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NICKEL-SORBITOL-DEXTRIN-CITRIC ACID COMPLEX

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Chelate complexes of nickel with sorbitol;dextrin;-sorbitol-dextrin; and -sorbitol-dextrin-citric acid are described. Complex formation with sorbitol alone is not satisfactory and dextrin is an essential component for its stability. With the exception of sorbitol complex others are stable between pH 10 to 4.2.

Key words: Nickel-chelate, Nickel complex, Nickel-sorbitol.

INTRODUCTION

Preparation and characterization of Ni-complex with sorbitol;-dextrin;-sorbitol-dextrin and -sorbitol-dextrincitric acid has been reported in this communication. Ironsorbitol [1a,b] dextrin-citric acid complex, which is used for the treatment of iron-deficiency anaemia, as an intramuscular preparation was described earlier. It was found that the iron-sorbitol complex is not sufficiently stable. On keeping for a few days at room temperature there appears sedimentation of fine dispersed ferric oxide particles and the percentage of iron in the preparation drops considerably. Later on after a few days more, the preparation turned into a gel. The isoelectric point, which is a better measure of stability of these chelates, is also at a higher pH of 6.5 to 7.5. Normally the stable carbohydrate [2,3] iron and nickel complex have isoelectric point of pH 4.5-5.5. However in conjunction with dextrin, and dextrincitric acid, the complex stabilizes.

Iron cobalt and nickel belong to the first tried of the Periodic Group VIII and the resemblance among them are more pronounced. We attempted to prepare cobalt and nickel complexes following the method used for the preparation of iron-complex. With cobalt, we did not succeed. However, nickel produced a complex with sorbitol, but again it was found to be unstable and the adjunction of dextrin was essential for its stability.

MATERIAL AND METHODS

 $NiSO_47H_2O$ (2.35 g) equivalent to 0.5 g elemental Ni was dissolved in boiled water (20 ml) and sodium hydroxide, 5 % (20 ml) was added to it dropwise with vigorous stirring. The green Ni (OH)₂ obtained was washed with tap and distilled water to free it from electrolytes. The wet hydroxide was taken into a porcelain dish and a calculated amount of hexitol, dextrin, citric acid and sodium hydroxide were admixed thoroughly with it. The contents were heated at 200° for different periods of time as indicated in the Tables. A dark brown cake was obtained which gave a clear solution when dissolved in water. At low temperature or when the time of heating is 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 H_2SO_4 and nitric acid (1:1) in a Kjeldahl flask till the organic matter was carbonized completely. Nickel sulphate thus obtained was estimated colorimetrically using dimethyl glyoxime [4] at 455 nm.

Stability on boiling. The aqueous solution of the complex containing 0.5 % nickel was boiled for 1 hr at 100° or for 30 min. 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 [5] and Robson. The Ni concentration in all solution was 1 mg/ml. After keeping the solution for 24 hrs. at room temperature, the precipitate was removed by cen'trifugation and the Ni content and pH in supernatant was determined. The results from these studies showed that the stable complexes precipitated within a pH range of 4.1-3.9 and there was no precipitation above pH 4.2.

Stability on admixture with saline. To a solution of 0.9 % sodium chloride (100 ml) was added 0.5 % nickel complex (10 ml) and admixed thoroughly and kept for 24 hrs at room temperature. The solution remained clear, showing no sedimentation, coagulation or gel formation. Stability on admixture with iron sorbitol-dextrin-Citric acid. Iron and nickel-sorbitol-dextrin-citric acid complexes containing elemental iron and nickel in the ratio of 10:1 were admixed thoroughly and kept for 24 hr at room temperature. The solution remained stable and clear.

Reaction on admixture with egg alubumin. Fresh egg albumin was prepared by mixing it with water in the ratio of 1:6 in accordance with the method of Hawk [6]. To this was added Ni SO₄ (0.47 %) and admixed thoroughly. The precipitation of egg albumin started on the addition of 0.3 mg elemental Ni.

The Ni complex was also added in the same manner, but no precipitation was observed even on the addition of upto 3 mg of elemental Ni.

The reaction with saline egg albumin was also the same.

Density and viscosity. The density and viscosity in poises refer to a solution containing 0.5 % elemental Ni, (sample No. 2, Table 2) 1.0629, 0.02558, (sample No. 1, Table 2) 1.0810, 0.02830, (sample No. 4, Table 2) 1.0619, 0.02817; (sample No. 1, Table 3) 1.0665, 0.02295 and (sample No. 1, Table 4) 1.0867, 0.02440.

DISCUSSION

The interaction of Ni with sorbitol alone took place smoothly as has been observed with other carbohydrates in a ratio of Ni 0.5 : sorbitol 15:NaOH 3 and 0.5 : 12 : 3 (Table 1, expt. 1 and 2). The complexes were stable even on boiling, but on keeping for few days turned into gel. Their isoelectric point was pH 10-9.5 and 9.5-9. The measure of stability on long boiling is only a rough indication. The isoelectric point or precipitation point with HCl is a more reliable measure and the lower the pH of precipitation the more stable would be the complex. This is due to the fact that these complexes are alkaline and binding of Ni with sorbitol is more firm if the pH of precipitation is lower towards the acidic side. This type of behaviour was also observed by us in iron - sorbitol [Ib] complex. We also found in the case of iron [2] saccharate that a preparation with precipitation pH of 6.5 - 7.5showed gel formation on keeping for a few days while that with pH of 4.9 - 5.2 remained stable for years. In the case of iron-saccharate the stability, however, can be varied by changing time of heating, temperature or porportion of the ingredients, but in the case of sorbitol, the pH of precipitation could not be lowered. Various ratios, change of temperature and time were tried without success. In conjunction with dextrin and citric acid, however the pH of precipitation dropped to 4.1-3.9 (Table 4, expt. 1 and 2). The incorporation of dextrin is essential

Table 1. Ni-sorbitol complex.

Ext. No.	Ratios of Ni:Sorbitol: NaOH	pH of the complex	Stability on long boiling	Metal in complex	Isoelectric point
1.	0.5:15:3	12.6	Stable	90.0	10 -9.5
2.	0.5:12:3	12.3	Stable	90.0	9.5-9
3.	0.5:10:3	12.2	Stable	63.0	8.5-8
4.	0.5: 8:3	10.8	Stable	25.38	8.5-8

Note. Best temp. : 200°; Time : 3.45 hr.

Table 2. Ni-Dextrin complex.

No.	Ratios of Ni-Dextrin : NaOH	pH of the complex	Stability on long boiling	Metal in the complex	Isoelectric point
1.	0.5.15:3	9.65	Stable	89.0	3.8-3.2
2.	0.5.12.3	9.95	Stable	82.0	4.6-4
Note	. Best temp.	200° Tu	me 3.20 hr	to Insmit	
Note	Table	200° Tu 3. Ni-Sorb	me 3.20 hr bitol-Dextr	in-complex	for the tree muscolar p
Note	Table	200° Tu 3. Ni-Sorb	me 3.20 hr pitol-Dextr	in-complex	ion the tra muscular p
Expt	Table	200° Tu 3. Ni-Sorb pH of the	ne 3.20 hr itol-Dextr Stability	in-complex Metal in	Isolectric
Expt No.	Table Ratios of Ni:Sorbitol:	200° Th 3. Ni-Sorb pH of the complex	ne 3.20 hr hitol-Dextr Stability on long	in-complex Metal in the	Isolectric point
Expt No.	Table Table Ratios of Ni:Sorbitol: Dextrin:NaOH	 200° Th 3. Ni-Sorb pH of the complex 	ne 3.20 hr hitol-Dextr Stability on long boiling	in-complex Metal in the complex	Isolectric point

Note: Best temp. : 200° Time: 3.75 hr.

10.6

0.5:10:8:3

2.

Table 4. Ni-Sorbitol-Dextrin-Citric acid complex.

Stable

91.0

5.5-4.7

Exp No.	t. Ratios of Ni:Sorbitol: Dextrin: Citric acid: NaOH	pH of the complex	Stability on long boiling	Metal in the complex	Isoelectric point
1.	0.5:10:8:3:3	9.7	Stable	98.0	4.1-3.9
2.	0.5:10:6:3:3	9.9	Stable	95.6	4.1-3.9

Note: Best temp. : 200° Time. 2.45 hr.

for the stability of the complex, since sorbitol alone does not form a stable complex.

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The fute obtained for density, viscosity and dielectric constitution are used for the starb of the physical properties of ware-emplene carbonate solvent mixitaries. Density measurement of the solvent of stored the properties of ware-empleted of barenetion between water and ethylotic carbonate through hydrogen of the moved the presence of interaction between water and ethylotic carbonate through hydrogen onling which would had to construction in the volveme of the interaction interaction in the volveme of the interaction in the volveme of the interaction are and also in the partial mole of the concentre through the volveme of the interaction interaction.

Act work. Solidit-valuent intriaction of herary system, Denisty-viscosity dielectric constant registrements of binary relative: Excess partial volume and devocion molar oscosity and dielectric unstant for EC-H, O system

INTRODUCTION

Ethylene carbonser, U.B. CH_2CO_3 (Et.) is a appute aptotic solvent with remarkable high indicartic constant (D= 83.6 at 40°). Furthermore if can be easily obtained its pare state. Although the freezing point of ethylene carbonate is 36.6°, this contopound is miscible with water upto a composition of nearly 90 wi % of EC at 25° which permits the preparation of muscal solvents covering as extremely wide range of dielectric constants. The resultant for that some kind of association is present. Also, the expected that some kind of association is present. Also, the associaof proton dottor group in pure EC and the weater basence of the carbonyi group do not permit the association of the solvent by hydrogen bonding. According to the Kirkwood factor and the value of the association of the weater basence of the carbonyi group do not permit the association of the solvent by hydrogen bonding. According to the Kirkwood ealertisted by Bounes [2] a critith degree of association between the solvent apolecules is observed.

From the above view the structural properties of the mixed system EC-water are of interest. Therefore density, viscosity, and dielectric constant measurements were expected to slied some more light on the structure of the solvent mixtures.

EXPERIMENTAL

Ethylene carbonate (BDH grade) was double distilled it reduced pressure and collected at 180°. The meldle cut of the distilation was used for the density, viscosity, and

Density measurements for water-ethylene earbonate mixtures at 23 .50 .45, 40 and 45° were made by using a potenesserer of accur 20 mi capacity. The pylenometer was calibrated with deuble distilled water at each temperature. A modified Unelotide suspended level viscometer was used for viscogity measurements by computing the flow of water-ethylene carbonate solvent mixtures with that of freshly prepared double distilled water whose viscogity is known at studied temperatures.

The apparatus and for the measurements of dielectric constant was z rodul Deleasance type "DR06" which has a frequency thege 0.1-12 MC/S. The adjustment was carried out on a cathode my tube. The turing condenser which has 4500 uniform divisions permitted fine adjustments and allowed a sensitivity of the order 10°. It is important to point out that a frequency of 5 MC/S was used for the measurement of the vola reading (S) for pure water and water-eihylottelearhousic mixtures.

The dielectric annumit (D) of a solution was calculated sing the equation

 $\mathbf{D} = \mathbf{AS} + \mathbf{C}$

where S is the scale reacing measured by the DeKameter. A and C are constants which can be readily evaluated by the least squares method taking into consideration pure water as a standard liquid. Substitution of the obtained values of the scale readings for pure water at different temperatures and the corresponding value of B (obtained from the (literature) [4], the values A and C could be obtained and axed for the evaluation of the dislective