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RECOVERING SEPARATION OF Cu(II) FROM DILUTE SOLUTIONS BY FLOTATION WITH ANIONIC COLLECTOR. CHARACTERIZATION OF THE COLLECTOR–COLLIGAND INTERACTION

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Abstract

The present paper reports the results of the determination of the composition and stereochemistry of the substances concentrated in the foam (sublate) during the separation of Cu(II) ion from dilute solutions (20–200 μg/ml) by flotation.

A 2-ethylhexanoic acid sodium hexanoate mixture was used as collecting agent.

Keywords: flotation, Cu(II) 2-ethylhexanoic-acid-sodium, collecting agent.

It is known that research in an interdisciplinary field like the flotation of ionic molecular and colloidal systems, involves fundamental problems of separation requiring a complex investigation of the phenomena [1], [2], [3]. The flotation of precipitates is a separation method with high separation efficiency ($R > 95\%$) in a very short flotation time (2–5 min.) [1–5].

These characteristics explain the choice of flotation for the separation of Cu(II) as $Cu(OH)_2$ precipitate, using sodium 2-ethylhexanoate in 2-ethylhexanoic acid as a collector. In the present paper studies on the composition and structure of the insoluble species concentrated in the foam obtained after the separation of Cu(II) by flotation from dilute aqueous solutions with 20–200 μg/ml concentration are described which clearly indicate the colligand–collector interaction [5], [6], [7].

The study is interesting mainly in respect of insoluble sublates with low concentration of the colligand ($1 \cdot 10^{-2} - 1 \cdot 10^{-4}$ mol/l) in which case isolation by common procedures in the aqueous phase is not efficient.

In the first stage of research the optimum conditions for the separation of Cu(II) from dilute solutions with sodium 2-ethylhexanoate in 2-ethylhexanoic acid as collector were determined.

The experimental results and the high separation yields (R > 95%) prove the efficiency of this method. In the literature [1], [6] two possibilities of the colligand–collector interaction are considered:

- the colligand–collector interaction is established in the solution and the hydrophobic product formed is adsorbed on the surface of the gas bubbles (the mobile phase of the system).
- in the first stage, the collector is adsorbed by the gas bubbles with the formation of an electrical field around it and the colligand ion is concentrated around it a counter ion.

The possibility of either mechanism depends on the nature of the colligand–collector interaction as follows [1], [6].

When an insoluble coordination combination is formed, the first mechanism is possible, when a compound of the ion pair type is formed, the sublate cannot exist in solution as a unit, therefore the second mechanism is possible.

The compound forming the sublate separated in the best conditions was studied by interpretation and correlation of the data of chemical and physicochemical analysis.

Experimental

1. Methods. Aqueous solutions of $CuSO_4 \cdot 5H_2O$ with a concentration of $3 \cdot 10^{-2}$ mol/l were adjusted to pH = 7.5 and 11.0 by adding 2 mol/l KOH, after which it was treated with collector under stirring at colligand–collector $C_C : C_{Cu(II)}$ molar ratios of 2 : 1 and 1 : 1.

The sample (3000 cm^3) was introduced into the flotation cell [1], [3] where it was diluted with pressurized water at $4 \cdot 10^5 N/m^2$ at a $V_{sample} : V_{water}$ ratio of 3 : 1. After 2–5 minutes the insoluble blue sublate obtained at the ligand surface was collected.

After drying at room temperature, the sublate was studied physicochemically for establishing the colligand–collector interaction type.

2. IR Spectra were recorded using a Perkin Elmer spectrophotommeter in the 400–4000 cm^{-1} range, using the KBr pellet technique.

3. Reflectance electronic spectra were recorded at room temperature by a Carl Zeiss Jena VSU-2G spectrophotometer, in the 360–1200 nm range using MgO as reference material.

4. Thermal analysis was made with a Paulik–Paulik–Erdey type derivatorgraph (MOM, Hungary), with simultaneous registration of the T, TG, DTG, and DTA curves in the 20–900 °C temperature range.

The curves were recorded in air atmosphere at a heating rate of 10 °C/min TG sensitivity = 200 mg, DTA sensitivity = 1/10, platinum crucibles, medium = static air, reference material = Al_2O_3, calcined at 1200 °C.

Results and Discussion

Six samples noted (1,... ,6) differing in the pH and the colligand–collector ratio (2 : 1; 1 : 1 and without collector) used during flotation were analysed for establishing the colligand–collector interaction. The characteristics of the samples are presented in *Table 1*.

Table 1
The characteristics of samples

No. of sample	Conc. of Cu(II) (mol/l) C_0	Collector: Cu(II) molar ratio	pH of flotation	Dilution $V_{\text{sample}} : V_{\text{water}}$
1.	$3 \cdot 10^{-2}$	–	7.5	3 : 1
2.	$3 \cdot 10^{-2}$	–	11.0	3 : 1
3.	$3 \cdot 10^{-2}$	2 : 1	7.5	3 : 1(A)
4.	$3 \cdot 10^{-2}$	2 : 1	11.0	3 : 1(C)
5.	$3 \cdot 10^{-2}$	1 : 1	7.5	3 : 1
6.	$3 \cdot 10^{-2}$	1 : 1	11.0	3 : 1

The IR spectra of two samples (No. 3 and No. 4; *Table 1*) were recorded for characterizing the structure of the compounds obtained. Literature [8], [9], [10] shows that in saturated alkylcarboxylic acids the influence of the carboxyl group appears only on the CH_2 group in α position. An intense band assigned to the shearing vibration of the CH_2 group next to the carboxyl group appears.

This vibration disappears in substituted acids, to which type 2–ethylhexanoic acid belongs.

The presence of the salt is characterized by two bands of the COO^- group. *Table 2* gives the characteristic IR frequencies and their possible assignations for the separated sublate.

The absence of the ν_{CO_2}-valence vibration (1550–1610 cm^{-1}), the replacement of the ν_{CO} (asym.) vibration in the sublate in comparison with the free ligand and also the presence in the spectra of sublate vibrations, with some bands near 3200–3400 cm^{-1} shows the possibility of a coordinated intersection with an O atom donor. The frequency δ_{MOH} present in the spectra of the sublate typical of the OH coordinated with central ion

Table 2

Characteristic IR frequencies (cm^{-1}) of the compounds and their probable assignation

No.	Compound	ν_{CO_2}		ν_{OH}	δ_{HOH}	ν_{CH}		δ_{HOH}		Observation
		asym.	sym.			asym.	sym.	asym.	sym.	
1.	R*-COO(H)	1200–1300	1550–1610	–	–	2800–3000	900–1000	1400–1480	1350–1400	ligand
2.	Hydroxo-complex pH = 7.5(A) sample 3	1050–1150	–	3200–3420	1550–1600	–	550–650	–	–	sublate
3.	Hydroxo-complex pH = 11.0(C) sample 4	1050–1150	–	3200–3420	1550–1600	–	550–650	–	–	sublate

R* = C_7H_{15}; 1. with NaCl and 2, 3 in KBr pellet

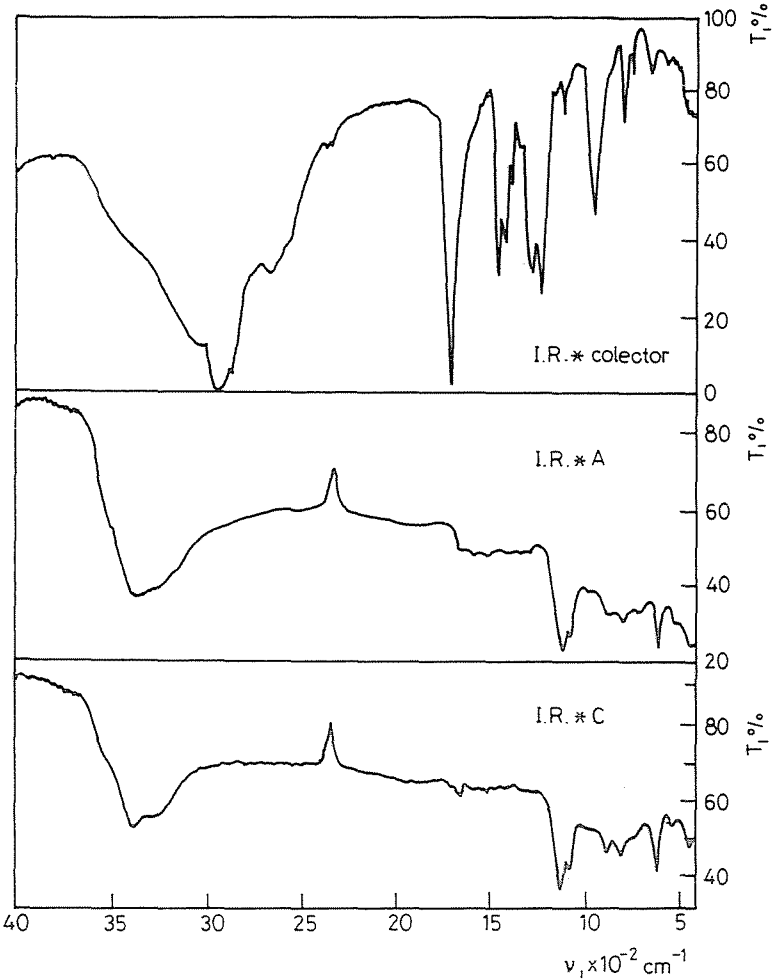


Fig. 1. IR spectra of the collector and sublated samples 3 and 4

shows a bonding with the O atom from the hydroxyl group, as presented in *Fig. 1*.

The ν_{CO} disappeared in both samples because the three-centrė delocalisation disappeared, only the –C–O– coordiantion bond remained unchanged.

The ν_{CH} (aliphatic) from the sublate is masked in the sublate by the ν_{OH}. In the sublate the C–O bond is shortened and the ν_{CH} is evidently replaced by another value of ν^* (600 cm^{-1}). We supposed a harder bond in the sublate, probably because of the inductive +I effect from the aliphatic chain.

The δ_{HOH} signal of sample A disappeared in the spectrum of sample C, because at ph = 11.0 the HO^- group is bonded in the place of water, $\Delta_{o(HO^-)} > \Delta_{o(HOH)}$ in octahedral structure with Jahn–Teller effect, with a configuration d^9 of the Cu(II) ion.

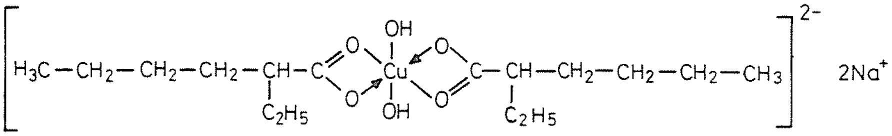
The electronic reflectance spectra for two samples (No. 3 and No. 4; *Table 1*) were recorded also in order to establish the most probable streochemistry of the sublates obtained.

In the electronic spectra of the compounds studied the positions of the most intense absorption bands are similar but they have different intensities and a slight shift towards higher values was observed for the sublate separated at pH = 11.0.

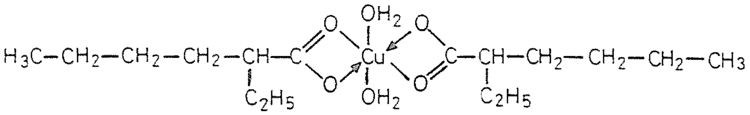
The electronic reflectance spectra show also a strong flat spectrum for sample A, probably because water is coordinated in the place of the HO^- group (C). The shift toward lower λ values shows the charge transfer.

All the spectral data have evidenced the probable structure of the separated compounds as proposed below:

(sample No. 3; *Table 1*)



(sample No. 4; *Table 1*)



The probable structure of the separated compounds should be verified by elemental analysis and also by conductivity determinations.

For obtaining some data on the thermal stability of the separated compounds [11] and of the products obtained by their thermal decomposition, the four samples (No. 3, 4, 5, 6; *Table 1*) and two samples of $Cu(OH)_2$ obtained at pH = 7.5 (sample No. 1; *Table 1*) and pH = 11.0 (sample No. 2; *Table 1*) were subjected to thermal analysis.

The DTA and TG curves obtained under the conditions mentioned above were similar for both series of analysed samples.

The DTA curves show an exothermal effect at 210 °C, due probably to the oxidation of the organic rest and an endothermal effect at 775 – 800 °C,

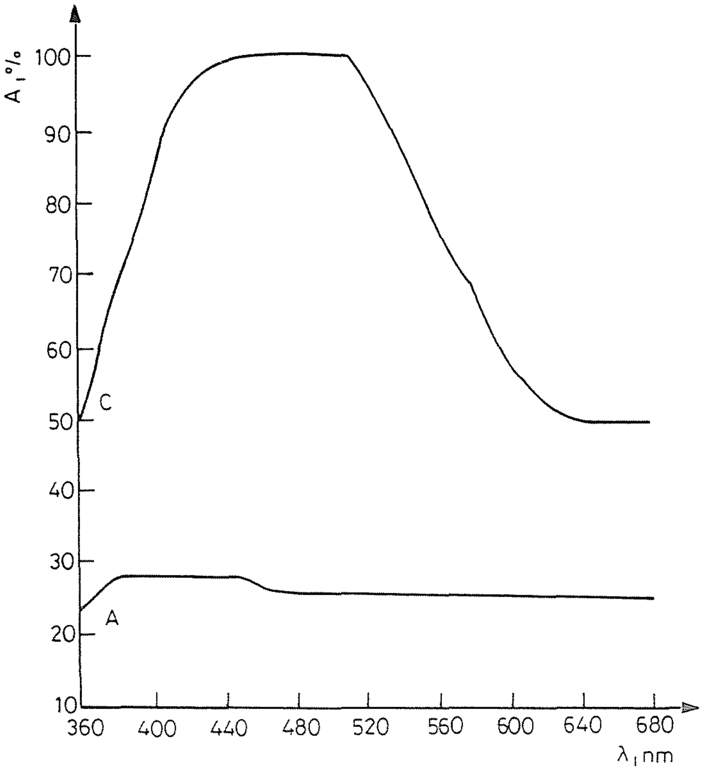


Fig. 2. The electronic reflectance spectra for sublated samples 3 and 4.

due to the decomposition of the hydroxo species to yield CuO as the final product of the transformation.

Both effects indicated by the DTA curves are accompanied by mass losses of the samples.

The DTA and TG curves characteristic of the compounds are given in *Fig. 3* (sublate at pH = 7.5) in comparison with $Cu(OH)_2$ at the same pH, with a $C_C : C_{Cu(II)}$ ratio of 2 : 1.

In *Fig. 4* is shown the sublate at pH = 11.0 in comparison with $Cu(OH)_2$ at pH = 11.0.

In *Fig. 5* is shown the sublate at pH = 7.5 with a $C_C : C_{Cu(II)}$ ratio of 1 : 1.

In *Fig. 6* is presented the sublate at pH = 11.0 with the same ratio.

The mass losses of the samples, calculated from the TG curve are similar to those obtained by stoichiometric calculations, and correspond to the formation of CuO.

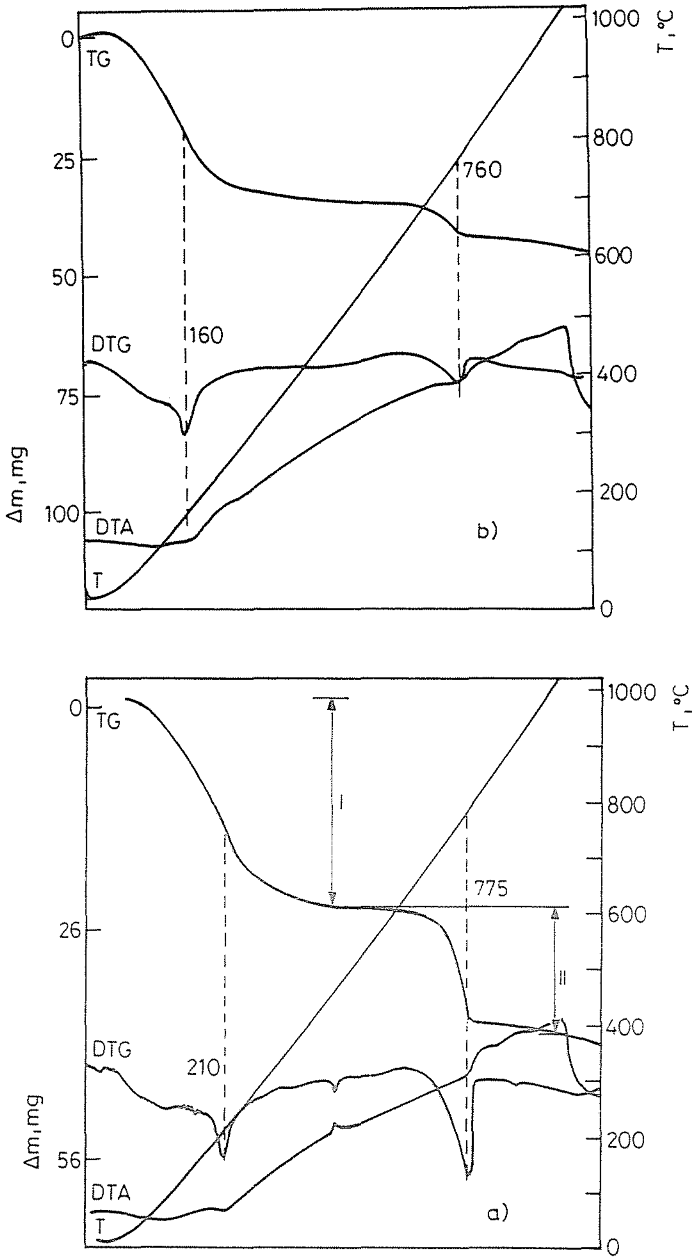


Fig. 3. Thermoanalytical curves of $Cu(OH)_2$: (3.a.) and sublates: (3.b) at pH = 7.5 and $C_C : C_{Cu(II)}$ molar ratio of 2 : 1

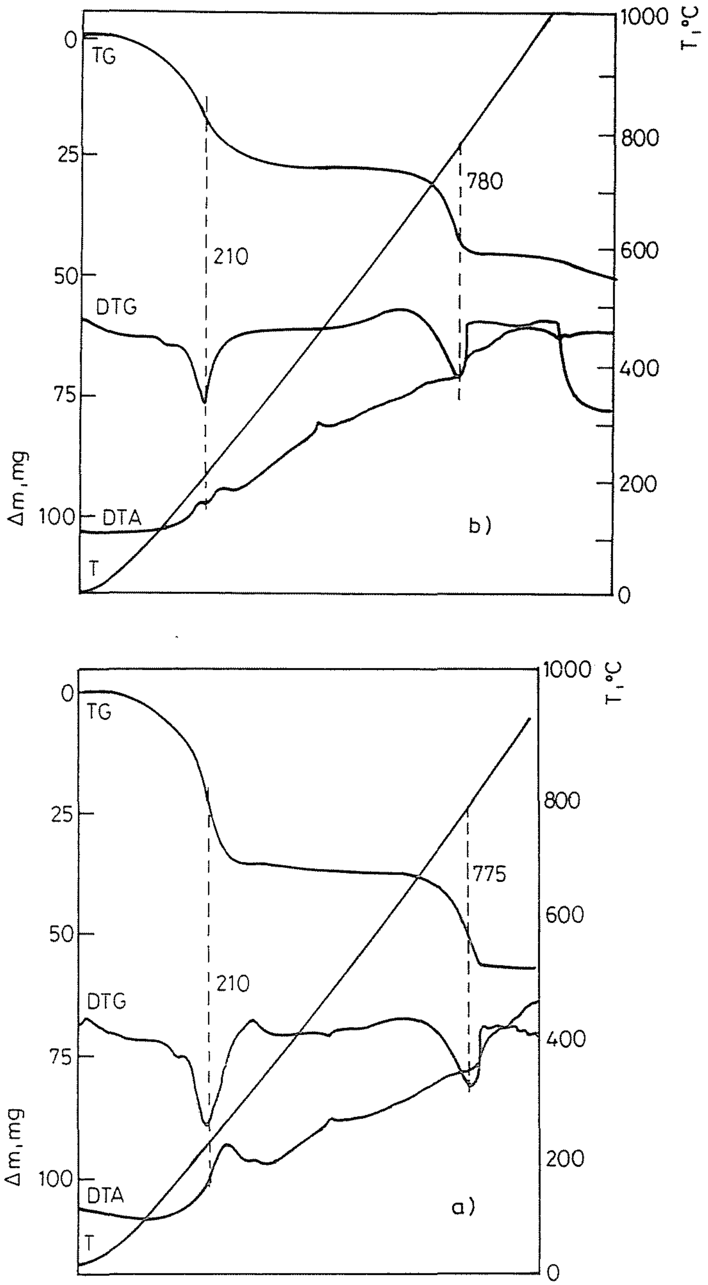


Fig. 4. Thermoanalytical curves of $Cu(OH)_2$: (4.*a*.) and sublates: (4.*b*) at pH = 11.0 and $C_C : C_{Cu(II)}$ molar ratio of 2 : 1

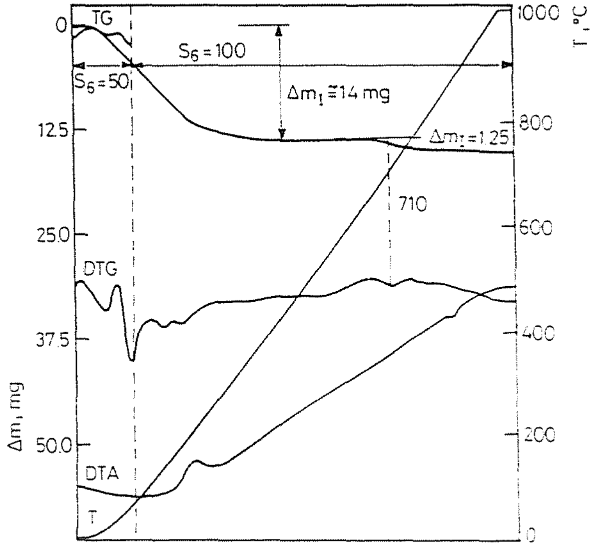


Fig. 5. Thermoanalytical curves of a sublate at pH = 7.5 and $C_C : C_{Cu(II)}$ molar ratio of 1 : 1

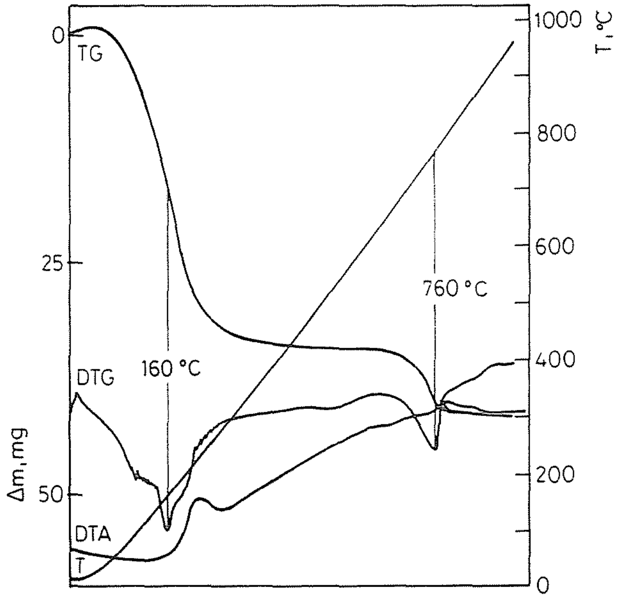


Fig. 6. Thermoanalytical curves of a sublate at pH = 11.0 and $C_C : C_{Cu(II)}$ molar ratio of 1 : 1

The DTA and TG curves of the four samples are similar to those of $Cu(OH)_2$ samples.

Conclusions

The results obtained show that the collector–colligand interaction in the separation product in the flotation of Cu(II) ion as a $Cu(OH)_2$ precipitate with the collector mixture 2-ethylhexanoic acid–sodium hexanoate is of the coordination type.

This type of interaction is special for the insoluble sublates separated at a $C_C : C_{Cu(II)}$ molar ratio of 2:1.

Our investigation offers a new field for using iono-molecular flotation as an efficient method for recovering Cu(II) from dilute solutions.

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