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Synthesis and Spectrophotometric Studies of 2-(2-Imidazolylazo)-5-Diethylamino Phenol

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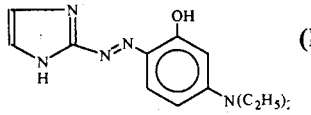
Abstract: In this paper, 2-(2-imidazolylazo)-5-diethylamino phenol (IZAPN) was prepared, the protonation behaviour and the condition of spectrophotometric determination of cobalt with this reagent are reported. The results show that the new colour reagent reacts with cobalt to from a stable purple red complex (1:3). However, the complex formed could be changed into another species with stable absorptivity by addition of mineral acid (1+1). The method is highly selective and sensitive and has been applied to the direct determination of cobalt in some alloys with satisfactory results.

Keywords: Synthesis, imidazolylazo spectrophotometry, cobalt.

In a search for new sensitive and selective organic reagents, a thorough study of some of the quinolylazo, pyridylazo compounds has been reported.[1-4] But triazolylazo and imidazolylazo compounds have not been studied. In an earlies paper,[5] we have reported the synthesis and spectrophotometric studies of 2-(1,3,4-triazolylazo)-5-diethylamino phenol and 2-(5-carboxy-1,3,4-triazolylazo)-5-diethylamino phenol. In this paper, 2-(2-imidazolylazo)-5-diethylamino phenol **(IZAPN)** was prepared, the conditions of its reaction with cobalt were studied. It was found that the reagent had high sensitivity and selectivity in the determination of microgram amounts of cobalt under the conditions established. The structure of the reagent is:



(IZAPN)

Experimental

High-purity (99.99%) cobalt was dissolved in nitric acid (1+1). The solution was finally diluted to 10 mg/L. Acetate acid and sodium acetate were used for pH5 adjustment. The solutions (1+1) of mineral acids were made from high-purity sulphuric, hydrochloric, nitric and perchloric acids. Concentration of **IZAPN** solution was 1×10^{-3} mol/L, in ethanol. All other reagents were of A. R. grade. Carlo Erba 1106 elemental analyzer (Italy), UV-265Fw spectrophotometer (Japan). IR-408 spectrophotometer (Britain) and pHS-3C pH meter (China) were used for analysis.

Preparation of 2-(2-imidazolylazo)-5-diethylamino phenol (IZAPN)

To a solution of 1.5 g (0.065 mol) of metal sodium in 30 ml of absolute ethanol, 2-amino-imidazole 4.15 g (0.050 mol) in 100 ml of anhydrous ether and 18 g (0.154 mol) of isopentyl nitrite were added, and the mixture was refluxed for 6h. 3-N,N-Diethylamino phenol 8 g (0.048 mol) in ethanol and hydrochloric acid (1+3) were added at 0-5℃ until the mixture was slightly acidic and the deep red color appeared. Crude reddish brown crystals were formed upon dilution with water (200 ml), which were filtered off, washed with water and the crude material was recrystallized from ethanol-water.

Analysis: $C_{13}H_{17}N_5O$ found: 60.52%C, 6.70%H, 26.89%N; calculated:60.21%C, 6.61%H, 27.01%N; IR (KBr, ν/cm^{-1}): 1630 (N=N), 1535 (⬡), 1300 (C-N), 3500 (OH), 1200-1250 (C_2H_5); ^{1}HNMR (ppm) δ_H: 1.1-1.2 (6H), 3.3-3.6 (4H), 6.6 (1H), 7.3-7.6 (2H), 8.1 (1H); Reddish brown powder (m.p.223-226℃).

Protonation behaviour of the reagent

The reagent is insoluble in water, but soluble in various organic solvents including ethanol, acetone and dioxane. The **IZAPN** proton-dissociation constants have values of pKa_1= 5.4 and pKa_2=10.9. The absorption spectra of the reagent at different pH values are shown in **Figure 1.**

Cobalt was determined as follows: A suitable aliquot of sample solution containing up to 10 μg of cobalt was transferred into a flask and 2.0 ml solution of **IZAPN** 1×10^{-3}mol/L was added, pH was adjusted to 5 with 5 ml of **HAc-NaAc** solution. After 10 min. 2 ml of hydrochloric acid (1+1), or sulfuric acid (1+1) was added. The mixture was diluted to volume. The absorption of the cobalt complex was measured at 570 nm against a reagent blank with 1-cm cells.

Results and Discussion

The coloured complexes are easily prepared by adding a few drops of a solution of **IZAPN** in ethanol to solutions of the metal ions at pH5. However, only cobalt complex can be changed to another species with stable absorptivity by addition of mineral acid (1+1), HCl, H_2SO_4, HNO_3 or $HClO_4$ and the molar absorptivity can be increased. Complexes of other ions were decomposed to the reagent upon addition of the acid. The results are shown in **Table 1.**

The absorption curves of **IZAPN** and its cobalt complex in 1.2 mol/L hydrochloric acid are shown in **Figure 2.** The absorption maximum of **IZAPN** is at 405 nm, but that of the complex is at 570 nm, $\Delta\lambda$ =165 nm.

Actually, 1.0 ml of 1×10^{-3}mol/L **IZAPN** solution is sufficient to complex 10 μg of cobalt. The color was formed in 10 min at room temperature. The absorbance was stable for at least one day. Beer's law is obeyed in the range of 0-0.4 mg/L of cobalt. The apparent molar absorptivity is 4.87×10^4L • mol^{-1} • cm^{-1} at 570 nm.

Table 1. Colour reaction of some metal ions with **IZAPN**

Ions	pH5	Molar Absorptivity ($L.mol^{-1}.cm^{-1}$)	Acid added			
			H_2SO_4	HCl	HNO_3	$HClO_4$
Reagent	yellow	3.2×10^4	yellow	yellow	yellow	yellow
Co^{2+}	purple red	b	purple red*	purple red*	purple red*	purple red*
Bi^{3+}	orange red	2.22×10^4	a	a	a	a
Cu^{2+}	purple red	3.54×10^4	a	a	a	a
Fe^{3+}	red brown	b	a	a	a	a
Pd^{2+}	purple red	b	a	a	a	a
Ni^{2+}	orange	2.96×10^4	a	a	a	a
V^{5+}	orange		a	a	a	a

a: No color reaction or decomposed to the color of reagent, b: molar absorptivity very small ,
*: molar absorptivity increased to $4.87\times10^4 L.mol^{-1}\cdot cm^{-1}$.

Numerous cations and anions were examined with the above mentioned method. The result showed, that most cations and anions had no effect at milligrams level, so the method is extremely selective and sensitive.

The empirical formula of the complexes was studied by the continuous and mole-ratio methods. The curves obtained indicate the formation of a complex 1:3(metal:reagent) in the presence 1.2 mol/L hydrochloric acid.

Figure 1. IZAPN Absorption spectra at different pH values. **IZAPN** against H_2O blank, **[IZAPN]**=4×10^{-5}mol/L, pH: 1,1.0; 2, 3.0; 3, 4.0; 4, 5.0; 5, 6.0; 6, 7.0; 7, 8.0; 8, 9.0; 9, 10.0; 10,11.0; 11,12.0.

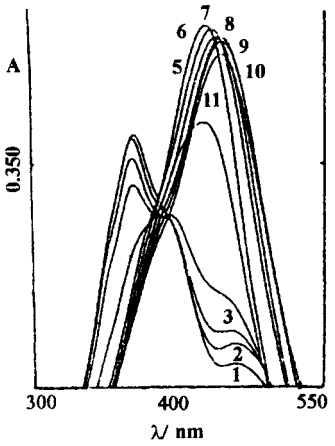
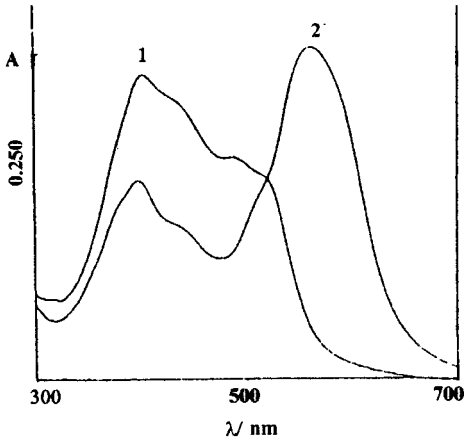


Figure 2. Absorbance curves of **IZAPN and** its cobalt complex in 1.2 mol/L hydrochloric acid **[IZAPN]**=4×10^{-5} mol/L, $[Co^{2+}]$= 6.79×10^{-6}mol/L. 1).**IZAPN** against H_2O blank.2).Complex against **IZAPN** blank



A sample of alloy (1 g) was dissolved in the usual way and cobalt was determined on an aliquot of the solution. Some results are shown in **Table 2**.

Table 2. Determinaion of cobalt in some alloys (n=6)

Alloy	Certificate (%)	Found (%)	RSD (%)
35CrMoV-250	0.012	0.0121	2.0
38CrMoAl-251	0.011	0.0110	1.8

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