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NOTE

2,4-Dihydroxy-5-Bromovalerophenone Oxime as a Gravimetric Reagent for Ni(II) and Cu(II) and Spectrophotometric Study of Complexes

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2,4-Dihydroxy-5-bromovalerophenone oxime (DHBVO) was developed as a new analytical reagent for the gravimetric estimation of divalent nickel and copper ions. In pH range of 3.0 to 6.0, this reagent gives a buff colored precipitate with Cu^{2+}. Job's method and mole ratio method revealed that the stoichiometry of the complex is 1:2, the Beer's law is obeyed up to 38.12 ppm of Cu^{2+}. The molar absorptivity at 420 nm was found to be 5.31×10^2 L mol^{-1} cm^{-1}. The stability constant of the complex is found to be 1.885×10^9. Ni^{2+} gives light green colured precipitate in pH range 7.0 to 9.0. Using both the above-mentioned methods, it was found that stoichiometry was 1:2. The molar absorptivity at 440 nm was found to be 1.79×10^2 L mol^{-1} cm^{-1}. The stability constant of the complex is found to be 1.24×10^9. Beer's law is obeyed upto 35.22 ppm of Ni^{2+}. The reagent can be used for the analysis of german silver alloy.

In the current scenario of analytical chemistry, many reagents are widely available. They include *o*-hydroxy ketoximes[1-3], phenyl hydrazones, thiosemicarbazones, chalcone oximes etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. In the following pages, we report the use of 2,4-dihydroxy-5-bromovalerophenone oxime (DHBVO) as a gravimetric reagent for Ni(II) and Cu(II). Spectrophotometric methods have been used to confirm the stoichiometry of complex and to determine the stability constants of complexes.

All the spectrophotometric measurements were done on Bausch and Lomb spectrophotometer (Spectronic 20) All the pH measurements were done on ELICO pH meter (LI-10T).

Synthesis of DHBVO: 2,4-Dihydroxyvalerophenone (resvalerophenone) was synthesized by the condensation of resorcinol with *n*-valeric acid in presence of anhydrous zinc chloride[4]. 2,4-Dihydroxy-5-bromovalerophenone was obtained by brominating resvalerophenone with bromine in glacial acetic acid. The oxime of this was prepared by usual method, using hydroxylamine hydrochloride and sodium acetate. The oxime recrystallised from ethanol. White crystals gave m.p. 146°C.

Gravimetric determination of copper: A 0.05 M solution of the reagent in 50% aqueous ethanol was used. Copper sulphate solution (0.05 M, 10 mL) taken in a clean beaker was diluted to about 100 mL with distilled water and pH of the solution was adjusted to 5.5 using sodium acetate-hydrochloric acid buffer. The solution was warmed at 60°C and small excess of reagent solution was added (0.05 M, 22 mL). A buff precipitate obtained was digested on water bath for 1 h at 60°C. The precipitate was filtered through a previously weighed sintered glass crucible (G-4) and washed with warm water followed by 50% aqueous ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110–115°C in hot air oven, cooled and weighed. The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots, keeping the optimum pH to evaluate its applicability.

Interference: To study the effect of foreign ions on gravimetric determination of Cu(II), 8–10 mg of various cations were added to a solution containing 31.77 mg Cu(II) at pH 5.5 and gravimetric estimations were done. It was observed that Sr(II), Ca(II), Zn(II), Ni(II), Mn(II), Ba(II), Mg(II) and Cd(II) do not interfere at this pH, but Fe(III) and Pd(II) interfered seriously. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

Gravimetric determination of nickel: A 0.05 M solution of the reagent in 50% aqueous ethanol was used. Nickel sulphate solution (0.05 M, 10 mL) taken in a clean beaker was diluted to about 100 mL with distilled water and pH of the solution was adusted to 8.0 by using ammonia-ammonium chloride buffer. The solution was warmed at 60°C and small excess of reagent solution was added (0.05 M, 22 mL). A light green precipitate obtained were digested on water bath for 60 min at 60°C. The precipitate was filtered through a previously weighed sintered glass crucible (G-4) and washed with warm water followed by 50% aqueous ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110–115°C in hot air oven, cooled and weighed. The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots, keeping the optimum pH to evaluate its applicability.

Interference: 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 Ni(II) at pH 8.0 and gravimetric estimations were done. It was observed that Sr(II), Ca(II), Zn(II), Pd(II), Ba(II), Mg(II) and Cd(II) do not interfere at this pH, but Mn(II), Cu(II) interfered seriously. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

Spectrophotometric study of Cu-DHBVO complex: A series of buffer solutions with pH value ranging from 3.0 to 6.0 were prepared using hydrochloric acid & sodium acetate; and acetic acid & sodium acetate. 5.0 mL of 0.05 M reagent solution was added to 2.0 mL of 0.01 M of Cu(II) ion solution at varied pH. The insoluble complex 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 spectra of the above solutions were recorded from 340 nm to 700 nm. It was found that Cu(II)-DHBVO absorbs maximum at 420 nm. This wavelength was used for all further studies. The absorbance was found maximum at pH 5.5 and hence this pH was used.

Different aliquots of Cu(II) solution were taken. Buffer solution was added to maintain pH 5.5. The excess of reagent was added to get precipitate of complex.

It was extracted with three 5.0 mL portions of chloroform and the combined extracts were diluted to 25 mL. The absorbance was measured at 420 nm. The absorbances were plotted against the concentration of Cu(II). It was found that Beer's law is obeyed up to 38.12 ppm of Cu(II). Molar absorptivity was calculated from graph and it was found to be 5.31×10^2 litre mole^{-1} cm^{-1}.

Job's method[5] and mole ratio method[6] were used to determine the stoichiometry of the complex. It was found to be 1:2 (M:L). This is in agreement with the stoichiometry found from gravimetry. The stability constants were calculated using the formula:

$$K_s = \frac{1-\alpha}{4\alpha^3 C^2}$$

where $\alpha = \frac{E_m - E_s}{E_m}$ (E_m is the maximum absorbance found from graph and E_s is the absorbance at stoichiometric molar ratio of the metal to the reagent in the complex).

The average stability constant found from two methods is 1.885×10^9.

$\Delta G°$ for complex formation at 25°C is –12.64 kcal/mol.

Spectrophotometric study of Ni-DHBVO complex: Studies were done in a same way as done for Cu(II). It was found that Ni(II)-DHBVO oxime absorbs maximum at 440 nm. The pH for maximum complex formation is 8.0. The complex obeys Beer's law up to 35.23 ppm of Ni(II). The complex has stoichiometry 1:2. Stability constant as determined by Job's method and mole ratio method was found to be 1.24×10^9. The standard Gibb's free energy change at 25°C for complex formation reaction was found to be –12.40 kcal/mole.

Analysis of german silver using DHBVO: Exactly 0.6028 g of german silver was taken and dissolved in 50 mL 1:1 nitric acid. The excess nitric acid was boiled off and the solution was diluted to 100 mL with distilled water.

10 mL aliquot was taken and Cu(II) (as prepared above) was determined at pH 5.0 as described earlier. The filtrate obtained after separating Cu(II) was concentrated and pH was raised to 9.0 and nickel was determined as described earlier. The experiment was repeated three times. Cu %, found: 56.47; reported: 56.00. Ni %, found: 19.22; reported: 19.00.

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