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NICKEL-FRUCTOSE CHELATE COMPLEX

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Chelate complexes of nickel with fructose and fructose high syrup have been prepared and characterized. These chelates are not homogenous. Nickel fructose contains three species of molecular weight 68,000, 37,000 and 20,000, while Ni-high fructose contains two molecular species of 66,000 and 50,000.

Key words: Nickel, Fructose and Chelate complexes.

Introduction

Iron, cobalt and nickel belong to the first triad of the periodic group III and the resemblence among them are more pronounced, Naqvi *et al.* [1] reported the preparation of sucrose, glucose and dextrin complex with Fe^{3+}, but their attempts to prepare a complex with fructose were not met with success. The preparation of a complex of Ni^{3+} with fructose has also not been reported in literature. Although, earlear Bari *et al.* [2] reported the preparation of complex of Ni^{3+} with sucrose and glucose. Later on Jafri *et al.* [3] reported the preparation of complexes of Ni^{3+} with sorbitol, dextrin and sor- bitol-dextrin-citric acid. Charley *et al.* [4] reported the preparation of Fe^{3+} chelate complex with fructose. They proposed a dimeric structure as shown in Fig. 1, based on its elemental analysis and molecular weight of 594. To ascertain whether fructose can form a complex with Ni^{3+}, present studies were undertaken. In this communication we have also determined their molecular weights, which are in the range of 22,000 to 68,000.

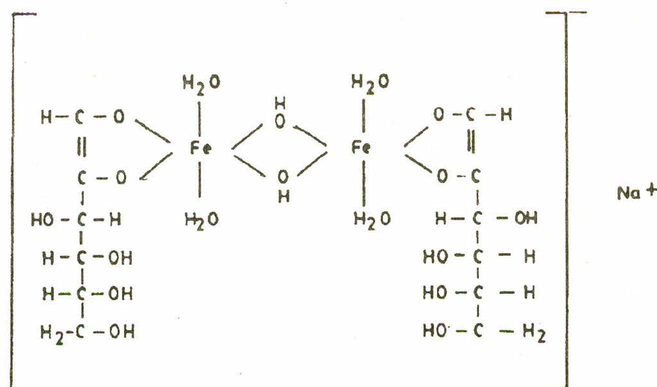

Fig. 1. Structure of Fe-fructose complex [4].

Schwietzer [5] proposed a polymeric structure for Fe^{3+}–hydroxide and its sucrose complex as indicated in Fig. 2a and 2b. Zaidi *et al.* [6] reported that iron-sucrose complex contain species of different molecular weight. Ni-fructose and fructose high syrup complex also contains species of different molecular weight, similar to iron-sucrose complex as indicated in Fig. 3.

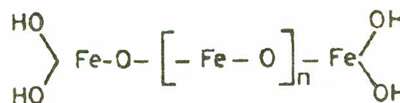

Fig.2a. -Polymeric Fe Hydroxide; n = ca4O.

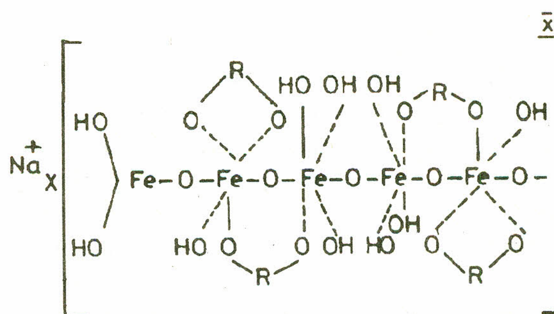

Fig. 2b. Structure of iron-sucrose complex [4].

Material and Methods

Materials. All chemicals used were of analar grade. Sephadex G-75 and dextrans of known mol.wt. were obtained from Pharmacia, Sweden. Iron dextran complex (Imferon) and high fructose syrup was obtained from the local market. Colorimetric estimation were carried out on Bausch and Lomb spectronic 20 and pH was determined on Titri pH meter type OP-401/2.

$NiSO_4 7H_2O$ (2.35 gm) equivalent to 0.5gm elemental Ni was dissolved in boiled water (20 ml) and sodium hydroxide 5% (20 ml) was added to it with vigorous stirring. The resulting green Ni $(OH)_2$ was washed with tap and distilled water to free it from electrolytes. The wet hydroxide was mixed with required amount of fructose, high fructose syrup and sodium hydroxide solution as indicated in the Tables. The contents were admixed throughly and heated at 200° in an electric oven. A dark brown cake was formed which gave a clear solution when dissolved in water. At low temperature or when the time of heating was shorter, the solution of the final product looks brownish and turbid against reflected light. The solution was centrifuged and nickel in the complex was estimated.

Estimation. The complex (1 ml) was digested with a mixture of sulphuric acid and nitric acid (1:1) in a Kjeldahl flask till the organic matter was carbonized completely. Nickel sulphate thus obtained was estimated colorimetricly using dimethylglyoxime [7] at 455 nm.

Stability on boiling. The aqueous solution of the complex containing 0.5% Ni was boiled for 1 hr. at 100° or for 30 mins at 115°. The solution remained clear.

Stability at different pH. The pH of the preparation in aqueous solution was regulated within the range of 1-8 with 0.1 to 1.0 N HCl in accordance with the method of Nissim and Robson [8]. The Ni concentration in all solutions was 1 mg/ml. After keeping the solution for 24 hrs at room temperaure the precipitate was removed by centrifugation and the Ni content and pH in supernatant was determined. The results from these studies showed that the stable complexes precipitate within a pH range of 4.1-3.9 and there was no precipitation above pH 4.2.

Stability on admixture with saline and iron-chelate. To a solution of 0.9% sodium chloride (100 ml) was added 0.5% Ni complex (10ml) and admixed throughly and kept for 24 hrs at room temperature. The solution remained clear, showing no sedimentation, coagulation or gel formation. Fe-sucrose complex and Ni-fructose complex containing elemental Fe and Ni in the ratio of 10:1 were admixed throughly and kept for 24 hrs at room temperature. The solution remained stable and clear.

Density and viscosity. The density and viscosity in milli poises refer to a solution containing 0.5% elemental Ni.

Separation of Ni-fructose and Ni-high fructose complex. Separation of Ni-fructose and Ni-high fructose complex was carried out by gel filtration on a Sephadex G-75 column. Five grams sephadex was suspended in enough 0.9% sodium chloride (500 ml) solution. The gel was allowed to swell for at least one day, before pouring into the column. After decanting the finer particles, the gel was poured into the column, 1.5 cm dia, slowly. On settling the gel about 500 ml saline was passed through the column. The hight of the column was 32cm.

The void volume (Vo) of the column was determined by passing blue dextran. Dextrans of known molecular weight were then passed and fractions of 5 ml were collected. Dextran in the fractions was estimated colorimetrically by Anthron method [9]. In this way total volume (v) was obtained and the column was calibrated by plotting V/Vo against the log mol.wt. of the above compounds. Iron dextran [10] complex (inferon), molecular weight 75,000 and iron-sucrose complex prepared by the method reported earlier [11] was passed through the column and fractions of 5 ml were collected. Iron in the fractions was estimated colorimetrically [7] by 2.2-bypyridine. The separation of the molecular species of iron-sucrose complex and their molecular weights are given in Fig. 3. Ni-fructose and Ni-high fructose were then passed through the column. The species of Ni-fructose and Ni-high fructose complex and their mol. wts. are given in Figs. 4 - 5.

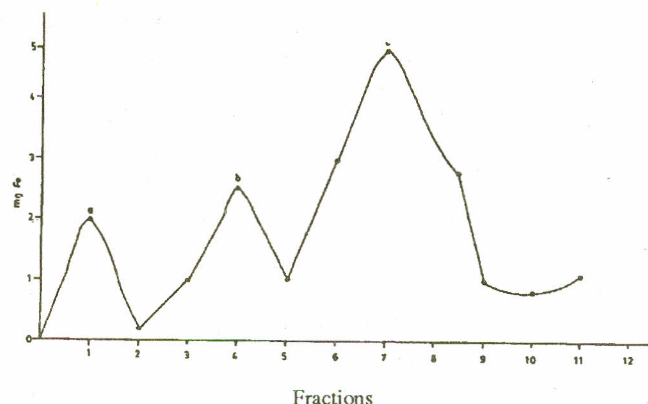

Fig 3. Iron sucrose complex showing molecular species. a=8.8% (M.Wt.95000); b= 18% (M.Wt.65000); c=45.4% (M.Wt.38.000).

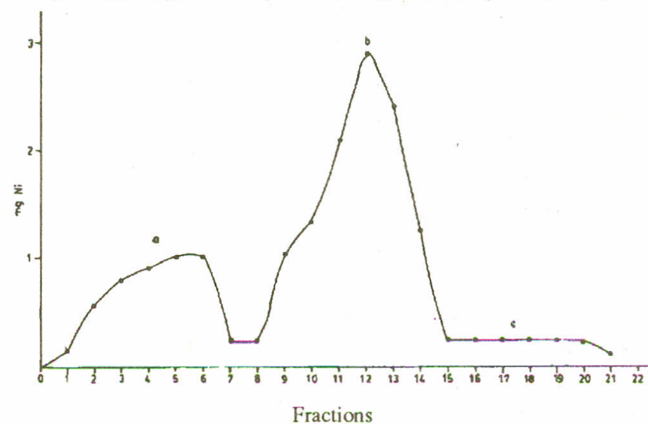

Fig.4. Ni high fructose complex showing the molecular species. a = 20% (M.Wt 66,000); b = 50% m.(Wt. 50,000); c = 30%; M. Wt. unidentified, fractions retained in the column.

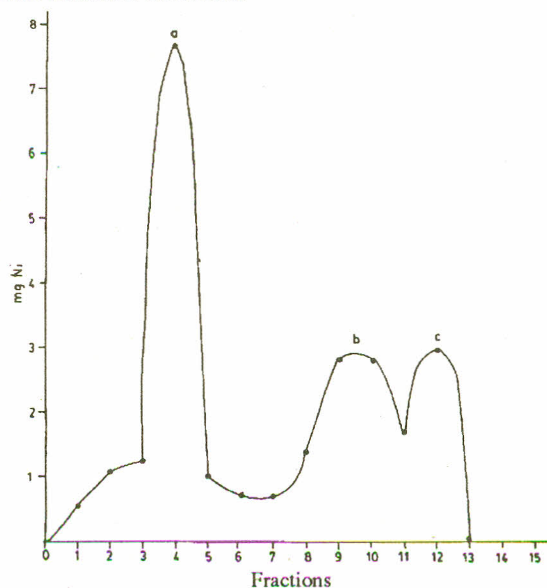

Fig. 5. Ni fructose complex showing moleculars species. a = 44% (M.Wt. 68,000); b = 40.6% (M.Wt. 37,000); c = 12% (M. Wt. 20,000).

Results and Discussion

Ni-fructose and Ni-high fructose complexes have been prepared. These complexes are polymeric and form colloidal solution in water. It was observed that green coloured freshly prepared Ni^{2+}-hydroxide obtained from Ni^{2+}-sulphate on boiling or keeping for few days changed into greyish black. It indicated that it has partially oxidized into Ni^{3+}-hydroxide. Earlier Baris *et al*. [2]. prepared Ni^{3+}-hydroxide by oxidizing Ni^{2+}-hydroxide with hydrogen peroxide for the preparation of the complex. Considering that Ni^{2+}-hydroxide gets auto-oxidized to Ni^{3+}, we omitted the oxidation step.

We observed in case of Co [11], that unless Co^{2+} is oxidized to Co^{3+}, formation of complexes with carbohydrates do not take place. Formation of the stable complex also do not take place when the precipitate of Ni^{3+}-hydroxide is not free from SO_4^- ions. In case of Fe^{3+}, we observed [12] that even the presence of Cl^- ions interfere in the formation of a stable complex. Long boiling of an aqueous solution of the complex is a measure of the stability, when the solutions are not precipitated in this operation they will remain stable for quite a long period of time-more than two years. However, it was observed that when Ni^{3+}-sucrose complex is admixed with 0.9% NaCl the solution remains stable at room temperature, similarly on admixture with Fe-sucrose complex there is no deterioration in the stability even on long boiling. This observation implies that 0.9% NaCl at room temperature does not destabilise the complex. The admixture of iron-sucrose shows that both the complexes are isotonic. The chelate complexes of Ni-fructose and Ni-high fructose are not homogeneous. Ni-fructose (fig. 5) contains three molecular species of mol.wt. 68,000 (44%): 37,000 (40.6%) and 37,000 (12 %), Ni-high fructose (Fig.4) have also got three molecular species of mol. wt 66,000 (20%) mol. wt. 50,000 (5%). mol. wt. unidentified (30%). These chelates resemble closely to the chelate of iron-sucrose complex (Fig. 3). It contained three molecular species: mol.wt. 95,000 (8.8%): mol.wt. 65,000 (18%); mol.wt. 38,000 (45.4%) while an unidentified species Ca (28%) of low mol.wt., which was retained in the column.

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