Monatshefte für Chemie 124, 1089–1098 (1993)

Monatshefte für Chemie
Chemical Monthly

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 ($\varepsilon = 1.15 \times 10^4\,\mathrm{l\,mol^{-1}\,cm^{-1}}$ at 595 nm) allows the determination of 1.95–8.86 $\mu\mathrm{g\,ml^{-1}}$ yttrium. Interferences and their elimination have been studied.

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

Säure-Base-Charakteristik von Naphthazarin und Lösungsgleichgewichte von Yttrium(III)-Chelaten

Zusammenfassung. Es wurden die spektralen Absorptions- und die Säure-Base-Charakteristiken von Naphthazarin (5,8-Dihydroxy-1,4-naphthochinon, *NAZA*) in Ethanol-Wasser (*v*/*v*, 50/50%) untersucht und die *pKa*-Werte bestimmt. Es wurden zwei Gleichgewichte bei *pH* 2.5–11.5, basierend auf der Säuredissoziation der nichtionisierten Form des Reagens, gefunden. Die Existenz dieser Gleichgewichte wurde durch potentiometrische *pH*-Titrationen überprüft, die Zusammensetzung, die molaren Extinktionskoeffizienten und die Stabilitätskonstanten der Chelate von *NAZA* mit Yttrium(III) wurden spektrophotometrisch bestimmt. Der Y(*NAZA*)-Monoligandenkomplex bei *pH* 5.5 ($\varepsilon = 1.15 \times 10^4\,\mathrm{l\,mol^{-1}\,cm^{-1}}$ bei 595 nm) ermöglicht die Yttriumbestimmung bei Konzentrationen von 1.95–8.86 $\mu\mathrm{g\,ml^{-1}}$. Störungen und ihre Vermeidung wurden untersucht.

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 Y^{3+} 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 Y^{3+} with this reagent. For this purpose, the spectral and acid-base properties of *NAZA* are examined. The acid-base equilibria of the reagent are characterized using spectral and potentiometric *pH* titration methods. In spite of the unique combination of properties that enable the ligand *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 *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 *pH* 3–9 were used for *pH* 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 *pH* were measured using a Radiometer *pH* meter (Model M63) equipped with a Radiometer combined-glass electrode (GK 2301C). The *pH* 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 *pH* values in 50% *v*/*v* ethanol were corrected as described by Douheret [8].

Results and Discussion

Spectroscopic and Acid-Base Properties of NAZA

In ethanol–water mixtures containing 50% (*v*/*v*) ethanol and at *pH* 2.5–11.5, the reagent, *NAZA*, exists in at least three different forms showing the absorption maxima at 505, 555, and 600 nm. The *pH*-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 $pH \leqslant 11.6$) and $\leqslant 8.8$. The association of the second proton in the bis α-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 (LH_2) and disappears completely at *pH* values > 8.9. At a *pH* of ~ 8.1, the spectrum of *NAZA* reveals an absorption at 555 nm by the monoionized form (LH^-) (c.f. Fig. 1). The latter band shifts to longer wavelengths on increasing the *pH* of the medium. The solution spectra of the reagent display a symmetrical and high intense band with $\lambda_{\max}$ at ~ 600 nm at $pH > 11.2$ corresponding to the dianionic form (L^{2-}).

The variation of absorbance with *pH* at 555 and 600 nm reveals the existence of two acid-base equilibria in solutions of *NAZA* (LH_2) within the *pH* range studied. These equilibria can be represented by the equations

$$LH_2 \rightleftharpoons LH^- + H^+, \qquad (1)$$

$$LH^- \rightleftharpoons L^{2-} + H^+. \qquad (2)$$

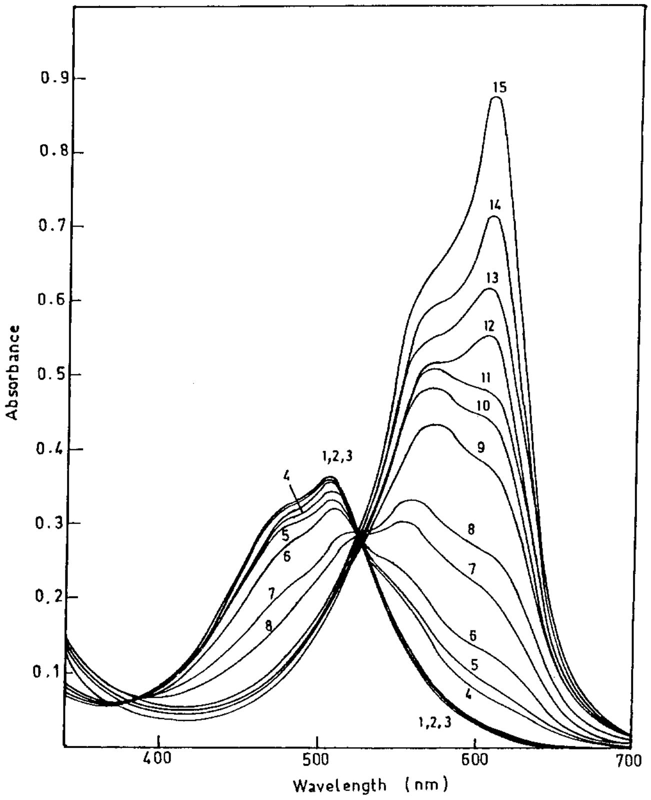

Fig. 1. Absorption spectra of $7.5 \times 10^{-5}\,M$ *NAZA* at different *pH* values, 50% (*v*/*v*) ethanol. *pH*: (1) 3.7; (2) 4.55; (3) 5.54; (4) 6.65; (5) 7.10; (6) 7.38; (7) 7.75; (8) 8.20; (9) 8.56; (10) 9.45; (11) 10.05; (12) 10.85; (13) 11.1; (14) 11.35; (15) 11.85

The shape of the band envelope can be correlated to the nature of the absorbing species. For LH_2 and the doubly ionised forms of the compound, the bis α-hydroxyl grouping can participate more or less equally in the charge-transfer process, and hence the electronic transitions would lead to single more or less symmetrical bands. The monoanionic species of *NAZA* is characterized by a less symmetrical or split CT band.

The absorbance versus *pH* graphs were interpreted according to the relationship [9]

$$\log(A - \varepsilon_1 C_L)/(\varepsilon_2 C_L - A) = q\,pH - pK_a, \qquad (3)$$

where C_L is the total reagent concentration in the final solution and ε_1 and ε_2 are the molar absorptivities of LH_x and LH_{x-1} forms, respectively, assuming that a particular acid-base equilibrium predominates for selected wavelengths. The graphical logarithmic analysis of the *A*-*pH* graphs was applied to different wavelengths and the deviations from the mean *pK* values were evaluated using

$$\sigma(pK) = \left[\frac{1}{N_\lambda - 1}\sum_{\lambda=1}^{N_\lambda}(p\bar{K} - pK_n)^2\right]^{1/2}, \qquad (4)$$

where $p\bar{K}$ is the mean value calculated from the *pK* values obtained from graphs of an individual wavelength *n*, and N_λ is the number of wavelengths used. Refined values of the acidity constants were calculated using general least squares method by treating the original data [$A = \mathrm{f}(pH)$] and calculating the estimated standard

Table 1. Dissociation constants of *NAZA* in 50% (*v*/*v*) ethanol, $I = 0.1\,M$ $NaClO_4$, 25 °C

Equilibrium	pK_{a_i}	
	Spectrophotometric method	Potentiometric *pH* titration method
$LH_2 \rightleftharpoons LH^- + H^+$	8.25 ± 0.02	8.38 ± 0.01
$LH^- \rightleftharpoons L^{2-} + H^+$	11.35 ± 0.03	11.22 ± 0.02

deviation concerning scattered experimental data [10]. The mean pK_{a_i} values of the reagent are given in Table 1.

The acid dissociation of *NAZA* was ascertained by titrating 50 ml of 75 mmol dm^{-3} perchloric acid and sodium perchlorate ($I = 0.1$ mol dm^{-3}, 25 °C) in the presence and absence of 0.25 mmol dm^{-3} of the reagent in an ethanol–water medium of (50% (*v*/*v*) ethanol) with 0.05 mol dm^{-3} sodium hydroxide and by using the differences in sodium hydroxide consumption between two such titrations for the calculation. In order to obtain reliable constants, at least six independent pairs of titration curves were recorded and the results were averaged. The *pH* titration curve of *NAZA* was characterized by two well-defined inflections at $a = 1$ and 2 (where a is the number of moles of alkali added per mole of reagent). The two inflection points can be unambiguously assigned to stepwise dissociation of the proton according to Eqs. (1) and (2). The corresponding acidity constants determined by *pH* titrations are given in Table 1. The values obtained are in good agreement with those determined by the spectrophotometric method.

In order to improve the precision of the equilibrium measurements in alkaline solution, linearization of the titrimetric data for the two equivalence points of *NAZA* was carried out using the computed Gran functions [11, 12],

$$W_t = \left(\frac{10^{-pH}}{\gamma_+} N_b v_b - \frac{10^{-pK_w}}{\gamma_- \gamma_+} V - K_a \frac{10^{pH - pK_w}}{\gamma_-} V\right), \tag{5}$$

$$B_t = V\left(10^{pH - pK_w} - \frac{10^{-pH}}{K_a} [L^{2-}] \gamma_-^2\right), \tag{6}$$

where N_b is the concentration of sodium hydroxide added and V is the total volume of solution being titrated. The $[L^{2-}]$ value was obtained, at different *pH* values, from the α-fraction diagram of the species. The value of pK_w was taken to be 14.38 ($I = 0.1$ mol dm^{-3}, 25 °C, 50% (*v*/*v*) ethanol). The ionic activity coefficient (γ_i) was calculated at $I = 0.1$ mol dm^{-3} by means of the Davies equation [13]

$$-\log \gamma = Az^2 \left\{ \left[\frac{\sqrt{I}}{(1 + \sqrt{I})} \right] - 0.2I \right\}. \tag{7}$$

The Gran plot gives reasonable agreement with the concentrations of the reagent to be titrated and allows for experimental errors of less than 1%.

In this study, the effect of hydroxide ions on the acid-basic equilibria of *NAZA* was examined. The ionization constants corresponding to equilibria (1) and (2) were checked using the relationship shown in Eqs. (8) and (9) [14],

$$pK_{a_1} = pH + \log\left(\frac{C_t - C_{\mathrm{NaOH}} - C_{\mathrm{H^+}} + C_{\mathrm{OH^-}}}{C_{\mathrm{NaOH}} + C_{\mathrm{H^+}} - C_{\mathrm{OH^-}}}\right) + \frac{AI^{1/2}}{1 + 4.56BI^{1/2}}, \qquad (8)$$

$$pK_{a_2} = pH + \log\left(\frac{2C_t - C_{\mathrm{NaOH}} - C_{H^+} + C_{\mathrm{OH^-}}}{C_{\mathrm{NaOH}} - C_t + C_{\mathrm{H^+}} - C_{\mathrm{OH^-}}}\right) + \frac{3AI^{1/2}}{1 + 4.56BI^{1/2}}, \qquad (9)$$

where C_t is the total initial concentration of *NAZA* allowing for the volume changes caused by the addition of titrant, and C_{NaOH} is the total concentration of NaOH added. The values of $C_{\mathrm{H^+}}$ and $C_{\mathrm{OH^-}}$ were calculated using the relations

$$-\log C_{\mathrm{H^+}} = pH + \log \gamma_{\mathrm{H^+}}, \qquad (10)$$

$$-\log C_{\mathrm{OH^-}} = pK_w - pH + \log \gamma_{\mathrm{OH^-}}. \qquad (11)$$

The constants A and B of the Debye-Hückel equation were taken to be 0.905 and 0.384, respectively [14].

The above data treatment gives precise values for the acid dissociation constants of *NAZA* in the medium employed.

Complexation Equilibria of Yttrium(III) with NAZA

The complexation equilibria of Y^{3+} with *NAZA* were studied in solutions containing 50% (*v*/*v*) ethanol at the *pH* range 3.8–8.2. The solution spectra were recorded in the presence of an excess of the metal ion, in equimolar solutions and in presence of excess reagent. The absorption spectra of equimolar solutions and those containing a preponderance of Y^{3+} are analogous and exhibit an absorption band at 590 nm. For solutions with excess of reagent, the spectrum reveals the formation of two complex species. In addition, to the band observed at 590 nm in the *pH* range 4.5–6.2 a new and intense absorption band of $\lambda_{\max}$ at 610 nm is observed in the *pH* range 6.4–7.2. The absorption bands characterizing the yttrium(III) complex species at *pH* 5.95 and 6.9 are shown in Fig. 2. The absorbance versus *pH* graphs for the above solutions show the ranges of formation of the complex species and existence of complex equilibria set in solution within the *pH* range studied.

The first complexation equilibrium is due to complexation of Y^{3+} with LH_2 form of the ligand according to the general equation

$$mY^{3+} + nLH_2 \xrightleftharpoons{{}^*K_{11}} Y_mL_nH_b^{(3m-q)+} + qH^+ \qquad (12)$$

(where $b = 2n - q$).

For solutions containing a preponderance of *NAZA*, the absorbance versus *pH* graphs indicate the presence of two complex equilibria that are sufficiently separated. The second rising part of these graphs is assumed to be due to a stepwise complex transition with further ligand species coordinated,

$$Y_mL_nH_b + pLH_2 \xrightleftharpoons{{}^*K_{21}} Y_mL_{n+p}H_c + qH^+ \qquad (13)$$

(where $c = b + 2p - q$).

All absorbance vs. *pH* graphs at various wavelengths and concentration ratios

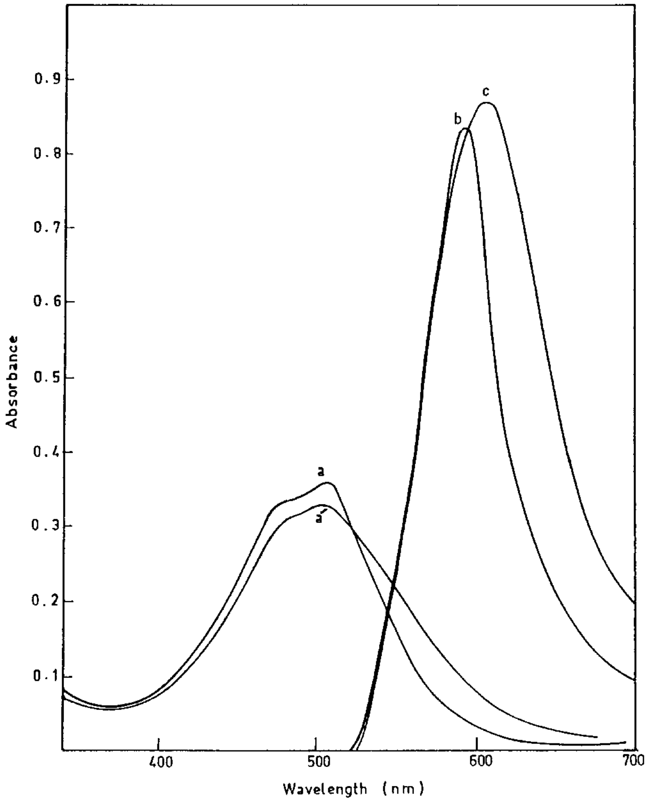

Fig. 2. Absorption spectra of Y^{3+}-binary complexes (50% (v/v) ethanol, (a) *NAZA* ($pH = 5.95$); (a') *NAZA pH* (6.95); (b) 1:1 Y^{3+}-*NAZA* ($pH = 5.95$); (c) 1:2 Y^{3+}-*NAZA* ($pH = 6.95$); (b, c versus reagent blank)

of components show a rapid decrease of absorbance above *pH* 7 owing to the hydrolysis of the complexed ligand.

A set of absorbance-*pH* graphs for varying metal ion excess was analysed under the conditions of the so-called "corresponding solutions" [15, 16] according to Eq. (14),

$$(pH)_i = \frac{m}{q}(-\log C_M) + \text{constant}, \tag{14}$$

where $(pH)_i$ represent the *pH* values for corresponding solutions, *m* is the number of metal ions bound in the chelate and *q* is the number of protons liberated during complexation. The results obtained reveal no evidence for the presence of any dinuclear complex in solution under the experimental conditions.

The absorbance vs. *pH* graphs for solutions with an excess of one component or equimolar solutions were interpreted by direct graphical and logarithmic analysis using the relations derived earlier by Sommer et al. [15, 16] and the generalized approach described previously [16–18].

By considering values of the acid dissociation constants of *NAZA* one can assume that the non-ionized form of this reagent is the prevalent ligand species in the *pH* range of complexation.

The following equilibria were assumed during the graphical analysis of the absorbance vs. *pH* graphs:

$$Y^{3+} + LH_2 \rightleftharpoons YLH^{2+} + H^+, \tag{A}$$

$$\mathrm{Y}L\mathrm{H}^{2+} + L\mathrm{H}_2 \rightleftharpoons \mathrm{Y}L_2\mathrm{H} + 2\mathrm{H}^+, \tag{B}$$

$$\mathrm{Y}L\mathrm{H}^{2+} + 2\mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{Y}L(\mathrm{OH})_2^- + 3\mathrm{H}^+, \tag{C}$$

$$\mathrm{Y}L_2\mathrm{H} + 2\mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{Y}L(\mathrm{OH})_2^- + \mathrm{H}^+ + L\mathrm{H}_2. \tag{D}$$

For solutions containing excess Y^{3+} or equimolar concentrations of components the analysis of the absorbance vs. *pH* graphs, in the *pH* range 4.5–6.2, using the appropriate transformations [15, 18] gives the best fit for equilibrium (A) and the formation of $\mathrm{Y}L\mathrm{H}^{2+}$ complex species. The existence of the latter complex equilibrium is also confirmed in solutions with preponderance of reagent as gathered from the analysis of the initially rising part of the absorbance vs. *pH* graph at 610 nm (*pH* 4.5–6.0).

In analyzing the second ascending part of the graph (at *pH* 6.4–7.2) it was found that equilibrium (B) and the formation of $\mathrm{Y}L_2\mathrm{H}$ species can be proved and characterized reliably.

For this complex equilibrium Eqs. (15) and (16) hold,

$$A-(C_L-2C_M)\bar{\varepsilon}_L/Z=\varepsilon_2 C_M+[(C_L-C_M)\bar{\varepsilon}_L/Z-(A-\varepsilon_1 C_M)][\mathrm{H}]^q/{}^*K_{22}C_L, \tag{15}$$

$$\log\{[(A-\varepsilon_1 C_M)-(C_L-C_M)\bar{\varepsilon}_L/Z]/[(\varepsilon_2 C_M-A)+(C_L-2C_M)\bar{\varepsilon}_L/Z]\}$$
$$= q\,pH+\log{}^*K_{22}+\log C_L, \tag{16}$$

where ε_1 and ε_2 are the molar absorptivities of the $\mathrm{Y}LH^{2+}$ and $\mathrm{Y}L_2\mathrm{H}$ chelates, respectively; $\bar{\varepsilon}_L=\varepsilon_{L\mathrm{H}_2}+\varepsilon_{L\mathrm{H}_2}[\mathrm{H}]/K_{a_1}$; $Z=1+K_{a_2}/[\mathrm{H}]$, n is the number of ligand molecules and q is the number of protons liberated during the formation of a particular complex species.

On the other hand, the coordination of a single Y^{3+} ion with *NAZA* at $pH \leqslant 6$ is confirmed independently by analysis of the $A=\mathrm{f}(C_M)$ dependence at $\lambda = 590$ and 610 nm using the following relations:

$$C_L/A=\frac{1}{\varepsilon_1}+[\mathrm{H}]^q/[(C_M-A)/\varepsilon_1]\varepsilon_1{}^*K_{11}, \tag{17}$$

$$\log[(A/\varepsilon_1 C_L-A)]=m\log[(C_M-A)/\varepsilon_1]+q\,pH+\log{}^*K_{11}. \tag{18}$$

All the absorbance-*pH* graphs at various wavelengths and concentration of components have a similarly shaped descending branch above *pH* 7.5, the shape of which is due to a hydrolysis effect. Side reactions involving the formation of hydroxo-complexes prevent the appearance of a defined plateau on the absorbance vs. *pH* graphs. The analysis of the descending part of these graphs for solutions with excess metal ion according to the general equation

$$M_mL_n\mathrm{H}_b+y\mathrm{H}_2\mathrm{O}\rightleftharpoons M_mL_n(\mathrm{OH})_y+q\mathrm{H} \tag{19}$$

indicate conclusively the hydrolysis of the $\mathrm{Y}L\mathrm{H}^{2+}$ complex to the hydroxocomplex $\mathrm{Y}L(\mathrm{OH})_2$ (equilibrium C). This complex transition is also confirmed in equimolar solutions above *pH* 7.0. The results obtained indicate that three protons are liberated during the complex transition and equilibrium (C) is predominant. The analysis of the descending branch (at $pH > 7.5$) for solutions with excess reagent confirmed the existence of the hydrolytic reaction (D) of the $\mathrm{Y}L_2\mathrm{H}$ complex.

The equilibrium constants ${}^*K_{11}$ and ${}^*K_{22}$ are related to the stability constants

B_{nq} by the expressions:

$$\log B_{11} = \log {}^*K_{11} + pK_{a_1}, \tag{20}$$

$$\log B_{22} = \log B_1 + \log {}^*K_{22} + pK_{a_1} + pK_{a_2}. \tag{21}$$

The stoichiometry of yttrium-*NAZA* complexes was further verified by the method of continuous variation. In solutions having $C_0 = C_M + C_L = 3.0 \times 10^{-4} M$ at *pH* 5.5, a component ratio of one to one (metal to ligand) was obtained. At *pH* 6.7, the maximum of the job plot corresponds to a ratio of 1:2.

As far as the complexation equilibria are concerned, the complex formation of *NAZA* with Y^{3+} does not compete with the deprotonation equilibrium of the free ligand under the present experimental conditions. From this study, it can be concluded that the only reacting species of the reagent is the nonionized form (LH_2) which is the prevalent one at the *pH* range of the study, and hence any contribution from the anionic form of *NAZA* in the complexation reaction can be precluded.

The calculated values of the equilibrium ($\log {}^*K$), stability constant ($\log B_{nq}$), and molar absorptivities of the complex species existing in the yttrium-*NAZA* binary system are given in Table 2.

The relative high values of B_{22} indicate that the bis *NAZA* complex tends to form simultaneously with the mono-ligand complex species. Such behaviour begins to occur at a *pH* of approximately 6.

The distribution of Y^{3+} species in the binary system has been calculated and plotted in Fig. 3. It is shown that the monoligand complex YLH^{2+} is formed to a

Table 2. Mean values of equilibrium constants ($\log {}^*K_{nq}$), stability constants ($\log B$) and molar absorptivity of yttrium(III) complexes with *NAZA*. Values are taken as averages for various component concentrations, 50% (*v*/*v*) ethanol, $I = 0.1 M$ ($NaClO_4$), 25°; (charges are omitted)

Equilibrium	Constant	log constant	Molar absorptivity $l\,mol^{-1}\,cm^{-1}$
$[MLH][H]/[M][LH_2]$	K_{11}^*	(-1.47 ± 0.01)[a] (-1.49 ± 0.02)[b] (-1.48 ± 0.02)[c]	$\varepsilon_1 = 1.15 \times 10^4$
$[ML_2H][H]^2/[MLH][LH_2]$	K_{22}^*	(-10.2 ± 0.03)[c]	$\varepsilon_2 = 0.881 \times 10^4$
$[ML(OH)_2][H]^3/[MLH]$	K_{OH}^*	(-21.4 ± 0.02)[a] (-21.37 ± 0.03)[b]	
$[ML(OH)_2][LH_2][H]/[ML_2H]$	$K_{\bar{OH}}^*$	(-11.22 ± 0.01)[c]	
$[MLH]/[M][LH]$	B_{11}	6.904[d]	
$[ML_2H]/[M][LH][L]$	B_{22}	16.3[e]	
$[ML(OH)_2]/[M][L][OH]^2$	B_{OH}	24.72[f]	

[a] From the absorbance versus *pH* graphs for solutions with excess of metal ion

[b] From the absorbance versus *pH* graphs for solution of equimolar concentrations

[c] From the absorbance versus *pH* graphs for solution with excess ligand

[d] $\log B_1 = \log K_{11}^* + pK_{a_1}$

[e] $\log B_2 = \log B_1 + \log K_{22}^* + pK_{a_1} + pK_{a_2}$

[f] $\log B_{OH} = \log K_{OH}^* + \log B_1 + pK_{a_2} + 2pK_w$

$= \log K_{OH}^* + \log B_2 - pK_{a_1} + 2pK_w$

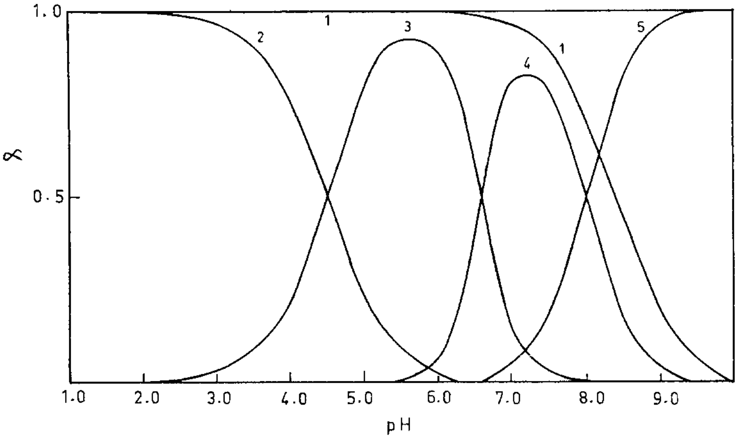

Fig. 3. Distribution curves for the components in the Y^{3+}-*NAZA* system (50% (*v*/*v*) ethanol, $I = 0.1\,M$ $NaClO_4$ curve (1) $\alpha = [LH_2]/C_L$, $C_L = 0.75 \times 10^{-4}\,M$; curves (2–5) $C_L = 5 \times 10^{-4}\,M$, $C_M = 1 \times 10^{-4}\,M$. (2) $\alpha = [Y^{3+}]/C_M$; (3) $\alpha = [YLH]/C_M$; (4) $\alpha = [YL_2H]/C_M$; (5) $\alpha = [YL(OH)_2]/C_M$

large extent at *pH* 5.5 and the overlap of YL_2H is quite apparent at $pH \geqslant 6$. Hydrolysis of the complexed ligand is negligible below *pH* 6.5.

Spectrophotometric Determination of Yttrium(III) with NAZA

According to the results of this study, the most suitable base for the spectrophotometric determination of yttrium (under our experimental conditions) is the complex formation of the monoligand complex YLH^{2+}. The latter complex does not require a rigid control of *pH* and possesses a reasonable stability. The optimum *pH* range for quantitative formation of the complex according to Eq. (A) is 5.5–5.8, which make the LH_2/LH^- acid-base equilibrium of the ligand to have no role in the complexation reaction at this *pH* range.

Procedure. A solution containing less than 0.22 mg of Yttrium(III) was transfered into a 25-ml calibrated flask and 2.5 ml of $2 \times 10^{-3}\,M$ *NAZA* and 2.5 ml of $0.1\,M$ $NaClO_4$ were added. The *pH* was adjusted to 5.8 and the solution was diluted to a volume with deionized water keeping the ethanol content of the medium at 50% (*v*/*v*). After thoroughly mixing the solutions, the absorbance was measured at 590 nm against a reagent blank similarly prepared but containing no Yttrium.

Calibration Graph and Reproducibility. Under the optimum conditions given above, a linear calibration graph for the Y^{3+}-*NAZA* system was obtained up to a concentration of $9.42\,\mu g\,ml^{-1}$ of Y^{3+} with a molar absorptivity of $1.15 \times 10^4\,l\,mol^{-1}\,cm^{-1}$ at 590 nm. A Ringbom plot showed that the optimum working range for the determination of Y^{3+} is 1.95–$8.86\,\mu g\,ml^{-1}$. The Sandell's sensitivity of the reaction of Y^{3+} was found to be $9.7 \times 10^{-3}\,\mu g\,cm^{-2}$. The reproducibility of the method was checked by analyzing a series of ten solutions having yttrium concentrations of $5.6\,\mu g\,ml^{-1}$. The relative standard deviation was found to be 0.8%. The proposed method is simple and rapid, it has the advantages of good reproducibility and sensitivity and highly stable reagent solutions, over bis-1,4-disubstituted anthraquinones [6, 19, 20] used for Yttrium determination.

Effect of Foreign Ions. The tolerance of the method to foreign ions was investigated with solutions containing 200 µg of Yttrium per 25 ml and various amounts of foreign ions. The concentrations indicated in parenthesis caused an error of not more than 2% in the absorbance measurements. The determination of Yttrium (III) as Y-*NAZA* binary complex was possible in the presence of any of the alkali metal or the alkaline earth ions, Cl^-, Br^-, NO_3^-, SO_4^{2-}, SO_3^{2-}, $B_4O_7^{2-}$, and acetate ions (16 mg); Th^{4+}, La^{3+}, Sc^{3+}, Zr^{4+}, Hg^{2+}, Fe^{3+}, and Ru^{3+} (5 mg), Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, and Ag^+ (3 mg). The tolerance ratio for many of these ions can be raised by using cyanide or NH_4CNS as masking agents. *EDTA* and fluoride ions interfere by reaction with Yttrium ion. Accordingly these reagents could not be used as masking agents.

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Received July 3, 1992. Accepted October 20, 1992