

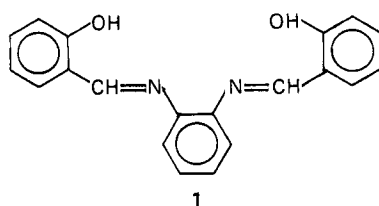
Bissalicylidene-*o*-phenylenediimine as a Solvent Extraction - Spectrophotometric Reagent for Nickel(II)

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By virtue of their co-ordinating nitrogen atoms Schiff bases show relatively high co-ordinating affinity towards transition metals and therefore offer possibilities as specific reagents for these elements that have not as yet been extensively explored. During the course of investigations into the use of Schiff bases in the solvent extraction of transition metals^{1,2} it was observed that bissalicylidene-*o*-phenylenediimine (**I**) extracted nickel(II) into toluene as an intense orange - red species. This colour is presumably related to the planar structure of the complex.³ In view of its apparent sensitivity for nickel(II), bissalicylidene-*o*-phenylenediimine has been investigated in more detail as a potential solvent extraction - spectrophotometric reagent for nickel(II).



Experimental

Reagents

Bissalicylidene-*o*-phenylenediimine was prepared by the slow addition of a solution of *o*-phenylenediamine (1.1 g in 20 ml of methanol) to a methanolic solution of salicylaldehyde

(2.5 g in 20 ml). Heat was evolved and the product formed as yellow - orange crystals. These were recrystallised from methanol (melting-point 164 °C).

Bissalicylidene-*o*-phenylenediimine nickel(II) was prepared by mixing methanolic solutions of bissalicylidene-*o*-phenylenediimine (0.5 g in 50 ml) and nickel acetate (0.42 g in 50 ml). The product separated as dark red crystals.

Standard nickel solutions were prepared from analytical-reagent grade nickel sulphate and standardised by complexometric titration.

Procedures

The distribution of nickel(II) between aqueous solution and bissalicylidene-*o*-phenylenediimine (10^{-2} mol l $^{-1}$) in toluene as a function of pH was measured by atomic-absorption spectroscopy using the nickel absorption line at 232 nm.

Proposed Analytical Procedure

To 10 ml of nickel(II) solution [the nickel(II) content being less than 10 μ g ml $^{-1}$] add 1 ml of ammonia - ammonium chloride buffer (pH 10) and shake for 10 min with 10 ml of bissalicylidene-*o*-phenylenediimine in toluene solution (10^{-2} mol l $^{-1}$). Separate the phases and measure the absorbance at 490 nm in 1-cm cells using the reagent solution pre-equilibrated with aqueous buffer as a blank.

Results and Discussion

Preliminary investigations established that extraction of nickel(II) by bissalicylidene-*o*-phenylenediimine in toluene (10^{-2} mol l $^{-1}$) is quantitative between pH 7.5 and 11.0. It was also shown that although the extent of the extraction is unchanged in this pH range, the rate of extraction increases with pH and decreases with increasing buffer concentration. Further unpublished work from this laboratory suggests that these two observations are related to the rate and mechanism of the formation of the complex between nickel(II) and the quadridentate reagent. At pH 10.5 shaking for 10 min was found to be sufficient for quantitative extraction.

The spectrum of the complex in toluene and that of the species extracted by the reagent (10^{-4} mol l $^{-1}$) in toluene are shown in Fig. 1.

For nickel(II) concentrations of 10 μ g ml $^{-1}$ (1.7×10^{-4} mol l $^{-1}$) or less the calibration graph at 490 nm is linear, the complex having a molar absorptivity of 8.62×10^3 l mol $^{-1}$ cm $^{-1}$. Sensitivity can be enhanced by using a 10:1 phase ratio for extraction.

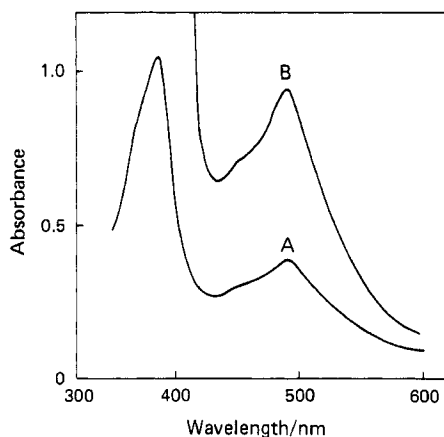


Fig. 1. A, Spectrum of bissalicylidene-*o*-phenylenediiminenickel(II) (5×10^{-5} mol l $^{-1}$) in toluene; B, spectrum of nickel(II) extract (10^{-4} mol l $^{-1}$) in toluene.

A study of interferences showed that the absorbance at 490 nm was unaffected by the presence of a ten-fold excess of magnesium(II), calcium(II), cadmium(II), cobalt(II), iron(II) or iron(III). However, copper(II) caused serious positive interference even when its concentration was lower than that of the nickel(II). This interference was removed by a preliminary extraction at pH 4 using the procedure previously recommended¹ for the solvent extraction - spectrophotometric determination of copper(II).

References

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