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2'-Hydroxy-4'-Butoxychalcone Oxime [HBCO] as an Analytical Reagent : Studies on Ni(II) Chelate

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Abstract: The ligand 2'-Hydroxy-4'-butoxychalcone oxime (HBCO) was developed as a new analytical reagent for the gravimetric and spectrophotometric analysis of Ni(II) ion. In the pH range of 8.0 to 10.0 this reagent gives light green complex with Ni(II). Job's method of continuous variation and Yoe and Jone's mole ratio method revealed the stoichiometry of the complex to be 1:2 [M:L]. The obeyence of Beer's law was studied and the molar absorptivity and Sandell's sensitivity were calculated. The reagent and its complex have been characterized by elemental analysis and IR spectra. The reagent has been used for the determination of Nickel content in German silver alloy.
Key words : Analytical reagent, Ni(II) chelate, 2'-Hydroxy-4'-butoxychalcone oxime(HBCO).

Introduction :

In the current scenario, large number of organic reagents have been employed for the detection and quantitative determination of metal ions. They include o-hydroxy ketoximes[1-2], phenyl hydrazones, thiosemicarbazones, chalcone oximes[3-5] etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. Here, we report the use of 2'-Hydroxy-4'-butoxychalcone oxime [HBCO] as an analytical reagent for Ni(II).

Experimental :

Instruments :

Spectrophotometric measurements were done on a "Milton Roy" (Spectronic 20D+) Spectrophotometer and "Shimadzu UV-160, UV-Visible Spectrophotometer". The IR spectra were recorded on "Perkin-Elmer" FTIR Spectrophotometer (RX-1) in KBr pallet. All pH measurements were done on Equip-Tronic pH meter (Model No.EQ 614).

Stock solution :

Stock solution of $NiSO_4.6H_2O$ (0.05 M) was prepared by dissolving 3.208 gm of $NiSO_4.6H_2O$ (A.R.) in minimum quantity of water and diluted to 250 ml with doubly distilled water. Concentrated sulphuric acid was added in little amount to prevent the hydrolysis of the salt. It was used after standardization[6] with EDTA.

Synthesis of Reagent [HBCO] :

Resacetophenone was prepared from resorcinol, glacial acetic acid and anhydrous zinc chloride according to the method of R. Robinson and R. C. Shah[7]. Resacetophenone was treated with butyl bromide and anhydrous potassium carbonate in acetone on a water bath at 65-70°C for six hours. On acidification with dilute HCl, 2-hydroxy-4-butoxy acetophenone was obtained. The 2-hydroxy-4-butoxy acetophenone was converted to chalcone by its condensation with benzaldehyde in presence of aqueous KOH for 24 hours at room temperature. The 2'-hydroxy-4'-butoxychalcone was converted to its oxime using hydroxylamine hydrochloride and sodium acetate. On crystallization from alcohol pure oxime in the form of light yellow crystals with m.p.178°C was obtained. Stock solution of reagent (0.05 M) was prepared by dissolving in 70% aqueous ethanol.

Gravimetric determination of Ni(II) :

Nickel sulphate solution (0.05 M, 10 ml) was taken in a clean beaker and diluted to about 100 ml with distilled water. A little excess of reagent solution was added (0.05 M, 22 ml). The pH of the solution was adjusted between 8.0 to 10.0 using $NH_3 + NH_4Cl$ buffer. A light green precipitate obtained were digested on water-bath for 60 minutes at 60°C. The precipitate were filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water followed by 70% aqueous ethanol to remove excess of the reagent. The chelate was dried to constant weight at 110°C in hot air oven, cooled and weighed as $Ni(C_{19}H_{20}O_3N)_2$. Duplicate experiments were performed in each case. The results are given in Table 1. The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots, keeping the optimum pH value to evaluate its applicability. The error in any case did not exceed 1.0%.

Interference from other ions :

To study the effect of foreign ions on gravimetric determination of Ni(II), 8-10 mg of various cations were added to a solution containing 29.33 mg Ni(II) at pH 9.0 and gravimetric estimations were done. It was observed that Sr(II), Ca(II), Na(I), K(I), Mg(II), Ba(II), Pd(II), Cd(II) do not interfere at this pH but Mn(II) and Cu(II) interfered seriously. Many common anions like nitrate, nitrite, sulphate, chloride, bromide, iodide were not found to interfere.

Table : 1:Gravimetric Determination Of Ni(II) Using HBCO

Ni(II) taken = 29.34 mg
Drying temperature = 110-115°C Salt = $NiSO_4.6H_2O$

pH	Ni(II) complex in g	Ni(II) found in mg	Error	
			in mg	%
8.0	0.3372	29.13	-0.21	-0.72
8.0	0.3376	29.17	-0.17	-0.58
8.5	0.3385	29.25	-0.09	-0.31
8.5	0.3384	29.24	-0.10	-0.34
9.0	0.3394	29.33	-0.01	-0.03
9.0	0.3393	29.32	-0.02	-0.06
9.5	0.3396	29.35	+0.01	+0.03
9.5	0.3398	29.36	+0.02	+0.07
10.0	0.3402	29.39	+0.05	+0.17
10.0	0.3406	29.43	+0.09	+0.31

Conversion factor = 0.0864

Spectrophotometric study of Ni(II)-HBCO chelate :
5 mg of chelate was extracted in 25 ml of chloroform and the absorption spectra was recorded in the range of 300 to 800 nm. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wavelength. A weak band is observed at 500 nm and hence all measurements were carried out at 500 nm.

Verification of Beer's law and optimum concentration range :

To 5 ml of solution (0.01 M) of the reagent HBCO, varying amount of the Ni(II) solution (0.005 M) was added and the pH was adjusted to 9.0, using [NH_3 + NH_4Cl] buffer. The insoluble complex was extracted in chloroform using three 5.0 ml, portions of chloroform and final volume of chloroform extract was adjusted to 25.0 ml. The absorbances of these solutions were measured at 500 nm against chloroform as blank. Absorbance values were plotted against metal concentration expressed in ppm. A straight line passing through the origin, indicating obeyance of Beer's law is obtained up to 117.38 ppm of Ni(II). The molar absorptivity of the Ni(II)-HBCO complex was found to be 1.24 x 10^2 lit.mol^{-1}.cm^{-1} and the Sandell's sensitivity is found to be 0.0473 µg/cm^2 at 500 nm.

Stoichiometry of complex :

Job's method of continuous variation[8] and Yoe and Jones mole ratio method[9] were used to determine the stoichiometry of the Ni(II)-HBCO complex. From both the methods, it was found to be 1:2 [M:L] ratio. This is in agreement with the stoichiometry found from gravimetry. The average stability constant found from two methods is 1.50 x 10^9. The Gibb's free energy change for complex formation reaction at 30°C was found to be -24.16 K.cal/mole.

IR Spectra :

Examination of the IR spectra of the chelates show that the band due to intramolecular hydrogen bonded O-H stretching of 2-hydroxy group disappears in the Ni(II)-HBCO complex. This results in revealing of two bands due to oximino -OH group at 3472 cm^{-1} and 3057 cm^{-1} in Ni(II) complex. The band due to the -C=N stretching which is observed at 1596 cm^{-1} in ligand is shifted to 1582-1585 cm^{-1} in complex. This may be due to coordination of metal through nitrogen. This is further supported by slight downward shift of ν NO from 1023 cm^{-1} in the ligand to 970 to 980 cm^{-1} in Nickel chelates. Thus, in the chelates, metal is covalently bonded with oxygen and coordinate bonded with nitrogen.

Gravimetric estimation of Ni(II) in German Silver using HBCO :

Preanalysed sample of german silver 0.6831 g was dissolved in nitric acid (1:1) by heating and excess of nitric acid was removed. The resulting solution was diluted to 100 ml in volumetric flask with distilled water.

An aliquot of above diluted solution (10 ml) was taken in a clean beaker and it was diluted to about 100 ml with distilled water and pH 5.0 was adjusted with sodium acetate and acetic acid buffer. The copper was determined gravimetrically using HBCO as per the procedure used for Ni(II). The filtrate obtained after filtering the copper complex was concentrated by evaporation and pH was raised to 9.0 with ammonium hydroxide and ammonium chloride buffer. The Ni(II) was determined gravimetrically using HBCO as per the procedure described previously.

Results : Estimation of nickel :

1.	Weight of Ni(II)-HBCO complex	= 0.2083 gm
2.	Nickel found in 10 ml diluted solution (Average of three determinations)	= 0.0180 gm
3.	Nickel found in German silver alloy sample	= 0.180 gm
4.	Percentage of nickel found in German silver alloy sample	= 26.35%
5.	Percentage of nickel reported in German silver alloy sample	= 26.00 %
6.	Percentage error	= +1.346 %

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