

2,4-Dihydroxy-5-BromoButyrophenone Oxime [DHBBO] as an Analytical Reagent : Studies on Ni(II) Chelate

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Abstract: The ligand 2,4-dihydroxy-5-bromobutyrophenone oxime [DHBBO] was developed as a new analytical reagent for the gravimetric and spectrophotometric analysis of Ni(II) ion. In the pH range of 7.0 to 10.0 this reagent gives light green precipitate with Ni(II). Job's method of continuous variation and Yoe and Jones mole ratio method revealed the stoichiometry of the complex to be 1:2. The obeyence of Beer's law was studied and the molar absorptivity and Sandell's sensitivity was calculated. The reagent and its complex have been characterized by elemental analysis and IR spectra. The complex was subjected to thermogravimetric analysis to study its decomposition pattern. The reagent has been used for the analysis of german silver.

Key words: Analytical Reagents, Ni(II) Chelate ,2,4-Dihydroxy-5-BromoButyrophenone Oxime [DHBBO] .

Introduction

In the current scenario, large numbers of organic reagents have been employed for the detection and quantitative determination of metal ions. Oximes, hydrazones, thiosemicarbazones, semicarbazones of aromatic aldehydes and ketones have been used as gravimetric and/or spectrophotometric reagents for different metal ions. 2-Hydroxy-4-ethoxyacetophenone oxime¹⁻³, 2-hydroxy-2-ethoxypropiophenone oxime⁴, 2-hydroxy-4-n-propoxybutyrophenone oxime⁵ and 2,4-dihydroxy-5-bromo-phenylacetophenone oxime⁶, 2-hydroxy-4-n-butoxy-5-bromopropiophenone thiosemicarbazone⁷, have been reported earlier. Here, we report the use of 2,4-dihydroxy-5-bromobutyrophenone oxime

[DHBBO] as a gravimetric and spectrophotometric reagent for Ni(II).

Experimental

Instruments

Spectrophotometric measurements were done on "Bausch and Lomb Spectrophotometer" and Shimadzu UV-160 A, UV-visible Spectrophotometer. All pH measurements were made on Elico pH meter LI-10T.

Stock solution

Stock solution of NiSO₄.6H₂O (0.05 M) was prepared by dissolving 3.208 gm of NiSO₄.6H₂O (A.R.) in minimum quantity of concentrated hydrochloric acid and diluted to 250 ml with doubly

distilled water. It was used after standardisation⁸ with EDTA.

Synthesis of Reagent [DHBBO]

Resbutyrophenone was prepared from resorcinol, butyric acid and anhydrous zinc chloride⁹. 2,4-Dihydroxy-5-bromobutyrophenone [DHBB] was prepared from resbutyrophenone and bromine in glacial acetic acid. It was crystallized from ethanol. The oxime of DHBB was prepared by the sodium acetate method. On crystallization from alcohol pure DHBBO in the form of colourless needles with m.p. of 123 °C was obtained. Stock solution of DHBBO (0.05 M) was prepared by dissolving the oxime in 70% aqueous ethanol.

Gravimetric determination of Ni(II)

An aliquot of Ni(II) (0.05 M, 10 ml) solution was diluted to 100 ml with distilled water and the pH of solution was adjusted in the range of 8.0 to 10.0 with suitable buffer. The solution was warmed and 22 ml of 0.05 M solution of DHBBO in ethanol was added till complete precipitation. The light green precipitate were digested on water-bath at 60-70 °C for 1 hr. and filtered through a previously weighed sintered glass crucible (G-4). The precipitate were washed with warm water and then finally with 70% aqueous ethanol to remove excess of reagent which might have precipitated on dilution. The precipitate were dried and weighed as Ni-(C₁₀H₁₁O₃NBr)₂. Duplicate experiments were performed in each case. The results are given in Table 1. Experiments were repeated with different aliquots of nickel. 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 29.35 mg of Ni(II) at pH 9.0 and gravimetric estimations were done. It was observed that Ca(II), Mg(II), Sr(II), Pd(II), Fe(III), Zn(II), Cd(II), Ba(II) and Al(III) do not interfere at this pH. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

Elemental analysis

Elemental Analysis of the reagent DHBBO and nickel complex was carried out on Carlo Erba elemental Analyser. The elemental analysis of the reagent and Ni(II) chelate is given in Table 2.

Spectrophotometric study of Ni(II)-DHBBO chelate

5 mg of chelate was dissolved in 25 ml chloroform and the absorption spectra was recorded in the range of 350 – 750 nm. It was observed that the absorbance of the coloured solution of chelate increase continuously towards the shorter wavelength. A plateau is obtained at 560 nm and this wavelength was used for spectrophotometric work.

Verification of Beer's law and optimum concentration range

To 6.0 ml (0.02 M) solution of the reagent DHBBO, varying amount of the nickel ion solution (0.007 M) was added; and the pH was adjusted to 9.0 using ammonium hydroxide and ammonium chloride buffer. The insoluble complex precipitated was extracted in chloroform using three 5.0 ml portions of chloroform and the final volume of the chloroform extract was adjusted to 25 ml. The absorbances of these solutions were measured at 560 nm against reagent blank. A straight line passing through the origin, indicating the obeyence of the Beer law was obtained upto 90.42 ppm of Ni(II) at 560 nm. The molar absorptivity of the Ni(II)-DHBBO complex was found to be 0.103 × 10⁵ lit.mol⁻¹.cm⁻¹. at 560 nm. The Sandell's sensitivity is found to be 0.57 µg/cm² at 560 nm.

Stoichiometry of complex

Job's method of continuous variation¹⁰ and Yoe and Jones mole ratio method¹¹ were used to determine the stoichiometry of the Ni(II)-DHBBO complex. From both the methods, it was found to be 1:2 [metal : ligand] ratio. This is in agreement with the stoichiometry found from gravimetry. The average stability constant found from two methods is 4.682 × 10⁸. The Gibb's free energy change for complex formation reaction at 30 °C was found to be -13.41 k.cal./mol.

Thermogravimetric Analysis

Thermogravimetric analysis of Ni(II) chelate was done on "Mettler M-3 Thermobalance TA-3000". It was found that there is no weight loss upto 200 °C indicating that the chelate can be safely dried without decomposition at 110 °C. The loss in weight above 200 °C is due to decomposition of chelate and loss of ligand molecules. Weight of final residue corresponds to NiO in case of Ni(II) chelate is in accordance with the formula (C₁₀H₁₁O₃NBr)₂Ni. The observed loss and weight of residue agree well with the loss and weight expected as per formula of chelate in which metal : ligand ratio is 1:2.

IR Spectra

The IR spectra of DHBBO shows two bands in O-H stretching region; one broad band at 3400 cm^{-1} due to phenolic 2-OH group and the other at 3100 cm^{-1} due to oximino -OH group. The band at 3400 cm^{-1} disappears in the IR spectra of complex because during complex formation, H of 2-hydroxy is removed and metal joins with the oxygen by covalent bond. The coordination of metal through N of oximino group may be shown by the downward shift of C=N stretching band, from 1630 cm^{-1} in ligand to 1610 cm^{-1} in chelate. The position of oximino -OH group changes from 3100 cm^{-1} in ligand to 3125 cm^{-1} in chelate, this also may be due to coordination metal through nitrogen.

Gravimetric estimation of Ni(II) in German silver using DHBBO

Preanalysed sample of german silver 0.6922 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 DHBBO 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 DHBBO as per the procedure described previously.

Table 1 Gravimetric determination of Ni(II) using DHBBO (Salt : $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, Ni(II) taken = 29.36 mg, Drying temp. = 110-115°C)

pH	Ni(II) complex in gm	Ni(II) found in mg	Error in mg	Error in %
8.0	0.2974	28.88	-0.48	-1.66
8.0	0.2968	28.82	-0.54	-1.87
8.5	0.2992	29.05	-0.31	-1.07
8.5	0.2998	29.11	-0.25	-0.86
9.0	0.3025	29.37	+0.01	+0.03
9.0	0.3023	29.35	-0.01	-0.03
9.5	0.3028	29.40	+0.04	+0.14
9.5	0.3031	29.43	+0.07	+0.24
10.0	0.3036	29.48	+0.12	+0.41
10.0	0.3039	29.51	+0.15	+0.51

Conversion factor: 1 gm of complex = 97.1 mg of Ni(II)

Table 2 Elemental analysis of reagent and Ni(II)-DHBBO

Compound	% C	% H	% N
	% found (% cal.)	% found (% cal.)	% found (% cal.)
DHBBO	43.66% (43.79%)	4.31% (4.38%)	5.07% (5.11%)
Ni(II)-DHBBO	39.74% (39.70%)	3.58% (3.64%)	4.65% (4.63%)

Results : Estimation of nickel :

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| 1. Weight of Ni(II)-DHBBO complex (average of three determination) | = 0.1359 gm |
| 2. Nickel found in 10 ml diluted solution | = 0.01320 gm |
| 3. Nickel found in German silver alloy sample | = 0.1320 gm |
| 4. Percentage nickel found in German silver alloy sample | = 19.07% |
| 5. Percentage nickel reported in German silver alloy sample | = 19.00% |
| 6. Percentage error | = + 0.37% |

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