Mixed-Ligand Complexes of Fe(II) & Cu(II) with Alizarin Maroon as a Primary Ligand & 5-Sulphosalicylic Acid as a Secondary Ligand

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Reactions of Fe(II) and Cu(II) with alizarin maroon (azm) as a primary ligand and 5-sulphosalicylic acid (ssa) as a secondary ligand have been studied spectrophotometrically and potentiometrically in 20% (v/v) ethanol and dioxane at an ionic strength $I = 100$ mmol dm^{-3} NaClO$_4$ and temperature = $25 \pm 0.1°$C. Based on the spectrophotometric studies, a method for the determination of Fe(II) and Cu(II) is proposed. The stability constants of the mono and mixed ligand complexes of Fe(II) and Cu(II) have been evaluated. The difference in stability constants, $\Delta \log K_M = \log K_M^{M\,(azm)}{}_{(azm)(ssa)} - \log K_M^{M}{}_{(ssa)}$ is found to be positive showing an astatistical increase in the values of mixed ligand stability constants.

In continuation of our work on the complexation equilibria of mixed ligand complexes in solution[1,2], we report here the spectrophotometric and potentiometric study of the reaction of Fe(II) and Cu(II) with alizarin maroon (3-amino-1,2-dihydroxy-anthraquinone) as a primary ligand and 5-sulphosalicylic acid as a secondary ligand. The pH-titration technique of Irving and Rossotti[3,4] and its modified form[5,6] were employed in the present study to determine the stability constants of the ternary complexes Fe(II)-azm-ssa and Cu(II)-azm-ssa. The measurements were carried out at $25 \pm 0.1°$C and at an ionic strength of 0.1 mol dm^{-3} (NaClO$_4$) in 20% (v/v) ethanol or dioxane. The absorption spectra of the mixed ligand complexes were also investigated. The fundamental conditions for the spectrophotometric determination of Fe(II) and Cu(II) complexes usign Fe(II)-azm-ssa and Cu(II)-azm-ssa ternary systems were established.

Materials and Methods

All the chemicals used were of AR grade. Dioxane was purified by recommended procedure[7]. A stock solution of azm (10^{-3} mol dm^{-3}) was prepared by dissolving an accurately weighed amount of the reagent in ethanol or dioxane. A solution of ssa (10^{-3} mol dm^{-3}) was prepared by dissolving the requisite amount of the pure reagent in deionised water. Fe(II) perchlorate was prepared from Fe(II) carbonate and perchloric acid. Cu(II) perchlorate was a Fluka reagent. The stock solutions of Fe(II) and Cu(II) (5×10^{-3} mol dm^{-3}) were prepared and standardised as recommended[8]. Standard solutions of NaOH (0.1 mol dm^{-3}) and HClO$_4$ (2.5×10^{-2} mol dm^{-3}) were prepared by accurate dilutions. Buffer solutions and solutions of diverse ions used for interference studies were prepared as mentioned elsewhere[9].

All pH-metric titrations were carried out at $25 \pm 0.1°$C using on Orion (M 501 A) digital pH-meter with a combined glass calomel electrode. The ionic strength of solutions was kept constant at 0.1 mol dm^{-3} (NaClO$_4$). All the measurements were carried out in 20% (v/v) ethanol or dioxane-water medium (20%, v/v), pH values were corrected for partially aqueous media as described previously[10]. The absorption spectra of solutions were recorded on a Pye-Unicam SP 8000 spectrophotometer in the range 350-750 nm using 1-cm mathed stoppered quartz cells.

Results and Discussion

Spectrophotometric studies

Recent work from this laboratory[11,12] on the acid-base properties of azm in aqueous solution or in water-ethanol (or dioxane) mixture indicated that the predominant form of this reagent within the pH range 3.0-6.0 is the monocationic species (H$_3$A$^+$) which undergoes stepwise ionisation on increasing the pH of the solution. The visible spectrum of azm exhibits an absorption band at $\lambda = 410$-420 nm in the pH range 3.5-6.0. This band shifts to longer wavelengths on adding the metal ion solutions. The spectra of Fe(II) and Cu(II)-azm 1:1 complexes measured with reagent blank as reference are characterised by an absorption band with λ_{max} near 620 and 630 nm respectively. The solution containing equimolar concentrations of azm and ssa undergoes a change in colour, from yellow to pink-violet when mixed with

Fe(II) or Cu(II) solution. The spectrum of the reaction mixture measured against a blank solution containing the same concentration of the two ligands shows an apparent decrease in the absorption at 410 nm and the appearence of a new band at 580 nm for Fe(II) and 540 nm for Cu(II) ternary system. This band is unambiguously due to the formation of a mixed-ligand complex of the metal ion with maximum colour development being attained at pH 5.8 for Fe(II) and at 5.4 for Cu(II) ternary systems.

Stoichiometry of the complexes

Job's method of continuous variation[13,14] was applied to find out the composition of the ternary complexes. The results indicate that the overall ratio of metal ion:azm:ssa is 1:1:1. The stoichiometric ratio of the complexes was also confirmed by applying the mole ratio method[15].

The reaction of Fe(II) or Cu(II) with azm and ssa can be represented by Eqs,

$$M^{2+} + H_3A^+ \rightleftarrows [M(HA)]^+ + 2H^+$$

$$[M(HA)]^+ + H_2L^- \rightleftarrows [M(HA)L]^{2-} + 2H^+$$
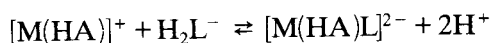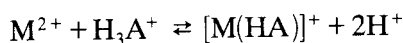
where H_2L^- is the mononegative charged species of the secondary ligand.

Spectrophotometric determination of Fe(II) and Cu(II)

An aliquot of the test sample containing 5-70 μg of Fe(II) or 10-60 μg of Cu(II) was transferred to a 25 ml calibrated flask and subsequently azm (5 ml, 10^{-3} mol dm^{-3}) added. The pH was adjusted to 5.8 for Fe(II) and 5.4 for Cu(II) and ssa (5 ml, 10^{-3} mol dm^{-3}) was added. The solution was diluted to the required volume with deionized water and the required amount of ethanol or dioxane. After thoroughly mixing the reaction mixture, the absorbance was measured at 580 nm for Fe(II) and 540 nm for Cu(II) against a reagent blank similarly prepared but containing no metal ion.

Effect of masking agents and foreign ions

The addition of EDTA as a masking agent causes an apparent decrease in the absorbance values and consequently could not be used. On the other hand, addition of fluoride ions as a masking agent upto 200-fold molar excess over Fe(II) or Cu(II) had no effect on the sensitivity of the proposed method. The effect of diverse ions at levels of 1-14 mg per 25 ml on the determination of metal ions was examined by the recommended procedure. There was no interference from 14 mg (200-

Table 1—Validity of Beer's Law

Metal ion	Metal ion per 25 ml (μg)	Metal ion (ppm) in the final conc.	Molar Absorptivity
	20% (v/v) Ethanol		
Fe(II)	5.0-40.0	0.20-1.60	10,000
Cu(II)	20.0-60.0	0.80-2.40	7,500
	20% (v/v) Dioxane		
Fe(II)	15.0-70.0	0.60-2.80	12,000
Cu(II)	10.0-45.0	0.40-1.80	7,000

Table 2—Negative Logarithms of Acidity Constants of the Ligands and Logarithms of the Stability Constants of Their Binary Complexes with Fe(II) and Cu(II)

[Ionic strength = 0.1 mol dm^{-3} NaClO$_4$; temp. = 25°C]

	$pK_{H_2L}^H$	pK_{HL}^H	M(II)	$\log K_{ML}^M$	$\log K_{ML_2}^{ML}$	$\log \beta_{ML_2}^M$
		20% (v/v) Ethanol				
azm†	9.10	11.20*	Fe(II)	6.20	5.05	11.25
			Cu(II)	5.20	4.56	9.76
ssa	3.10	12.60	Fe(II)	5.10	4.70	9.80
			Cu(II)	4.96	4.57	9.53
		20% (v/v) Dioxane				
azm††	9.50	11.50*	Fe(II)	6.40	5.40	11.80
			Cu(II)	5.49	4.59	10.08
ssa	2.90	11.40	Fe(II)	5.85	5.50	11.35
			Cu(II)	5.15	4.38	9.63

† $pK_{H_3L^+}^H = 6.75$

†† $pK_{H_3L^+}^H = 7.55$

*Ref. 11.

Table 3—Logarithms of the Equilibrium Constants of the Ternary M-azm-ssa Systems and Some Related Data

[Ionic strength = 0.1 mol dm^{-3} NaClO$_4$; temp. = 25°C]

Metal ion	$\log \beta^{M}_{M(azm)(ssa)}$	$\log K^{M(azm)}_{M(azm)(ssa)}$	$\log K^{M(ssa)}_{M(ssa)(azm)}$	$\Delta \log K$	$\log X$
		20% (v/v) Ethanol			
Fe(II)	11.75	5.55	6.65	0.75	2.45
Cu(II)	10.80	5.60	5.84	0.64	2.21
		20% (v/v) Dioxane			
Fe(II)	13.10	6.70	7.25	0.85	3.05
Cu(II)	11.33	5.84	6.18	0.69	2.95

fold excess) of Li$^+$, Na$^+$, Ba^{2+}, Cl^{-1}, I$^-$, NO$_3^-$ and SO$_4^{2-}$ or 8 mg (100 fold excess) of Mg^{2+}, Ca^{2+}, Al^{3+}, Br$^-$, CO$_3^{2-}$, SO$_3^{2-}$ and HPO$_4^{2-}$. Among the anions investigated, CN$^-$ causes a serious negative error even when present in only ~ 20-fold excess.

The validity of Beer's law was examined. Calibration graphs obtained were linear over the range 1×10^{-5}-1×10^{-4} mol dm^{-3} of Fe(II) or Cu(II). The moalr absorptivities of the ternary systems are given in Table 1. Ten identical samples each with a final metal ion concentration of 1×10^{-5} mol dm^{-3} were tested according to the recommended procedure and their absorbances were measured. The relative standard deviation was found to be less than 0.004 absorbance unit.

Potentiometric studies

The proton-association constant $pK^{H}_{H_3A^+}$ and the dissociation constant $pK^{H}_{H_2A}$ of azm in ethanol-water and dioxane-water medium (20%, v/v) were determined using Irving-Rossotti pH-titration technique[3,4] (Table 2). The details regarding the potentiometric method have been reported earlier[12]. The values of the dissociation constants of 5-sulphosalicylic acid (ssa) were also determined potentiometrically under the same experimental conditions. The metal-ligand titration curves exhibit two inflections at $m = 2$ and $m = 4$ (m = nol of base added per mol of metal ion) indicating the formation of [M(HA)]$^+$ and [M(HA)$_2$] binary complexes.

The formation constants corresponding to the equilibria (1 and 2) were calculated and the values are given in Table 2.

$$M + 2 \text{ azm} \rightleftarrows M(\text{azm})_2 \quad \beta^{M}_{M(azm)_2} \quad \ldots (1)$$

$$M + 2 \text{ ssa} \rightleftarrows M(\text{ssa})_2 \quad \beta^{M}_{M(ssa)_2} \quad \ldots (2)$$
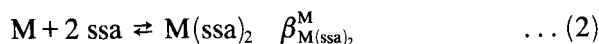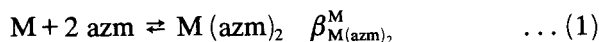
Potentiometric titration curves for ternary systems containing M(II)-azm and ssa exhibit two inflec-

tions at $m = 3$ and $m = 4$. The divergence of mixed ligand curves from binary curves indicates that the deprotonation of azm or ssa in the ternary systems occurs at a lower pH. This means that the ternary complexes are more stable than the corresponding binary systems. The values of the formation constant of the general equilibrium

$$M + \text{azm} + \text{ssa} \rightleftarrows M(\text{azm})(\text{ssa}) \quad \beta^{M}_{M(azm)(ssa)} \quad \ldots (3)$$
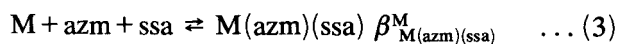
are given in Table 3.

One way to quantify the stability of ternary complexes is according to equation (4)[16], i.e., by comparing the differences in stability, e.g., for the reaction between M(ssa) and (azm).

$$\Delta \log K_M = \log K^{M(ssa)}_{M(ssa)(azm)} - \log K^{M}_{M(azm)},$$
$$= \log K^{M(azm)}_{M(azm)(ssa)} - \log K^{M}_{M(ssa)} \quad \ldots (4)$$

The other approach commonly used to quantify the stability of a ternary complex is based on the equilibrium constant, X, as defined by equation (5)[17,18]; $\log X$ may be calculated according to Eq. (6).

$$X = M(\text{azm})(\text{ssa})]^2 / [M(\text{azm})_2][M(\text{ssa})_2] \quad \ldots (5)$$

$$\log X = 2 \log \beta^{M}_{M(ssa)(azm)}$$
$$- \left(\log \beta^{M}_{M(azm)_2} + \log \beta^{M}_{M(ssa)_2} \right)$$
$$= \left(\log K^{M(azm)}_{M(azm)(ssa)} - \log K^{M(ssa)}_{M(ssa)_2} \right)$$
$$+ \left(\log K^{M(ssa)}_{M(ssa)(azm)} - \log K^{M(azm)}_{M(azm)_2} \right)$$
$$\ldots (6)$$

The calculated values of log X are listed in Table 3. The values obtained show an astatistical increase

in the stability of the mixed ligand complexes $(\log X_{stat} = 0.6)$[18,19].

The higher stability of the complexes formed in dioxane (20%, v/v) may be due to the fact that the protonation and the stability constant values are more sensitivie to the dielectric constant of the medium. In dioxane-water mixtures of low dielectric constant, these values were expected to be significantly higher than those for the aqueous-ethanol medium. This may also be ascribed to the predominant basic property of dioxane[20].

The higher stability of Fe(II) chelates may be due to the resonance stabilisation energy derived through the coordination with ligands having aromatic ring system[21].

References

1 Idriss K A, Seleim M M, Hassan M K, Abu-Bakr M S & Sedaira H, *Analyst*, **110** (1985) 705.
2 Idriss K A, Seleim M M, Saleh M S & Hashem E Y, *Polyhedron*, **5** (1986) 1525.
3 Irving H M & Rossotti H S, *J chem Soc*, (1953) 3397.
4 Irving H M & Rossotti H S, *J chem Soc*, (1954) 2904.
5 Chidambaram M V & Bhattacharya P K, *J inorg nucl Chem*, **32** (1970) 3271.
6 Chidambaram M V & Bhattacharya P K, *Indian J Chem*, **9** (1971) 1294.
7 Vogel A I, *A text book of practical organic chemistry* (Longmans Green, London) 1956, 177.
8 Scott W & Furman, *Standard methods of chemical analysis*, 6th Edn (Van Nostrand, New York) 1962.
9 Idriss K A, Seleim M M, Abu-Bakr M S & Saleh M S, *Analyst*, **107** (1982) 12.
10 Douheret G, *Bull Soc Chim Fr*, (1967) 1412.
11 Idriss K A, Awad A M, Seleim M M & Abu-Bakr M S, *Bull Soc Chim Fr*, (1981) 180.
12 Idriss K A, Seleim M M, Abu-Bakr M S & Saleh M S, *Indian J Chem*, **21A** (1982) 395.
13 Job P, *Ann Chim (Rome)*, **10** (1928) 113.
14 Shirif F G & Awad A M, *J inorg nucl Chem*, **24** (1962) 79.
15 Yoe G H & Jones A L, *Ind Engng Chem, Anal Ed*, **16** (1944) 111.
16 Fischer B E & Siegl H, *Inorg Chem*, **18** (1979) 425.
17 Martin R B & Prados R, *J inorg nucl Chem*, **36** (1974) 1665.
18 Dewit R & Watters J J, *J Am chem Soc*, **76** (1954) 3810.
19 Kida S, *Bull chem Soc Japan*, **29** (1958) 805.
20 Sahai R, Agrawal & Kushwaha S S S, *J Indian chem Soc*, **59** (1982) 1121.
21 Irving H & Williams R J P, *J chem Soc*, (1983) 3206.