Polarographic Separation of Cobalt from Nickel

By

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With 3 Figures in the Text

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Most of the reported work on polarography of cobalt has been done with a view to effect its determination in presence of nickel. The base electrolytes used either form complexes with one of the two ions or lead to polarization of the electrodes, resulting in preferential reduction of one of these cations. Amongst the former may be mentioned pyridine, ammonia, acetophenone and thiocyanate. The latter type includes tartarates, ethylenediamine, triethanolamine, ammonia and dimethylglyoxime. Of the various other methods investigated for separation of cobalt and nickel, the use of catalytic waves of cystine, cysteine and other proteins in presence of cobalt in small quantities, the oxidation of cobalt to the trivalent state, polarography in non-aqueous media and in mixtures of complexing salts (ethylenediaminetartarates, K$_2$P$_2$O$_7$ and EDTA + KCN) are noteworthy.

The supporting electrolytes used in most of these polarographic studies have nitrogen as the complexation centre. To ascertain whether the phenomenon was generally applicable, a number of nitrogen compounds having an active nitrogen complexing atom (e.g., urea, hydrazine, phenylhydrazine, quinoline, quinoline ethyliodide, aniline) were tried as supporting electrolytes in the polarography of cobalt and nickel.

Preliminary studies revealed that quinoline and aniline were ineffective because of their low solubility in water, while quinoline ethyliodide was itself reduced at the D.M.E. The separations with the remaining compounds were also not very marked, but a mixture of urea with pyridine and hydrazine showed promise. The present communication reports these latter studies in some detail.

Experimental

All chemicals used in these studies were of E. Merck's extra pure grade. Hydrazine, phenylhydrazine, quinoline, aniline and pyridine were all redistilled, only constant boiling fractions being used. Cobaltous chloride and nickel chloride were from B.D.H. AnalR. samples.

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Solutions. Cobalt(II) chloride solution was approximately 0.1 M and was standardized by the anthranillic procedure. Approximately 0.1 M nickel(II) chloride solution was standardized by the dimethylglyoxine method. Fresh solutions of gelatine were prepared every day.

Current-voltage curves were drawn in the usual manner with a Leeds and Northrup Electrochemical Type E. The polarographic cell was a jacketted pyrex beaker of 25 ml capacity, covered with a three hole rubber bung. Water from a thermostat maintained at 35 ± 0.1°C was circulated in the jacket during the course of a recording. The saturated calomel reference electrode (S.C.E.) was coupled to the cell through a KCl-agar bridge. Oxygen was removed from the test solution by streaming purified hydrogen and the surface of the solution was kept flushed with a slow flow of hydrogen during the recording. The capillaries used for polarograms in pyridine-urea and hydrazine-urea had a rate of flow of 2.7428 mg and 2.4140 mg per second respectively with open circuit. At a 50.0 cm mercury head, the drop time 't' was 3.0 and 3.5 seconds respectively. The height of the polarographic waves was measured by the method of Muller, allowance being made for residual currents in the determination of the diffusion current data.

Polarographic Behaviour of Cobalt an Nickel

Effect of pH

The effect of pH variation on the characteristics of the two cations was investigated in pyridine-urea and hydrazine-urea base electrolytes.

Rising pH values caused the cobalt half wave potentials to shift to more negative values in general. The effect, however, was not very consistent and a slight shift towards positive values was observed in the pH range 4.0—5.0. From 5.0—6.5 the $E_{1/2}$ was more or less constant but beyond this stage there was a marked shift to negative potentials; but the waves were ill defined. Cobalt was precipitated in solutions more alkaline than pH 8.5. In urea-hydrazine the cobalt $E_{1/2}$ were shifted towards positive potentials with increasing basicity and cobalt precipi-