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On the Discriminating and Stability Increasing Properties of Alizarin Maroon in Mixed-Ligand Complexes of Yttrium(III)

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The stability constants of the yttrium(III) mixed ligand complexes (1 : 1 : 1) containing alizarin maroon (*azm*) and as a second ligand salicylic acid (*sa*), 5-sulphosalicylic acid (*ssa*), 5-nitrosalicylic acid (*nsa*), 2,2′-bipyridyl (*bipy*) and 1,10-phenanthroline (*phen*) have been determined potentiometrically in 20% (*v*/*v*) ethanol-water medium ($I = 100\,\text{mmol}\,\text{dm}^{-3}$ $NaClO_4$, 25 ± 0.1 °C). The complexation equilibria of the different biligand systems were demonstrated. All of these mixed-ligand complexes are considerably more stable than expected from purely statistical reasons. The results obtained were discussed in relation to the nature of the secondary ligands involved. For the equilibrium, $Y(azm)_2 + Y(L)_2 \rightleftharpoons 2\,Y(azm)(L)$, the following constants, $\log X$, were determined: Y(*azm*)(*sa*) 3.11 (0.46); Y(*azm*)(*ssa*) 2.76 (0.33); Y(*azm*)(*nsa*) 3.02 (0.48); Y(*azm*)(*bipy*) 3.96 (0.99); Y(*azm*)(*phen*) 4.33 (1.07). The constants given in parentheses correspond to $\Delta \log K_Y = [\log K^{Y(azm)}_{Y(azm)(L)} - \log K^{Y}_{Y(L)}]$.

(Keywords: Yttrium(III) mixed-ligand complexes; Stability constants; Spectrophotometry; Alizarin maroon)

Die stabilitätserhöhenden Eigenschaften von Alizarin-Maron in Yttrium(III)-Komplexen mit gemischten Liganden

Es wurden die Stabilitätskonstanten der 1 : 1 : 1-Yttrium(III)-Komplexe mit Alizari-Maron (*azm*) und mit einer Reihe weiterer Zweitliganden [Salizylsäure (*sa*), 5-Sulfosalizylsäure (*ssa*), 5-Nitrosalizylsäure (*nsa*), 2,2′-bipyridyl (*bipy*) und 1,10-Phenanthrolin (*phen*)] potentiometrisch in 20% (*v*/*v*) Ethanol-Wasser ($I = 100\,\text{mmol}\,\text{dm}^{-3}$ $NaClO_4$, $t = 25 \pm 0.1$ °C) bestimmt. Es werden die Komplexierungsgleichgewichte der verschiedenen Zweiligandensysteme angeführt. Alle gemischtligandigen Komplexe zeigten eine deutlich höhere Stabilität, als nach rein statistischen Überlegungen zu erwarten wäre. Die Ergebnisse werden in Relation zur chemischen Natur der Sekundärliganden gesetzt. Für das Gleichgewicht $Y(azm)_2 + Y(L)_2 \rightleftharpoons 2\,Y(azm)(L)$ wurden folgende Konstanten $\log X$ ermittelt: Y(*azm*)(*sa*) 3.11 (0.46); Y(*azm*)(*ssa*) 2.76 (0.33); Y(*azm*)(*nsa*) 3.02 (0.48); Y(*azm*)(*bipy*) 3.96 (0.99); Y(*azm*)(*phen*) 4.33 (1.07). Die Werte in Klammern entsprechen $\Delta \log K_Y = [\log K^{Y(azm)}_{Y(azm)(L)} - \log K^{Y}_{Y(L)}]$.

Introduction

Most of the physico-chemical studies of Y(III) mixed ligand complexes in solution were carried out using certain ligand combination containing *EDTA*, rhodamine S or nitrilotriacetic acid as primary ligands. Ternary complexes of yttrium with methyl xylenol blue-N-hexadecyl-trimethyl ammonium chloride [1], xylenol orange-N-hexadecyl pyridinium bromide [2], arsenazo(III)-diphenylguanidine (*DPG*) and eriochrome black *T-DPG* [3] systems have been also studied. Mixed ligand complexes of Y(III) containing substituted anthraquinones have hitherto not been reported. In continuation of our studies of the complexation equilibria of mono- and biligand systems in solution [4–7] we report here the complex formation between Y(III) and alizarin maroon (*azm*) using salicylic acid (*sa*), 5-nitrosalicylic acid (*nsa*), 5-sulphosalicylic acid (*ssa*), 2,2′-bipyridyl (*bipy*) or 1,10-phenanthroline (*phen*) as secondary ligands, the aim being to establish the equilibria existing in solution and to characterise the stability constants of the Y(III) ternary complexes. An *Irving* and *Rossotti* *pH*-titration technique [8] and its modification [9, 10] were employed in this work, measurements were made at 25 ± 0.1 °C with an ionic strength of 100 mmol dm^{-3} ($NaClO_4$) in 20% (*v*/*v*) ethanol. The participation of a heteroaromatic N base with good π-acceptor properties enhances the stability of ternary complexes of Y(III) also containing an oxygen donor ligand (*azm*). The use of Y(*azm*)(*ssa*) ternary complex in the spectrophotometric determination of trace amounts of Y(III) was studied and the optimum conditions were established.

Experimental

Analytical grade reagents and deionised water (or pure ethanol) were used for preparation of solutions. $10^{-3}\,M$ stock solutions of *azm* or secondary ligand (*sa, ssa, nsa, bipy* or *phen*) were prepared by dissolving the accurately weighed amount of the reagent in ethanol. A solution of yttrium(III) ($10^{-3}\,M$) was prepared using Analar yttrium nitrate and standardized as recommended [11]. Standard solutions of NaOH (0.1 *M*) and $HClO_4$ ($2.5 \cdot 10^{-2}\,M$) were also prepared. More dilute solutions of the reagents were obtained as required by accurate dilution. Buffer solutions and solutions of diverse ions used for interference studies were all prepared as mentioned elsewhere [12].

All *pH*-metric titrations were carried out at 25 ± 0.1 °C using an Orion (M 601 A) digital *pH*-meter with a combined glass-calomel electrode. The ionic strength of solutions was kept constant at 0.1 *M* ($NaClO_4$). Measurements were carried out in 20% (*v*/*v*) ethanol-water medium. Correction of *pH* readings in this medium was made as described previously [4]. The absorption spectra of solutions were recorded on a Pye Unicam SP 8000 spectrophotometer in the range 350–750 nm using 1-cm matched stoppered quartz cells.

Dissociation Constants of the Ligands and Stability Constants of Binary and Ternary Complexes

The acid-base properties of *azm* in aqueous solutions or in water-ethanol mixtures have been studied by *Idriss* et al. [13, 14]. The results proved that the predominant form of *azm* in acidic medium is the monocationic species H_3A^+, which undergoes stepwise ionization on increasing the *pH* of the solution. The proton association constant $pK^{\mathrm{H}}_{\mathrm{H}_3A^+}$ and the ionization constant $pK^{\mathrm{H}}_{\mathrm{H}_2A}$ of *azm* in 20% v/v ethanol-water medium corresponds to the equilibria (a) and (b)

$$\mathrm{H}_3A^+ \rightleftharpoons \mathrm{H}_2A + \mathrm{H}^+ \qquad (pH\,6\text{–}8) \tag{a}$$

$$\mathrm{H}_2A \rightleftharpoons \mathrm{H}A^- + \mathrm{H}^+ \qquad (pH\,8.5\text{–}10.5) \tag{b}$$

were evaluated using the *Irving-Rossotti pH*-titration technique.

The values of the dissociation constants of the secondary ligands used in this work were also determined potentiometrically under the same experimental conditions (Table 1). The stability constants of the binary complexes were calculated from titration graphs in which the metal : ligand ratio was 1 : 2. The conditions of measurements for the titrations of the ternary complexes were the same as for the binary ones, but the solutions contained equivalent amounts of *azm*, Y(III) and secondary ligand. The experimental details were similar to those described earlier.

Results and Discussion

The ligand titration curve for *azm* in the cationic form (Fig. 1) was below the acid curve and showed a moderate inflection at $a = 1$ followed by a steep inflection at $a = 2$ (a, moles of base added per mole of ligand) indicating the stepwise ionization of the ligand.

The metal-ligand titration curves (Fig. 2) exhibit two inflections at $m = 2$ and $m = 4$ (m, moles of base added per mole of metal ion) indicating the formation of $[\mathrm{Y}(\mathrm{H}A)]^{2+}$ and $[\mathrm{Y}(\mathrm{H}A)_2]^+$ binary complexes. The low concentration of the metal ion used was likely to prevent the formation of polynuclear complexes. The corresponding equilibria may be represented as follows:

$$\mathrm{Y} + azm \rightleftharpoons \mathrm{Y}(azm), \quad K^{\mathrm{Y}}_{\mathrm{Y}(azm)} \tag{1}$$

$$\mathrm{Y}(azm) + azm \rightleftharpoons \mathrm{Y}(azm)_2, \quad K^{\mathrm{Y}(azm)}_{\mathrm{Y}(azm)2} \tag{2}$$

The corresponding constants for the binary complexes of Y(III) with the secondary ligands used in this study (Eqs. 3 and 4) as depicted from the titration graphs are included in Table 1.

$$\mathrm{Y} + L \rightleftharpoons \mathrm{Y}L, \quad K^{\mathrm{Y}}_{\mathrm{Y}L} \tag{3}$$

$$\mathrm{Y}L + L \rightleftharpoons \mathrm{Y}L_2, \quad K^{\mathrm{Y}L}_{\mathrm{Y}L_2} \tag{4}$$

The mixed ligand titration curves of Y(III), *azm* and *sa*, *nsa*, *bipy* or *phen* in a 1 : 1 : 1 molar ratio exhibit a single steep inflection at $m = 3$. In ternary systems involving *ssa* as secondary ligand, inflections are obtained at $m = 3$ and $m = 4$ (cf. Fig. 1). The composite curve drawn theoretically by the graphical addition of the horizontal distance of the Y-*azm* curve to the titration curve of the secondary ligand is not superimposable with the mixed ligand titration curve, thereby confirming the formation of the Y-*azm*-*L* complexes.

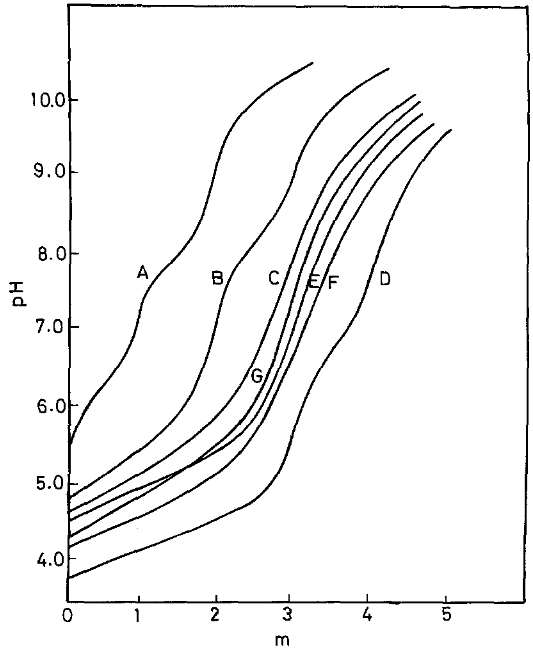

Fig. 1. Potentiometric titration curves for triprotonated *azm*, 1 : 2 Y(III)-*azm* and 1 : 1 : 1 Y-*azm*-secondary ligand (L) ternary systems. [m = moles of alkali per mole of metal ion.] For A, the abscissa represents the moles of alkali added per mole of ligand (a). A triprotonated *azm* (H_3A^+); B Y(III) + *azm* (1 : 2); C Y(III) + *azm* + *sa* (1 : 1 : 1); D Y(III) + *azm* + *ssa* (1 : 1 : 1); E Y(III) + *azm* + *nsa* (1 : 1 : 1); F Y(III) + *azm* + *bipy* (1 : 1 : 1); G Y(III) + *azm* + *phen* (1 : 1 : 1)

The value of the formation constant of the general equilibrium (5) was calculated by considering the species H, H_3A, H_2A, HA, H_2L, HL, L, Y, YHA, $Y(HA)_2$, YL, YL_2 and $Y(HA)(L)$.

$$Y^{3+} + azm + L \rightleftharpoons Y(azm)(L), \; B^{Y}_{Y(azm)L} \qquad (5)$$

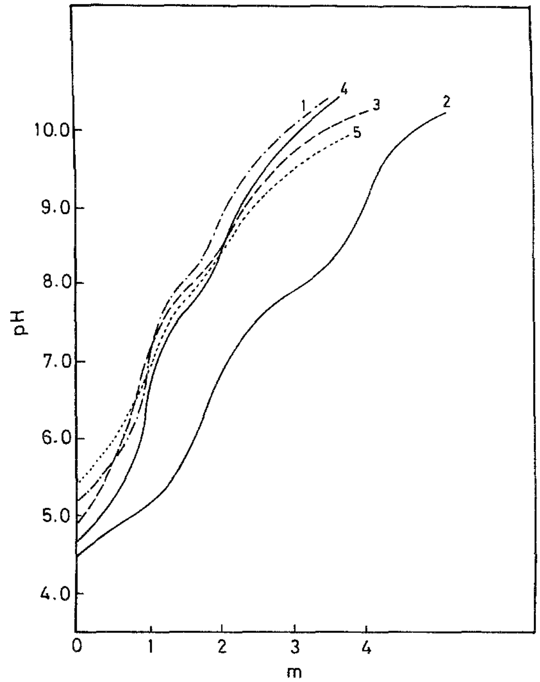

Fig. 2. Potentiometric titration curves of 1 : 2 Y(III)-secondary ligand (*L*) binary systems. [$I = 100\,\mathrm{mmol\,dm^{-3}}$ $NaClO_4$, 25 °C; 20% (*v*/*v*) ethanol.] [*m* = moles of alkali per mole of metal ion.] *L* = *1 sa, 2 ssa, 3 nsa, 4 bipy, 5 phen*

The overall stability constant $B^{Y}_{Y(azm)L}$, which was determined experimentally, is connected with $K^{YL}_{YL(azm)}$ and $K^{Y(azm)}_{Y(azm)L}$ by Eqs. (6) and (7), respectively:

$$\log K^{YL}_{YL(azm)} = \log B^{Y}_{YL(azm)} - \log K^{Y}_{YL} \tag{6}$$

$$\log K^{Y(azm)}_{Y(azm)L} = \log B^{Y}_{Y(azm)L} - \log K^{Y}_{Y(azm)} \tag{7}$$

There are two convenient ways to characterize the stability of mixed ligand complexes. One is based on the difference of stability constants, $\Delta\log K$ [15], (Eqs. 3, 4, and 8)

$$\begin{aligned}\Delta\log K_{Y} &= (\log K^{Y(azm)}_{Y(azm)L} - \log K^{Y}_{YL}) \\ &= \log K^{YL}_{YL(azm)} - \log K^{Y}_{Y(azm)} \end{aligned} \tag{8}$$

and the other on the disproportionation constant $\log X$ [16, 17] (Eqs. 9, 10, and 11)

$$Y(azm)_2 + YL_2 \rightleftharpoons 2\,Y(azm)L \tag{9}$$

$$\log X = 2\log B^{\mathrm{Y}}_{\mathrm{Y}(azm)L} - (\log B^{\mathrm{Y}}_{\mathrm{Y}(azm)2} + \log B^{\mathrm{Y}}_{\mathrm{Y}L2}) \qquad (10)$$

$$= (\log K^{\mathrm{Y}(azm)}_{\mathrm{Y}(azm)L} - \log K^{\mathrm{Y}L}_{\mathrm{Y}L2}) + (\log K^{\mathrm{Y}L}_{\mathrm{Y}(azm)L} - \log K^{\mathrm{Y}(azm)}_{\mathrm{Y}(azm)2}) \qquad (11)$$

In general, negative values for $\Delta\log K$ [Eq. (8)] are expected. The statistical values of $\Delta\log K$ obtained for coordination of two different bidentate ligands to a regular and to a distorted octahedral coordination sphere are -0.4 and a -0.9 [18] respectively. The statistical value for $\log X$ of a metal ion is the same, namely 0.6 [17, 19].

Table 1. *Negative logarithms of the acidity constants of the ligands and logarithms of the stability constants of their binary* Y(III) *complexes* [$I = 100\,\mathrm{mmol\,dm^{-3}}$; 25 ± 0.1 °C; 20% (*v*/*v*) ethanol]

Ligand (*L*)	$pK^{\mathrm{H}}_{\mathrm{H}_2L}$	$pK^{\mathrm{H}}_{\mathrm{H}L}$	$\log K^{\mathrm{Y}}_{\mathrm{Y}L}$	$\log K^{\mathrm{Y}L}_{\mathrm{Y}L_2}$	$\log B^{\mathrm{Y}}_{\mathrm{Y}L_2}$
azm[a]	9.10	11.20 [13]	5.78	4.65	10.43
sa	4.65	13.86 [23]	5.30	3.45	7.75
ssa	3.10	12.60 [24]	4.28	3.52	7.80
nsa	2.86 [10]	9.85	4.18	3.46	7.64
bipy	—	4.60	4.45	3.60	8.05
phen	—	4.28	4.80	3.75	8.55

[a] $pK^{\mathrm{H}}_{\mathrm{H}_3L^+}$ for *azm* = 6.75

According to our results, the formation of Y(III)-*azm* and Y(III)-*L* binary complexes and the complex equilibrium for the Y(III)-*azm-L* ternary system can be represented by the following schemes:

Y(III)-*azm* complexes

$$\mathrm{Y}^{3+} + \mathrm{H}_3A^+ \rightleftharpoons [\mathrm{Y(H}A)]^{2+} + 2\,\mathrm{H}^+,\ K^{\mathrm{Y}}_{\mathrm{Y}(azm)} \qquad (12)$$

$$[\mathrm{Y(H}A)]^{2+} + \mathrm{H}_3A^+ \rightleftharpoons [\mathrm{Y(H}A)_2]^{+} + 2\,\mathrm{H}^+,\ K^{\mathrm{Y}(azm)}_{\mathrm{Y}(azm)2} \qquad (13)$$

$$\mathrm{Y}^{3+} + 2\,\mathrm{H}_3A^+ \rightleftharpoons [\mathrm{Y(H}A)_2]^{+} + 4\,\mathrm{H}^+,\ B^{\mathrm{Y}}_{\mathrm{Y}(azm)2} \qquad (14)$$

Binary and ternary systems containing *sa* or *nsa*

$$\mathrm{Y}^{3+} + \mathrm{H}L^- \rightleftharpoons [\mathrm{Y}L]^{+} + \mathrm{H}^+,\ K^{\mathrm{Y}}_{\mathrm{Y}L} \qquad (15)$$

$$[\mathrm{Y}L]^{+} + \mathrm{H}L^- \rightleftharpoons [\mathrm{Y}(L)_2]^{-} + \mathrm{H}^+,\ K^{\mathrm{Y}L}_{\mathrm{Y}L_2} \qquad (16)$$

$$\mathrm{Y}^{3+} + 2\,\mathrm{H}L^- \rightleftharpoons [\mathrm{Y}(L)_2]^{-} + 2\,\mathrm{H}^+,\ B^{\mathrm{Y}}_{\mathrm{Y}L_2} \qquad (17)$$

$$\mathrm{Y}^{3+} + \mathrm{H}_3A^+ + \mathrm{H}L^- \rightleftharpoons [\mathrm{Y(H}A)L] + 3\,\mathrm{H}^+,\ B^{\mathrm{Y}}_{\mathrm{Y}(azm)L} \qquad (18)$$

$$[\mathrm{Y}(\mathrm{H}A)]^{2+} + \mathrm{H}L^{-} \rightleftharpoons [\mathrm{Y}(\mathrm{H}A)L] + \mathrm{H}^{+},\ K^{\mathrm{Y}(azm)}_{\mathrm{Y}(azm)L} \tag{19}$$

$$[\mathrm{Y}(\mathrm{H}A)_2]^{+} + [\mathrm{Y}L_2]^{-} \rightleftharpoons 2\,[\mathrm{Y}(\mathrm{H}A)L],\ X \tag{20}$$

Binary and ternary systems containing *ssa*

$$\mathrm{Y}^{3+} + \mathrm{H}_2L^{-} \rightleftharpoons [\mathrm{Y}(L)] + 2\,\mathrm{H}^{+},\ K^{\mathrm{Y}}_{\mathrm{Y}L} \tag{21}$$

$$\mathrm{Y}(L) + \mathrm{H}_2L^{-} \rightleftharpoons [\mathrm{Y}(L)_2]^{3-} + 2\,\mathrm{H}^{+},\ K^{\mathrm{Y}L}_{\mathrm{Y}L_2} \tag{22}$$

$$\mathrm{Y}^{3+} + 2\,\mathrm{H}_2L^{-} \rightleftharpoons [\mathrm{Y}L_2]^{3-} + 4\,\mathrm{H}^{+},\ B^{\mathrm{Y}}_{\mathrm{Y}L_2} \tag{23}$$

$$\mathrm{Y}^{3+} + \mathrm{H}_3A^{+} + \mathrm{H}_2L^{-} \rightleftharpoons [\mathrm{Y}(\mathrm{H}A)L]^{-} + 4\,\mathrm{H}^{+},\ B^{\mathrm{Y}}_{\mathrm{Y}(azm)L} \tag{24}$$

$$[\mathrm{Y}(\mathrm{H}A)]^{2+} + \mathrm{H}_2L^{-} \rightleftharpoons [\mathrm{Y}(\mathrm{H}A)L]^{-} + 2\,\mathrm{H}^{+},\ K^{\mathrm{Y}(azm)}_{\mathrm{Y}(azm)L} \tag{25}$$

$$[\mathrm{Y}(\mathrm{H}A)_2]^{+} + [\mathrm{Y}L_2]^{3-} \rightleftharpoons 2\,[\mathrm{Y}(\mathrm{H}A)L]^{-},\ X \tag{26}$$

Binary and ternary systems containing *bipy* or *phen*

$$\mathrm{Y}^{3+} + L\mathrm{H}^{+} \rightleftharpoons [\mathrm{Y}L]^{3+} + \mathrm{H}^{+},\ K^{\mathrm{Y}}_{\mathrm{Y}L} \tag{27}$$

$$[\mathrm{Y}L]^{3+} + L\mathrm{H}^{+} \rightleftharpoons [\mathrm{Y}L_2]^{3+} + \mathrm{H}^{+},\ K^{\mathrm{Y}L}_{\mathrm{Y}L_2} \tag{28}$$

$$\mathrm{Y}^{3+} + 2\,L\mathrm{H}^{+} \rightleftharpoons [\mathrm{Y}L_2]^{3+} + 2\,\mathrm{H}^{+},\ B^{\mathrm{Y}}_{\mathrm{Y}L_2} \tag{29}$$

$$[\mathrm{Y}(\mathrm{H}A)]^{2+} + L\mathrm{H}^{+} \rightleftharpoons [\mathrm{Y}(\mathrm{H}A)L]^{2+} + \mathrm{H}^{+},\ K^{\mathrm{Y}(azm)}_{\mathrm{Y}(azm)L} \tag{30}$$

$$\mathrm{Y}^{3+} + \mathrm{H}_3A^{+} + L\mathrm{H}^{+} \rightleftharpoons [\mathrm{Y}(\mathrm{H}A)L]^{2+} + 3\,\mathrm{H}^{+},\ B^{\mathrm{Y}}_{\mathrm{Y}(azm)L} \tag{31}$$

$$[\mathrm{Y}(\mathrm{H}A)_2]^{+} + [\mathrm{Y}L_2]^{3+} \rightleftharpoons 2\,[\mathrm{Y}(\mathrm{H}A)L]^{2+},\ X \tag{32}$$

The stability constants presented in Table 2 show that the ternary complexes are more stable than their corresponding binary complexes.

Table 2. *Logarithms of the equilibrium constants of the ternary* $\mathrm{Y}^{3+}/azm/L$ *systems and some related data* [$I = 100\,\mathrm{mmol\,dm^{-3}}$, 25 ± 0.1 °C; 20% ($v/v$) ethanol]

Ligand (L)	$\log B^{\mathrm{Y}}_{\mathrm{Y}(azm)L}$ [a]	$\log K^{\mathrm{Y}(azm)}_{\mathrm{Y}(azm)L}$ [b]	$\log K^{\mathrm{Y}L}_{\mathrm{Y}L(azm)}$ [c]	$\Delta\log K$ [d]	$\log X$ [e]
sa	10.8	4.76	6.50	0.46	3.11
ssa	10.65	4.61	6.37	0.33	2.76
nsa	10.70	4.66	6.52	0.48	3.02
bipy	11.22	4.97	6.55	0.99	3.96
phen	11.65	5.34	6.58	1.07	4.32

[a] Eq. (5); [b] Eq. (7); [c] Eq. (6); [d] Eq. (8); [e] Eqs. (10) and (11)

The observance of $\Delta \log K$ and $\log X$ values shows that ligands (L) containing nitrogen donor atoms form more stable ternary complexes. The order of stabilities of the mixed ligand complexes towards the secondary ligand is *phen* > *bipy* > *sa* > *nsa* > *ssa*. The higher stability for the ternary complex involving *sa* or *nsa* compared to that containing *ssa* may be ascribed to the neutralization of charge in these ternary complexes compared with the binary ones. The lower stability of the complex involving *ssa* may also be due to the presence of the electron-withdrawing sulphonic group.

Among the secondary ligands studied, *phen* and *bipy* form the most stable ternary complexes owing to the interaction between the π-systems of the two ligands bound to Y(III). The higher stability of Y(*azm*)(*phen*) or Y(*azm*)(*bipy*) relative to the other ternary complexes can be ascribed to the π-accepting qualities of the heteroaromatic N-base. The latter induces a stronger ligand field at the Y(III) ion than the salicylate dianion. The stabilization of the Y-*azm*-*phen* system can be understood by considering that 1,10-phenanthroline not only induces a strong ligand field to metal σ-bonding but also acts as a powerful π-acceptor.

Absorption Spectra

The absorption spectra of *azm* are characterised by a main absorption band at $\approx$ 420 nm within the *pH* range 4.0–6.5. A *ssa* solution (10^{-4} *M*) shows no measurable absorbance above 400 nm. The spectra of the Y(III)-*azm* (1 : 1) complex with reagent blank as reference exhibit an absorption band at $\lambda = 540$ nm. The solution containing equimolar concentrations undergoes a change in colour from yellow to blue when mixed with Y(III) solution. The spectrum of the reaction mixture against a blank solution containing the same concentration of the two ligands shows an apparent decrease in the absorption at 420 nm and exhibits a new band at 590 nm. The formation of the mixed ligand complex of Y(III) with *azm* and *ssa* is accompanied by a bathchromic shift in the absorption spectrum, with maximum colour development in the *pH* range 5–6 (Fig. 3).

Spectrophotometric Determination of Y(III)

A solution containing less than 150 μg of yttrium was introduced into a 25 ml calibrated flask, then 2.5 ml of 10^{-1} *M EDTA* solution and 2.5 ml of 10^{-3} *M azm* were added. The *pH* was adjusted to 5.5–6 with a buffer solution, 2.5 ml of 10^{-3} *M ssa* were added and the solution was diluted to the proper volume with redistilled water and the requiste amount of ethanol (20% *v*/*v*). After thoroughly mixing the reaction mixture, the absorbance was measured at 590 nm against a reagent blank similarly prepared but containing no yttrium.

The influence of foreign ions at levels of 1.5–15 mg per 25 ml on the estimation of Y(III) was studied for a sample containing 77.8 μg of Yttrium by the recommended procedure. There was no interference from 15 mg (ca. 200 fold excess) of Li^+, Na^+, Ba^{2+}, Mg^{2+}, Mn^{2+}, Hg^{2+}, Mo^{6+}, Cl^-, Br^-, NO_3^-, SO_3^{2-}, SO_4^{2-} and NO_2^-; 8 mg (ca. 100 fold excess) of Cr^{3+}, Pb^{2+}, Zn^{2+}, CO_3^{2-} and I^-, Co^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, CN^-, and HPO_4^{2-} could be masked by the addition of $1 \cdot 10^{-2} M$ *EDTA*. The

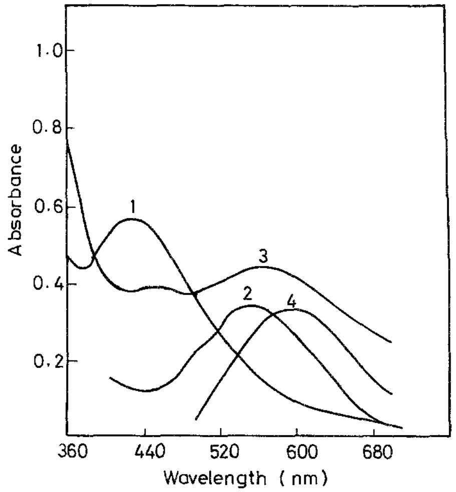

Fig. 3. Absorption spectra of Y (III)-*azm-ssa* ternary complex in 20% (*v*/*v*) ethanol (*pH* = 6.1); [Y(III)] = $0.5 \cdot 10^{-4} M$; *1 azm*, *azm-ssa* (both give the same spectrum); *2* 1 : 1 Y(III)-*azm* (vs. *azm*); *3* 1 : 1 : 1 Y(III)-*azm-ssa* (vs. buffer containing 20% ethanol); *4* 1 : 1 : 1 Y(III)-*azm-ssa* (vs. reagent blank)

negative interference due to La(III) and Fe^{3+} was completely eliminated by increasing the concentration of *EDTA* to $2.5 \cdot 10^{-2} M$. Among the anions investigated, fluoride caused a serious negative error even when present only in a 10-fold excess. The presence of ~ 1 mg of F^- seems to prevent any reaction between Y(III) and *azm*.

Test solutions with different concentrations of metal ion were prepared by the recommended procedure. The system adhered to *Beer*'s plots over the range 0.889–6.401 ppm of Y(III). The molar absorptivity was found to be $1 \cdot 10^4 \, L\,mol^{-1}\,cm^{-1}$.

The reproducibility of the method was examined by using the solution contained 88.9 μg of Yttrium. From the data obtained by seven determinations, the standard deviation was calculated to be 0.003 absorbance unit.

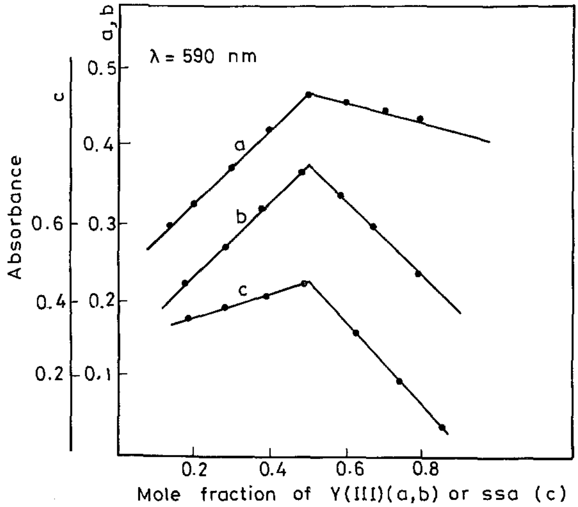

Fig. 4. *Job*'s plots: *a* Y(III)-*ssa* (in presence of excess *azm*); *b* Y(III)-*azm* (in presence of excess *ssa*); *c ssa-azm* [in presence of excess Y(III)]

Job's [20, 21] method of continuous variation was applied to establish the composition of the ternary Y(III)-*azm-ssa* complex. The molar fractions of two of the components were varied continuously, keeping their combined concentration constant, and keeping the third component in a large excess for all solutions in the series. Under these conditions, the ternary system was modified to a quasi binary system. The results shown in Fig. 4 indicate that the overall Y(III)-*azm-ssa* complex has a 1 : 1 : 1 composition at the *pH* of the study. The stoichiometry of the ternary system was also determined by applying the mole-ratio method [22].

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