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NOTE

2′,4′-Dihydroxy-5′-bromochalcone Oxime as a Spectrophotometric Reagent for Cobalt(II) and Manganese(II)

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2′,4′-Dihydroxy-5′-bromochalcone oxime (DHBCO) has been synthesized and used as a new spectrophotometric reagent for Co(II) and Mn(II). In pH range 8.0–10.0, this reagent gives dark violet coloured complexes with Co(II) and Mn(II). Job's and mole-ratio methods revealed that the stoichiometry of both the complexes is 1 : 1. Both the complexes obey the Beer's law over a wide range of concentration. The molar absorptivities and Sandell's sensitivities have been calculated. The stability constants at 27°C and Gibb's free energy changes have also been calculated. Applicability has been checked by using the reagents to determine manganese in ore samples.

Key Words: Spectrophotometric reagent, 2′,4′-Dihydroxy-5′-bromochalcone oxime, Cobalt(II), Manganese(II).

In the current scenario of analytical chemistry, many organic reagents are widely used as analytical reagents. They include *o*-hydroxyketoximes[1-2], phenylhydrazones, thiosemicarbazones, chalconeoximes[3-7] etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. Here we report the use of 2′,4′-dihydroxy-5′-bromochalcone oxime (DHBCO) as a spectrophotometric reagent for Co(II) and Mn(II).

All the spectrophotometric measurements were done on Shimadzu UV-160A, UV-Visible spectrophotometer and all the pH measurements were done on Equip-tronic pH-meter (EQ-614).

Synthesis of DHBCO

Resacetophenone was synthesized as per reported method[8]. 2,4-Dihydroxy-5-bromoacetophenone was obtained by brominating resacetophenone with bromine in glacial acetic acid. 2′,4′-Dihydroxy-5′-bromochalcone was prepared by condensation of 2,4-dihydroxy-5-bromoacetophenone and benzaldehyde in ethanol and aqueous solution of KOH. The oxime of this was synthesized by the usual method using hydroxylamine hydrochloride and sodium acetate. The oxime was recrystallised from ethanol. Light green coloured crystals with m.p. 190°C. (nitrogen, found: 4.08%, calculated: 4.19%).

Spectrophotometric study of Co(II)-DHBCO complex

A series of buffer solutions with pH value ranging from 8.0 to 10.0 were prepared using ammonia and ammonium chloride. In 1.0 mL of 0.005 M Co(II) solution, 3.0 mL of 0.02 M ethanolic solution of DHBCO were added and the pH of the solutions were adjusted to 8.0–10.0 by using buffer solutions. The appearance of dark violet colour indicates complex formation. These coloured solutions were diluted to 25 mL with 70% aqueous ethanol. The spectra of the above solutions were recorded from 350 to 800 rim. It was found that in Co(II)-DHBCO absorption spectra there is a shoulder at 400 rim. A wavelength of 400 rim is selected for all further studies. The absorbance was found maximum at pH 9.0 and hence this pH was used.

Different aliquots of Co(II) solution were taken and buffer solution was added to maintain pH 9.0. The excess of the reagent was added to obtain dark violet coloured complex. The contents were diluted to 25 mL as usual. The absorbance was measured at 400 nm. The absorbance was plotted against the concentration of Co(II). It was found that Beer's law is obeyed up to 18.86 ppm of Co(II). The molar absorptivity was calculated from graph and it was found to be 2.384×10^3 L mol^{-1} cm^{-1} and Sandell's sensitivity was found to be 0.024 μg of Co(II)/cm^2. Job's and mole-ratio methods[10] were used to determine the stoichiometry of the complex. It was found 1 : 1 [M : L]. The stability constants were calculated using the formula

$$K_s = \frac{1-\alpha}{c\alpha^2} \qquad \text{where } \alpha = \frac{E_m - E_s}{E_m}$$

where E_m = the maximum absorbance found from graph

E_s = the absorbance at stoichiometric molar ratio of the metal to the reagent in the complex.

The average stability constant found from the two methods is 1.43×10^6. The standard Gibbs free energy (ΔG^0) for complex formation at 27°C is –8.45 kcal/mol.

Spectrophotometric study of Mn(II)-DHBCO complex

Studies for Mn(II) complex were done in a same manner as for Co(II) complex. It was found that in Mn(II)-DHBCO absorption spectra there is a shoulder at 450 nm and hence this wavelength was selected for analytical work. The pH for maximum complex formation is 9.5. The complex obeys Beer's law up to 10.99 ppm of Mn(II). The molar absorptivity was calculated from the plot of absorbance against the concentration of Mn(II) and it was found to be 4.415×10^3 L mol^{-1} cm^{-1} and Sandell's sensitivity was found to be 0.1 of Mn(II)/cm^2. The complex has stoichiometry 1 : 1 [M : L]. The stability constant as determined from Job's and mole-ratio method was found to be 5.84×10^6. The standard Gibb's free energy change (ΔG^0) at 27°C for complex formation reaction was found –9.28 kcal/mol.

The advantage of using this reagent for spectrophotometric determination of Mn(II) and Co(II) is that the molar absorptivities are high and hence it can be

used to determine these ions even at low concentration level. Further the reagent has high molecular weight.

Determination of manganese in pyrolusite ore

Pyrolusite ore sample was treated with 1 : 1 hydrochloric acid and the solution was filtered to remove silica and other insoluble matter. Finally the filtrate was diluted to 100 mL. 3.0 mL of the above solution was taken in a 50 mL volumetric flask and diluted up to the mark with double distilled water. The complex was formed by taking 2.0 mL aliquot and by adding suitable buffer; excess reagent and diluted to 25 mL. Absorbance was measured at 450 nm and mg of manganese was determined from Beer's law calibration plot. Percentage of Mn: found 55.2; reported 54.9.

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