Spectrophotometric and Conductometric Study of Chelate of Divalent Copper with 2-Hydroxy-1, 4-naphthoquinone (Lawsone)

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SURVEY of literature reveals that 2-hydroxy-1, 4-naphthoquinons (Lawsone) has found its application in qualitative and quantitative estimations of various metals¹⁻⁴. Recently Jain et al.⁵ have reported the cholate of Lawsone with lanthanum. The present communication reports on the nature of structure, stability constant, free energy of formation and state of hybridisation of Cu⁺⁺: Lawsone chelate.

Experimental

Standard solutions of Lawsone (K. K. Laboratories +.N.C. Plain view, New York, A.R.) and cupric hloride (B.D.H. AnalaR) were prepared by dissolving the respective compound in double distilled iethyl alcohol (absolute).

To isolate the complex, 200 ml. of Lawsone (alcoholic) solution was added slowly to the beaker containing 200 ml of cupric ion (0.01 M) with constant stirring. After addition the solution was warmed and allowed to stand overnight. The brownish red coloured crystals appeared, were filtered and washed several times with ice-cooled water and dried at 70°-76°.

The isolated complex was analysed for metal content gravimetrically.

Baush and Lomb Spectronic-20 spectrophotometer for absorbance measurements, Perkin-Elmer infracord spectrophotometer for infra-red spectra and Gouy's magnetic balance for magnetic susceptibility, were used.

Results and Discussion

It has been observed that the order of addition of reactants had no appreciable effect on absorbance.

Nature of chelate

To find the nature of chelate formed and working wave length Garg, Singh and Kotyal⁶ method was used. For this, mixtures containing equal proportions of cupric chloride and 2-hydroxy-1,4-naphthoquinons were mixed and the absorbance measured. The absorption maximum of the complex (brownish red in cólour) was found to be 440 nm.

Composition of the chelate

The composition of the chelate was established by the methods of Job's continuous variation, molar ratio⁸, slope ratio⁹ and Dey¹⁰. A large number of observations were taken at λ_{max} i.e. 440 nm, and it was found that the ratio of Cu⁺⁺: Lawsone in the chelate is 1:2. Job's method using conductance measurements also gave the same interaction ratio.

Evaluation of stability constant and free energy

The stability constant calculated from the absorbance data by molar ratio method is 2.5×10^8 and free energy formation as calculated from $-\Delta F$ = $RT \ln K$ is -11.6K. Cals per mole.

Molecular formula of the chelate

On analysis the % of Cu, C, H and O are determined to be 15 3%, 57.1%, 2.2% and 23.2% respectively and the calculated values are 15.5%, 57.2%, 2.4% and 23.4% respectively for the formula $(C_{10}H_5O_3)_2Cu$.

Nature of chelate

Information regarding the nature of bonding was observed from I.R. Spectra of the complex. The O-H band at 3125 cm⁻¹ in the ligand has completely disappeared in the complex indicating thereby that proton is liberated during complex formation. The C=O stretching vibration in free ligand is disappears in complex indicates that Co-ordination of Lawsone is through carbonyl oxygen.

On the basis of infra-red studies the structure of the complex may be.

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