

Spectrophotometric Study of Copper(II), Nickel(II) and Palladium(II) Complexes of Bis(Benzoylacetone)meso-Stilbeneimine (BA2S) Using Solvent Extraction Technique

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Summary: The spectrophotometric study of copper(II), nickel(II) and palladium(II) complexes BA2S has been made here. The reagent and metal complexes were characterised by UV, VIS and IR methods [1] by copper, nickel and palladium from an aqueous solution into chloroform using reagent was optimised. The copper, nickel and palladium were extracted upto 94,64, and 97 percentages respectively.

Introduction

In performing spectrophotometry an avoidance of overlapping absorption bands of solvents or contaminants has been made, and this only happens in excess reagents that was found to be present in sample. The assurance in achieving successful and an accurate results the solvents were examined and tested based on physical spectral characteristics and their purity. It has been not exhibit extraneous impurity peaks in the spectral region. The evaluation of solution stability and its absorbance have been kept in view from time to time.

It has been found that many organic compounds absorb quite strongly by double beam spectrophotometer, while only a limited number of inorganic ions

do, and it is normal procedure of inorganic absorption spectrophotometry to add a molecule or reagent species to the solution of an inorganic ion which will react with it and in process bring about marked change in spectral absorption characteristics of the reagent.

Since iron(II) ion was found weakly coloured a complexing agent 1,10-phenanthroline [2] was added to form an ion association species that was found suitable for the determination of small amounts of iron.

In present work copper(II), nickel(II), and palladium(II) complexes were prepared by reported

method [3] and spectrophotometric studies were carried out on Hitachi-220 spectrophotometer followed the pattern of solvent extraction of copper(II), nickel(II) and palladium(II) complexes of meso-BA2S at pH 6.5 (acetic-acetate buffer) in chloroform.

The pH measurements were made using (CD 620 digital WPA) pH meter with glass electrode and saturated reference electrode.

Results and Discussion

Complexation and solvent extraction

Metal ion solution (0.5-1 mL) containing (100-100 ug) of copper, nickel and palladium was added to (2 mL) acetic-acid buffer at pH 6.5 alongwith addition (4 mL) of methanol and (4mL) of 0.8% w/v reagent in chloroform followed by (1.0 g) of potassium bromide. The solution was warmed for 20 minutes and shaken on mechanical shaker (Gallen-Kamp) for one hour. The organic layer so obtained was separated and required absorbance maxima of 555 nm, 408 nm, and 404 nm, respectively against the reagent in chloroform using Spectrophotometer (Hitachi-220). The percentage extraction for each of metal ions was evaluated from the standard calibration curves as drawn from pure complexes are shown in Fig-1(a). The absorbance concentration relation for different metal ions are shown in Table-2.

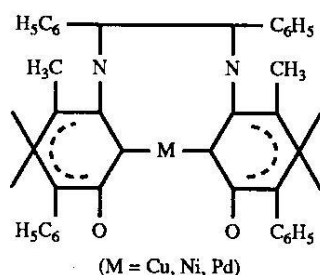


Fig.1(a): Showing structure of copper, nickel and palladium complexes of meso-BA2S.

Experimental

1. Preparation of N'-benzoyl-N'-acetyl meso-stillbenediimine

A mixture of freshly prepared by hydrolysis of amarine (100 g), acetic anhydride (175 mn) and fused sodium acetate (3 g) were gently refluxed for 3 hours

on heating mentle. The product was cooled and treated carefully with water (200 mL). The solution was heated again for two hours. The precipitate was filtered, washed with ethanol. The colourless precipitate was dried between 150-200°C.

2. Preparation of meso-stillbenediimine

The diimine was prepared by hydrolysis of N'-benzoyl-N'-acetyl meso-stillbenediimine with sulphuric acid (1:1) as under:

N'-benzoyl-N'-acetyl meso-stillbenediimine (75 g) was heated with (500 mL) water and conc H₂SO₄ (500 mL) water to a boiling point. The current of steam was passed to remove benzoic acid. After three hours when the hydrolysis was completed, mixture was cooled and cautiously treated with ammonia, total volume being kept as small as possible. When the addition of (600 mL) of ammonia was completed, the mixture was left over night. The mixture was filtered through glass wool and was made alkaline in cold solution of ammonia. The meso-stillbenediimine [4] separated out as colourless leaflets which were filtered and recrystallised from hot water. The m.p. was found 120°C and yielded 15 g.

3. Preparation of meso-BA2S reagent

A mixture of freshly prepared meso-stillbenediimine (0.525 g) and benzoylacetone (1g) was heated on water-bath for two hours and was allowed to stand over night at room temperature. Precipitates obtained were washed with ether and recrystallised in benzene m.p. 255°C.

4. Preparation of meso-BA2S reagent

Each (0.2 g) of the metal chlorides (Cu, Ni, and Pd) were dissolved in (5 mL) acetonitrile separately. Mixture was refluxed on an electric plate till clear solution was obtained. An equimolar amount (.5) of reagent in (5 mL) benzene was added to the reflux solution. The mixture was refluxed for eight hours, and was allowed to stand at room temperature of 30 minutes. Most of solvent was removed by simple distillation technique. The residue was recrystallized from n-hexane and washed with acetone. Infrared spectra were recorded on Unicam SP 1025 Infrared spectrophotometer using KBr nujol mull techniques. All absorptiometric studies were carried out on Hitachi-220 spectrophotometer. Recorded melting points are shown in Table-1.

Table 1: Metal complexes of BA2S.

Complex	m.p.
Copper	288°C
Nickel	291°C
Palladium	278°C

Table-2. Metal BA2S complex absorbance-concentration in chloroform.

Metal	concentration (mg/mL)	Absorbance maxima	Absorbance
Copper	0.5	555.0 nm	0.224
	0.1	555.0 nm	0.423
	1.5	555.0 nm	0.617
Nickel	0.2	555.0 nm	0.733
	0.5	408.0 nm	0.094
	0.1	408.0 nm	0.287
Palladium	1.5	408.0 nm	0.652
	0.2	408.0 nm	1.375
Palladium	0.5	404.0 nm	0.228
	0.1	404.0 nm	0.539
	1.5	404.0 nm	0.794
	0.2	404.0 nm	0.980

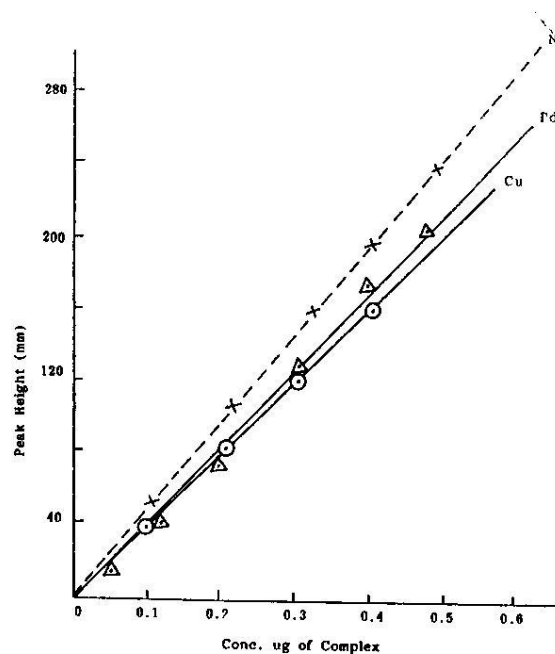


Fig. 1(b): Calibration curves of copper, nickel and palladium complexes.

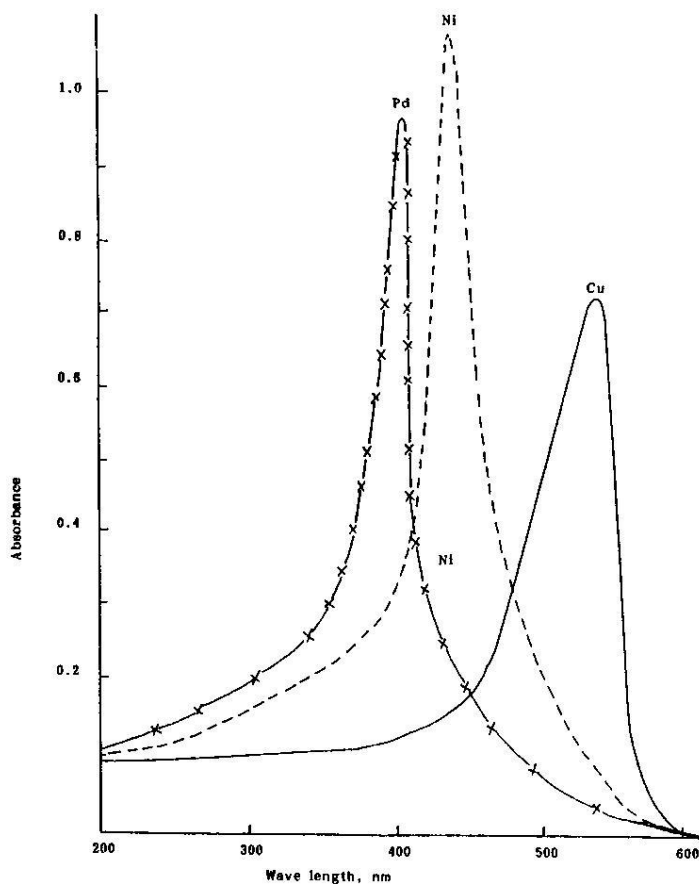


Fig. 1(c): Absorption band spectra of copper, nickel and palladium complexes.

The structure of metal organic complex is shown in Fig-1(a).

The ability of meso-BA2S reagent to form complex with metal ions and their extraction from an aqueous solution into chloroform is critical for the development of this useful analytical technique. When an aqueous solution of metal ions were shaken with the reagent in chloroform for 30 minutes, the percentage of metal ions extracted was only 30% in the initial work.

Here, the effect of pH 6.5 (acetic-acetate buffer), the addition of salt NaBr, heating time along with shaking and effect of methanol as solvent were monitored. It may be noted that the change in pH on the extraction of copper, nickel, and palladium were also evaluated by the addition of appropriate buffer solutions from pH 5-10 but pH 6.5 (acetic-acetate buffer) remained effective. The % age extraction was increased by the addition of methanol because of increased distribution of the reagent in an aqueous phase and addition of different salts NaNO₃, KBr and NaBr were tried in improving the percentage extraction of metal ions, but however NaBr remained more effective. The extraction of copper, nickel and palladium were also pH dependent when the extraction at pH 5 for copper was 70% which finally increased at pH 6.5 to 94% and nickel and palladium were 54

percentage similarly and raised to 64% for nickel only at pH 6.5.

Under similar conditions the complexation and extraction of palladium was slow in the initial stage and improved on the addition of 1g of KBr as salting ion and on heating for 30 minutes at 50-55°C. Other solvents like *n*-hexane, benzene, xylene, dioxine and methylisobutyl ketone [5] were applied and tested but each time a decrease in percentage extraction was observed. The effect of pH 6.5 (acetic-acetate) remained more significant and metal ions were extracted satisfactorily in chloroform. The calibration curves so obtained for copper, nickel and palladium as shown in Fig-1(b) had obeyed Beers Law when recorded at 555 nm, 408 nm, and 404 nm respectively. The absorption band shapes are given in Fig. 1 (c).

References

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