

Identification of the Formed Complex During Extraction of Copper (II) from Sulphuric Acid by Means of Sodium Diethyldithiocarbamate (SDDT)

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The sulphuric acid is widely used in many industrial applications, due to its interesting physico-chemicals properties, along with its low cost.

Generally, the fresh or recycled sulphuric acid used in industry is contaminated by cations such as Fe^{3+} , Zn^{2+} , Cu^{2+} and which are impurities and may influence its physico-chemicals properties.

This present work concerns the study of the complexation step involved in a liquid-liquid extraction purification process for the purification of sulphuric acid solutions of different molar concentrations, contaminated by Copper cations. The complexing agent tested is the sodium diethyldithiocarbamate (SDDT).

Different reliable techniques of analyses like TGA, DSC, UV-vis, XR and elementary analyses were used to demonstrate that the acidity did affect neither the complexing agent nor the formed complex.

The obtained results compared very well with reported values in the literature and hence reinforcing the adopted approach.

1. Introduction

Sulphuric acid is an important chemical which is involved in many sensitive industrial fields such as textile, car batteries manufacturing, production of fertilizers through superphosphate and ammonium sulphate, metallurgical, fabrication of explosive materials, etc. However, very often any freshly produced or recycled sulphuric acid is contaminated by heavy metal cations, mainly Fe^{3+} , Zn^{2+} and Cu^{2+} (Martin, 1999), a fact which may greatly influence the processes involved in the above cited industrial fields, from both economical and environmental considerations. Hence, these impurities must be imperatively removed, requiring then a treatment of the acid. Various techniques do exist to achieve this task and one can cite filtration, flotation, electrolysis, precipitation and liquid-liquid extraction which is the main topic of the present study.

In fact in the literature many research works were reported and dealt with the elimination of heavy metal cations like iron, cobalt, nickel, cadmium, etc. from sulphuric acid solutions, using liquid-liquid extraction and the main conclusion was that the efficiency of this separation technique depended upon the considered complexing agent. Consequently this has been the main motivating factor to carry out the present

experimental work where the elimination of Cu^{+2} from synthesized sulphuric acid solutions of concentrations ranging from 0.2 to 7M at 25 °C, is considered with sodium diethyl dithiocarbamate (SDDT, $\text{C}_5\text{H}_{10}\text{NS}_2\text{Na}$) as the complexing agent to form $\text{Cu}(\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4)$ ($\text{Cu}(\text{DDT})_2$) (Skoog, 2003), at a pH of 8.5, a value within the range of 4 to 11 as suggested by (Mendham et al., 2006; Skoog et al., 2003).

The approach is similar to that generally used for the extraction of heavy metals in an acidic medium, by organophosphorus and oximes extractants (Amine et al. 2004; Simpson et al., 2004).

The extraction is based on the following two main steps:

1. A complex formation between the present ionic species in the solution and the complexing agent;
2. A phase separation after a migration of the formed complexes into the organic phase.

However in the literature, some research workers insinuated that a high acidity may lead to a decomposition of SDDT giving CS_2 (Sceney et al., 2003; Zegmunt and Bacerzak, 2000). This has then encouraged the study of the stability of the formed complex, by following the colour of the aqueous phase, before any contact with the chloroform organic phase, which shifted from brown to green, when the acid concentration reached 4M. An identification of the formed complexes was then necessary to confirm whether the induced colour change of the aqueous phase is due to any complex decomposition or not, by means of reliable techniques of analysis such as the thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-rays (XR), UV-vis, and an elemental analysis.

Also the production process of metallic pollutants free sulphuric acid is characterised by an important aspect which consists of the thermal decomposition of the formed metal dialkyldithiocarbamates, leading to compounds having widespread industrial applications such as foam rubber, fungicides, effective heat stabilisers, anti-oxidants, etc. Therefore the present process has more than one advantage since it can lead to clean sulphuric, to preserve the environment by reducing the emissions and finally to form promising species with important industrial applications as reported in the literature (Baron et al, 2002; Faraglia et al, 2002).

2. Experimental

2.1 Methods and materials

Sulphuric acid and the sodium diethyldithiocarbamate (SDDT) were of analytical grade and supplied by Sigma Aldrich Company. Hydrated copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was obtained from Panreac Quimica, Spain.

The thermogravimetric measurements were performed using a TGA Q50 V6.7 Build 203 analyser, operating with a heating rate of 5 °C/min under air atmosphere. A DSC92 SETARAM was used for the measurements of the SDDT complex melting temperature and the corresponding enthalpy. UV-vis spectra were obtained by means of a Shimadzu 1601 UV/vis spectrophotometer.

2.2 Extraction procedure

The experiments were carried out in two separate Erlen- Meyers containing 50 mL of a 0.5 and 7M sulphuric acid solutions, of a Cu^{2+} mass concentration of 1 g/L. A mass of 4 g of SDDT and a volume of 50 mL of chloroform were added to each solution. The resulting solutions were agitated mechanically for one hour at an agitation speed of 600 rpm. The system is then left at rest for 15 minutes in order for the system to reach equilibrium and the organic phase was separated from the aqueous one kept under the vapour aspirator to evaporate the organic solvent. The obtained complexes are kept at 50 °C in a desiccator ready for analysis.

3. Results and discussion

3.1 XR and UV-visible analyses

The analyses of the two samples spectra show the existence of crystalline structure of monoclinic type.

It is also established that the SDDT reacts selectively with non absorbing species to give products which highly absorb in the UV or the visible. This is presently confirmed for the case of Copper.

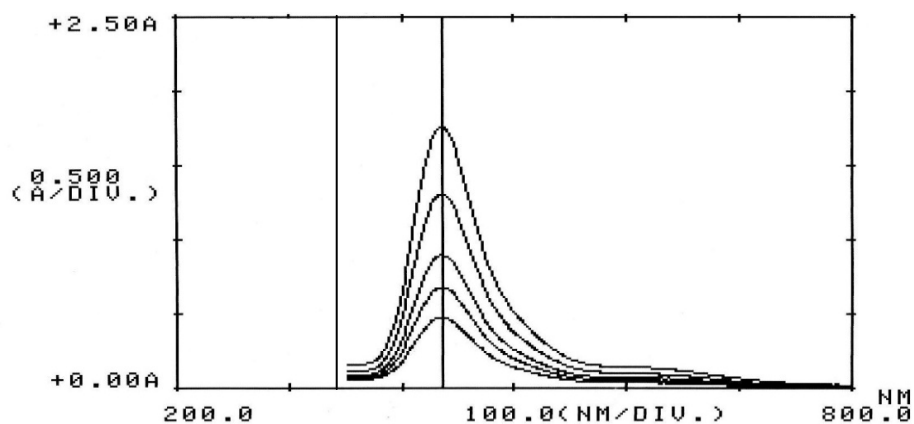


Figure 1: UV-Visible spectra of the organic phase for different sulphuric acid concentrations in the range 0.2-7M, $[\text{Cu}^{2+}] = 63 \text{ mg/L}$, agitation speed = 600 rpm and agitation time 1 h.

Figure 1 shows similar spectra for solutions of the same Copper mass concentration of 63 mg/L but with different acid concentration in the range of 0.2 to 7M and at a pH varying from 0.45 to 1.66 with a maximum wavelength λ_{max} equal to 436 nm, confirming exactly the value given in the literature for the $\text{Cu}(\text{DDT})_2$ complex in Chloroform (Mendham et al., 2006; Skoog, 2003). Therefore one may conclude that the acidity did not really affect the SDDT which can safely be used as a complexing agent

at pH values less than 4. To confirm this result an elementary analysis was also carried out as shown in the following section.

3.2 Elementary analysis

The results for the elementary analysis for C, H, N, S and Cu for the two samples are shown in the following Table 1 where it can easily be seen that the respective percentages for each element are very close and hence the complex is the same compound and is Cu (C₁₀H₂₀N₂S₄) indeed.

Table 1: Elemental analysis for both complexes

	Complex1	Complex2	Calculated
C%	34.23	31.11	33.35
H%	5.67	5.67	5.60
N%	7.64	6.96	7.78
S%	34.35	33.07	35.62
Cu%	16.69	14.58	17.64

3.3 Study of the thermal decomposition

The TG curves of Figure 2 show an initial decomposition at lower than 200 °C. The decomposition of complex 1 proceeds essentially in one stage and shows a mass loss of 76.51 % and an approximate decomposition temperature of 220 °C with a residue of 23.39 % at 350 °C. Complex2 proceeds in two stages and shows a first decomposition at lower than 100 °C and a mass loss of 6.68 %. This can be explained by the presence of water and/or solvent. A second decomposition of 70.06 % is also shown at an approximate temperature of 220 °C and a residue of 23.26 %.

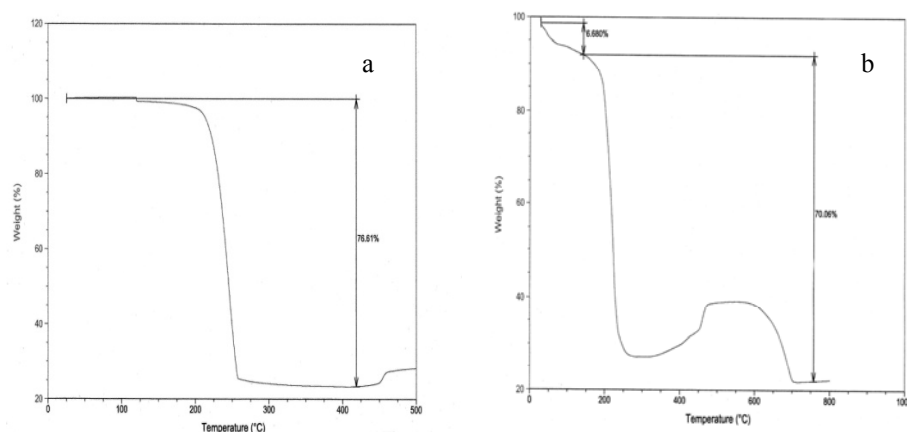


Figure 2: TG Thermograms, (a) Complex1 and (b) Complex2.

From the literature, the residue for both complexes is Cu₂S with a theoretical percentage of 26.55 %, close to the obtained values (Ali et al., 2004; Ringkasan, 1982; Sceney et

al., 1976; Singhal et al., 2004). At temperature over 400 °C, the increase of the mass is due to CuSO₄ in the air (Singhal et al., 2004). Therefore it can be concluded once more that both complexes are Cu (C₁₀H₂₀N₂S₄) and that the acidity did not have any influence, neither on the complexation reaction nor on the formed complex.

The TG results were also confirmed by the results given the DSC curve of Figure 3 where three distinct endothermic peaks are shown, corresponding, respectively, to 43.9 °C, 150.8 °C and 200.7 °C.

The first and second peaks are probably due the presence of some remaining water or Chloroform in the complex crystals, whereas the third peak corresponds to the melting of the complex with an onset temperature of 196.61 °C and a melting enthalpy of ΔH=38.113 kJ/mol.

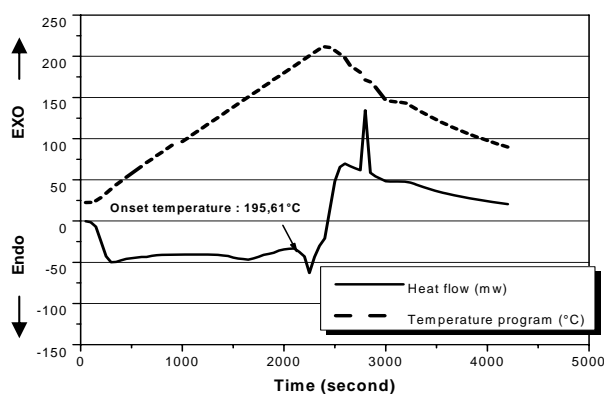


Figure 3: DSC thermogram for the complex.

These values are in an excellent agreement with the reported values of 197 °C and 41.27 kJ/mol for Cu (C₁₀H₂₀N₂S₄) (Stephenson, 1987).

4. Conclusion

The results confirms that the sodium diethyldithiocarbamate (SDDT) can be used efficiently in the purification of sulphuric acid when eliminating the heavy metals cations such as Cu²⁺, by liquid-liquid extraction, with Chloroform as the diluent. In fact with acid concentrations between 0.2 and 7M and at a pH in the range of 0.45 to 1.66, an extraction rate between 86.7 % and 97 % could be achieved. These figures are close to those obtained for the case of the elimination of the cations Fe³⁺ from sulphuric acid solutions of concentrations ranging from 0.5 to 1M with an extraction rate lying in the range of 85.46 - 97.8 % (Souheila and Hassan, 2009).

Finally, through this study, it can be ascertained that the SDDT can be safely used as a complexing agent for the elimination of Cu²⁺ from sulphuric acid solutions of different

molar concentrations by liquid-liquid extraction, at a pH less than 4, without any degradation by the acidity and the resulting complex is $\text{Cu}(\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4)$.

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