Acid-Base Characteristics of Naphthazarin and Solution Equilibria of Yttrium(III) Chelates

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Summary. The spectral absorption and acid-base characteristics of naphthazarin (5,8-dihydroxy-1,4-naphthoquinone, NAZA) in ethanol water medium containing 50% (v/v) ethanol have been studied, and the pKa values determined. Two equilibria are established in solution at pH 2.5–11.5, based on the acid dissociation of the nonionized form of the reagent. The existence of these equilibria is confirmed by potentiometric pH titrations and the precision of the equilibrium study is improved. The composition, molar absorptivities and stability constants of the chelates of NAZA with yttrium(III) have been determined spectrophotometrically under the conditions encountered in this study. The complexation equilibria existing in solution are discussed. The Y(NAZA) monoligand chelate formed at pH 5.5 (ε = 1.15 x 10^41 mol⁻¹ cm⁻¹ at 595 nm) allows the determination of 1.95–8.86 µg ml⁻¹ yttrium. Interferences and their elimination have been studied.

Keywords. Yttrium(III) determination; Naphthazarin; Spectrophotometry; Complexation equilibria.

Introduction

Although several procedures have been proposed in the last decade for direct or extraction spectrophotometric determination of yttrium [1–6], there is a need for a simple, rapid and sensitive method with faster colour development which does not require rigid control of pH. In this paper detailed studies on the complexation equilibria of Y³⁺ with 5,8-dihydroxy-1,4-naphthoquinone (Naphthazarin, NAZA) in 50% (v/v) ethanol were carried out, the aim being to establish the equilibria existing in solution and to determine the optimum conditions favouring direct
spectrophotometric determination of $\text{Y}^{3+}$ with this reagent. For this purpose, the spectral and acid-base properties of $\text{NAZA}$ are examined. The acid-base equilibria of the reagent are characterized using spectral and potentiometric $p\text{H}$ titration methods. In spite of the unique combination of properties that enable the ligand $\text{NAZA}$ to be utilized in some novel applications, no studies have yet been reported involving the complex equilibria of metal ions with this reagent.

**Experimental Part**

All chemicals were of analytical-reagent grade and de-ionized water (or pure ethanol) was used for the preparation of solutions. A stock solution of $\text{NAZA}$ of concentration of $2 \times 10^{-3}$ $M$ was prepared by dissolving the accurately weighed amount of the purified reagent in ethanol. More dilute solutions were obtained by appropriate dilution. A $5 \times 10^{-3}$ $M$ solution of yttrium nitrate was prepared by dissolving the required amount of the AnalaR product in re-distilled water. The metal content of the solution was determined as recommended [7]. Solutions of lower concentrations were obtained by accurate dilution. Solutions of diverse ions used for interference studies were prepared using AnalaR products of nitrates, acetates or chlorides of the metal ions and potassium or sodium salts of the anions to be tested. Thiel buffers (boric acid, borax, succinic acid and sodium sulphate) of $p\text{H}$ 3–9 were used for $p\text{H}$ adjustment in the interference experiments.

The absorption spectra of the solutions were recorded on a Perkin-Elmer Lambda 3B spectrophotometer in the range 400–700 nm using 1-cm matched stoppered silica cells. Values of $p\text{H}$ were measured using a Radiometer $p\text{H}$ meter (Model M63) equipped with a Radiometer combined-glass electrode (GK 2301C). The $p\text{H}$ meter was calibrated regularly before use with standard buffer solutions. All the spectrophotometric and potentiometric measurements were performed in 50% $v/v$ ethanol–water at 25 °C. The $p\text{H}$ values in 50% $v/v$ ethanol were corrected as described by Douheret [8].

**Results and Discussion**

**Spectroscopic and Acid-Base Properties of $\text{NAZA}$**

In ethanol–water mixtures containing 50% ($v/v$) ethanol and at $p\text{H}$ 2.5–11.5, the reagent, $\text{NAZA}$, exists in at least three different forms showing the absorption maxima at 505, 555, and 600 nm. The $p\text{H}$-dependence of the absorbance at ionic strength of 0.1 $M$ (NaClO$_4$) measured at various wavelengths indicates gradual association of protons with the oxygen of the bis-hydroxyl substituents at $p\text{H}$ ≤ 11.6 and ≤ 8.8. The association of the second proton in the bis $\alpha$-hydroxylic grouping is accompanied by a slight change in the optical properties of the reagent. The absorption band at 505 nm is caused by the nonionized species of the reagent ($L\text{H}_2$) and disappears completely at $p\text{H}$ values > 8.9. At a $p\text{H}$ of ~ 8.1, the spectrum of $\text{NAZA}$ reveals an absorption at 555 nm by the monoionized form ($L\text{H}^-$) (c.f. Fig. 1). The latter band shifts to longer wavelengths on increasing the $p\text{H}$ of the medium. The solution spectra of the reagent display a symmetrical and high intense band with $\lambda_{\text{max}}$ at ~ 600 nm at $p\text{H}$ > 11.2 corresponding to the dianionic form ($L^2^-$).

The variation of absorbance with $p\text{H}$ at 555 and 600 nm reveals the existence of two acid-base equilibria in solutions of $\text{NAZA}$ ($L\text{H}_2$) within the $p\text{H}$ range studied. These equilibria can be represented by the equations

\begin{align*}
L\text{H}_2 & \rightleftharpoons L\text{H}^- + H^+, \quad (1) \\
L\text{H}^- & \rightleftharpoons L^2^- + H^+. \quad (2)
\end{align*}