baia Mare, 17-19 May 1995;
16. G. Oprea, C. Mihali – Studia Univ. Babes Bolyai, Ser. Chemia, vol. 43(1-2), p. 116-125,1998, Cluj Napoca;
17. A. Rigbom, Les complexes en chimie analitique, Ed. Duond, Paris, 1967.