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*NOTE*

# 2,4-Dihydroxy-5-Bromovalerophenone Oxime as a Gravimetric Reagent for Pd(II) and Mn(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 palladium and manganese ions. In the pH range of 2.0 to 5.0, this reagent gives a golden yellow coloured precipitate with $Pd^{2+}$. Job's method and mole ratio method revealed that the stoichiometry of the complex is 1 : 2. Beer's law is obeyed up to 63.78 ppm of $Pd^{2+}$. The molar absorptivity at 440 nm of complex was found to be $5.01 \times 10^2$ L $mol^{-1}$ $cm^{-1}$. The stability constant of the complex is found to be $2.45 \times 10^9$. $Mn^{2+}$ gives dark green coloured precipitate in pH range 8.5 to 9.0. Using both the above-mentioned methods, it was found that stoichiometry was 1 : 1. The molar absorptivity at 420 nm was found to be $3.9 \times 10^3$ L $mol^{-1}$ $cm^{-1}$. The stability constant of the complex is found to be $1.61 \times 10^6$. Beer's law is obeyed up to 6.60 ppm of $Mn^{2+}$. The reagent can be used for the analysis of pyrolusite ore.

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 this work, we report the use of 2,4-dihydroxy-5-bromovalerophenone oxime (DHBVO) as a gravimetric reagent for Pd(II) and Mn(II). Spectrophotometric methods have been used to confirm the stoichiometry of complex and to determine the stability constants of the complexes.

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

*Synthesis of DHBVO:* Synthesis of DHBVO is as reported earlier[4].

*Gravimetric determination of Palladium:* A 0.05 M solution of the reagent in 50% aqueous ethanol was used. Palladium chloride solution (0.01 M, 20 mL) taken in a clean beaker was diluted to about 100 mL with distilled water and pH of the solution was adjusted to 2.0 using sodium acetate-hydrochloric acid buffer. The solution was warmed at 60°C and a small excess of reagent solution was added (0.05 M, 9.0 mL). A golden yellow precipitate obtained were digested on water bath for 1 h at 60°C. The precipitates were 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 a 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 Pd(II), 8–10 mg of various cations were added to a solution containing 21.282 mg Pd(II) at pH 2.5 and gravimetric estimations were done. It was observed that Ca(II), Sr(II), Mg(II), Mn(II), Ni(II), Zn(II), Cd(II), Na(I), K(I), Ba(II) do not interfere at this pH, but Fe(III), Co(II), Cu(II) interfere seriously. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

*Gravimetric determination of managanese:* A 0.05 M solution of the reagent in 50% aqueous ethanol was used. Manganese sulphate solution (0.05 M, 10 mL) taken in a clean beaker was diluted to about 100 mL with distilled water. A small excess of reagent DHBVO was added (0.05 M, 22 mL). Then the pH was adjusted to 9.0 using ammonia-ammonium chloride buffer. The dark green precipitates of manganese chelate formed were kept at room temperature for about 24 h. 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. The chelate was dried to constant weight at 90°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 Mn(II), 8–10 mg of various cations were added to a solution containing 27.47 mg Mn(II) at pH 9.0 and gravimetric estimations were done. It was observed that Sr(II), Ca(II), Zn(II), Pd(II), Ba(II) and Mg(II) do not interfere at this pH, but Cu(II), Ni(II) interfered seriously. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

*Spectrophotometric study of Pd-DHBVO complex:* A series of buffer solution with pH value ranging from 2.0 to 5.0 were prepared using hydrochloric acid and sodium acetate. 5.0 mL of 0.05 M of the reagent solution was added to 2.0 mL of 0.01 M of Pd(II) ion solution at varied pH. The insoluble complex was extracted in chloroform using three 5.0 mL portions of chlorofirm 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 Pd(II)-DHBVO absorbs maximum at 440 nm. This wavelength was used for all further studies.

Different aliquots of Pd(II) solution were taken. Buffer solution was added to maintain pH 2.5. The excess of reagent solution 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 440 nm. The absorbances were plotted against the concentration of Pd(II). It was found that Beer's law is obeyed upto 63.786 ppm of Pd(II). Molar absorptivity was calculated from graph and it was found to be $5.01 \times 10^2$ L $\text{mole}^{-1}$ $\text{cm}^{-1}$.

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 wer calculated using the formula:

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

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 $2.45 \times 10^9$.

$\Delta G°$ for complex formation at 25°C is −12.80 kcal/mol.

*Spectrophotometric study of Mn-DHBVO complex:* Studies were done in the same way as done for Pd(II) but extraction was carried out in ethyl acetate instead of chloroform. It was found that Mn(II)-DHBVO oxime absorbs maximum at 420 nm. The complex obeys Beer's law upto 6.60 ppm of Mn(II). The complex has stoichiometry 1 : 1. Stability constant as determined by Job's method and mole ratio method was found to be $1.61 \times 10^6$. The standard Gibb's Free energy change at 25°C for complex formation reaction was found to be −8.46 kcal/mole.

The stability constants here calculated using the formula:

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

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).

*Analysis of pyrolusite ore using DHBVO:* An exact quantity of pyrolusite ore (0.9907 g) was weighed and dissolved in 10 mL concentrated hydrochloric acid. The excess acid was boiled off. This process was repeated thrice and the solution was filtered to remove silica. The solution was diluted to 100 mL with distilled water. 10 mL aliquot was taken and Mn(II) was determined at pH 9.0 as described earlier. The experiment was repeated three times. Mn %, found: 56.10; reported: 55.61.

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