

Ternary complexes in the spectrophotometric determination of trace amounts of silver(I) and cadmium(II)

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Abstract. The reaction of silver(I) and cadmium(II) with 1,10-phenanthroline (PHEN) and Eosin (2,4,5,7-tetrabromofluorescein) gives coloured association complexes. The solution spectra of the mixed-ligand complexes are characterised by high intensity ($\epsilon \sim 10^4$) metal-to-ligand charge-transfer bands at 540-555 nm. The optimum conditions for the spectrophotometric determination of Ag(I) or Cd(II) have been established. A simple, sensitive and selective method was proposed for the determination of traces of the metal ions either in aqueous or organic media. In the presence of EDTA only aluminium and cyanide interfere.

Keywords. Ternary complexes; spectrophotometry; silver; cadmium.

1. Introduction

The formation of mixed-ligand complexes using fluorescein compounds as secondary ligands has recently been reported (El-Ghamry 1968, 1969; Poluektov and Sandu 1970; Tananaiko and Gorenshtein 1974, 1975). The colour reactions were particularly used as the basis of reliable methods of determining Cu(II) (Bailey *et al* 1966), Co(II) (Hadad *et al* 1976) and Pd(II) (Dagnall *et al* 1968). The present paper includes spectrophotometric studies of the mixed-ligand complexes of Ag(I) and Cd(II) with 1,10-phenanthroline and eosin. The possibility of using the ternary complexes formed for the micro-determination of the metal ions is examined.

The preliminary results of this study showed that the ternary complexes are characterised with an apparent stability either in the aqueous or non-aqueous media when the optimum conditions are adopted. The colour reaction is instantaneous and the established procedure will not operate, like some of the existing methods, in alkaline solutions where precipitation of many metal ions is liable to take place. The carboxylic group in eosin favour extraction of the ternary complex into organic solvent.

2. Experimental

Ag(I) and Cd(II) solutions were prepared from the analytically pure nitrate reagents and standardised by conventional methods (Scott and Furman 1962). 10^{-3} M solutions of eosin and 1, 10-phenanthroline (PHEN) were prepared by dissolving the appropriate amount of the solid (E. Merk) in twice distilled water. 0.1 M solution of EDTA was prepared using the Analar product. Buffer solutions of pH 2.5–8 consisting of citric acid and disodium hydrogen phosphate were prepared as recommended (Perrin and Dempsey 1974).

Spectrophotometric measurements were carried out at room temperature (ca. 25°C) with a UNICAM SP 8000 spectrophotometer with 1 cm silica cells. For aqueous media, a series of solutions were prepared containing 1 ml of 10^{-1} M EDTA, 0.5 ml of 10^{-3} M phenanthroline, 7.5 ml of 10^{-4} M eosin and 0–14 ml of 10^{-4} M Ag(I) or Cd(II) solution. The pH was adjusted to pH 5.5–6.4 for Ag(I) or pH 4.4–5 for Cd(II) determinations respectively. The whole volume was made up to 25 ml with twice distilled water. After thorough mixing, the absorbance was measured at 540 or 545 nm against a reagent blank similarly prepared, but containing no metal ion.

1.00 ml of 10^{-4} M $\text{AgNO}_3 = 10.78 \mu\text{g Ag(I)}$,

1.00 ml of 10^{-4} M $\text{Cd(NO}_3)_2 = 11.25 \mu\text{g Cd(II)}$.

For examining the effects of interfering ions, solutions of such ions were added before the Ag(I) or Cd(II).

For extraction experiments, 0–14 ml of 1×10^{-5} M Ag(I) or Cd(II) solution 1 ml of 10^{-1} M EDTA and 0.5 ml of 10^{-4} M eosin were mixed in 100 ml separatory funnels, and the volume made up to 25 ml. After adding 25 ml of chloroform (or nitrobenzene), the mixture was shaken vigorously for 5 min and allowed to stand for 10 min. The organic layer was transferred to a beaker containing sodium sulphate and thence to the spectrophotometer cell, where the absorbance was measured over the range 500–600 nm against a reagent blank obtained in the same way.

3. Results and discussion

3.1. Absorption spectra

The absorption spectrum of 5 ml of 10^{-4} M eosin diluted to 25 ml of solution shows an absorption peak at 510 nm (figure 1, curve a). The presence of 5 ml of 10^{-4} M Ag(I) or Cd(II) produces no significant change in colour or absorption spectrum, but on adding 0.5 ml of 10^{-3} M Phen., the colour changes from orange-yellow to pink. The peak at 510 nm decreases and a new peak appears at 540–555 nm. The maximum colour development was obtained at 5.8–6.4 for Ag(I) complex and at pH 4.0–4.5 for the Cd(II) complex.

3.2. Effect of masking agents and extraneous ions

The addition of EDTA up to 100-fold molar amount relative to Ag(I) or Cd(II) had no effect on the sensitivity. The effects of eighteen cations; Al(III), As(III),

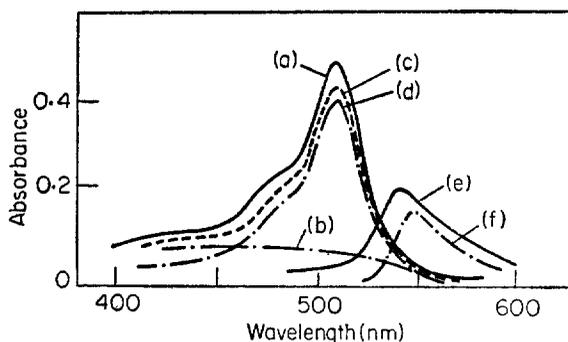


Figure 1. Absorption spectra in aqueous solutions of (a) eosin, eosin and metal ion, or 1,10-phenanthroline and eosin, (all give essentially the same spectrum). (b) Ag(I) or Cd(II) and eosin measured against eosin; (c) Ag/Phen./eosin measured against silver; (d) Cd/Phen./eosin measured against cadmium; (e) Ag/Phen./eosin; (f) Cd/Phen./eosin measured against Phen./eosin.

Ba(II), Ca(II), Co(II), Cu(II), Cr(III), Ce(III), Fe(II), Fe(III), Hg(II), Mg(II), Mn(II), Ni(II), Pb(II), Th(IV), U(VI), Zn(II) and 13 anions: Br^- , Cl^- , CN^- , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, F^- , HPO_4^{2-} , I^- , NO_2^- , NO_3^- , S^{2-} , SO_3^{2-} and SO_4^{2-} were investigated for their interferences in the presence of 100-fold molar amount of EDTA relative to Ag(I) or Cd(II). The results show that only aluminium(III) and cyanide interfere seriously under these conditions.

3.3. Stoichiometry of the complexes

The stoichiometry of the ternary complexes was determined by Job's method of continuous variation (Job 1928, 1936) and the mole ratio method (Yoe and Jones 1944). The results shown in figure 2 indicate that the overall ratio of Ag : Phen. : TBF or Cd : Phen. : TBF ternary complexes is 1 : 1 : 1 i.e. the normal charged chelate formed between silver(I) or cadmium(II) and 1,10-phenanthroline associates with the negatively charged eosin.

3.4. Solvent extraction

The extraction of ion-association complexes involving fluorescein derivatives is only achieved satisfactorily with chloroform or nitrobenzene. These solvents were also able to extract the present ternary complexes. In combination with the use of EDTA as a broad-range masking agent, the extraction procedure provides an extremely selective and sensitive method for the determination of silver or cadmium. Another important advantage of the extraction method is the higher molar absorptivities obtained as compared with the aqueous method. The absorption spectra obtained from a solution containing 0.5 ml of 10^{-1} M EDTA, 0.5 ml of 10^{-3} M Phen, 0.5 ml of citric acid-phosphate buffer, and 7.5 ml of 10^{-4} M TBF, extracted into 25 ml of chloroform or nitrobenzene (reagent blank) show a peak at 535 nm and a shoulder at 510 nm (figure 3 curve 1). The addition of 5.0 ml of 2×10^{-5} M metal ion solution to the above solution followed by extraction into

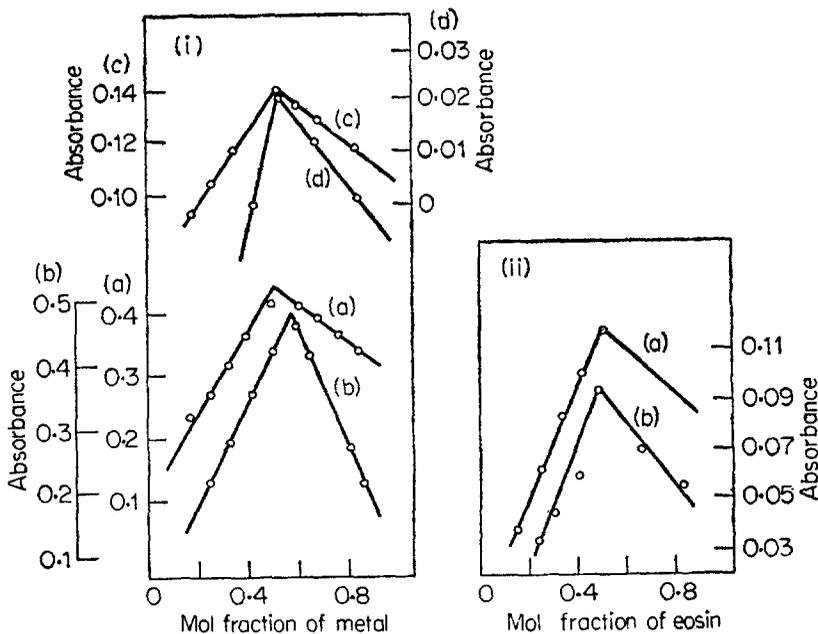


Figure 2. Job's plots. (i)-(a) eosin-Ag (in excess Phen.) varying ratios of 1×10^{-4} M eosin and silver nitrate, (b) eosin-Cd (in excess phen.) varying ratios of 1×10^{-4} M eosin and cadmium nitrate, (c) Phen.-Ag (in excess eosin) varying ratios of 5×10^{-4} M Phen., and silver nitrate, (d) Phen.-Cd (in excess eosin) varying ratios of 5×10^{-4} M Phen., and cadmium nitrate. (ii) Eosin-Phen. (in excess metal) varying ratios of 5×10^{-4} M eosin and phen., plus 0.5 ml citric acid-phosphate buffer and 5.0 ml of 5×10^{-4} M (a) Silver nitrate, (b) Cadmium nitrate diluted to 25 ml with redistilled water.

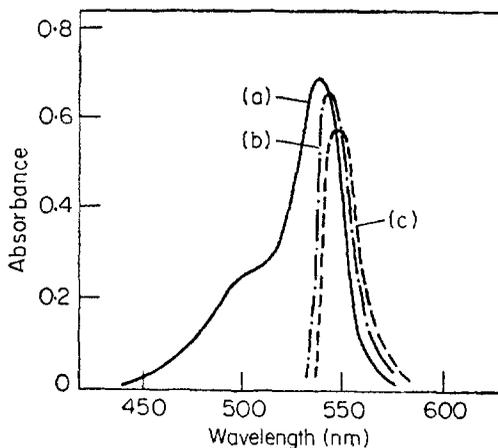


Figure 3. Absorption spectra in non aqueous solutions of: (a) Phen./eosin ; (b) Ag/Phen./eosin, (c) Cd/Phen./eosin vs Phen./eosin.

Table 1. Validity of Beer's Law.

Procedure	Metal ion	Micrograms of metal ion per 25 ml	Metal ion in the final concentration (ppm)	Molar absorptivity
Aqueous medium	Ag(I)	18.75-150	0.75-6.0	12500
	Cd(II)	20.0-112.5	0.80-4.5	8750
Solvent extraction	Ag(I)	4.0-25.75	0.16-1.03	31250
	Cd(II)	4.25-30.00	0.17-1.20	25000

chloroform or nitrobenzene resulted in a peak at 540-555 nm (figure 3 curves *b* and *c*) (reagent blank).

3.5. Calibration curves and Beer's Law

By following the established procedure, the validity of Beer's Law was examined in both aqueous and organic media. The results obtained are summarised in table 1. Calibration graphs obtained were rectilinear over the ranges: Ag(I), $0.5 \cdot 58 \times 10^{-5}$ M and $0.9 \cdot 5 \times 10^{-6}$ M, Cd(II), $0.4 \cdot 45 \times 10^{-5}$ M and $0.1 \cdot 08 \times 10^{-5}$ M for the aqueous and organic systems respectively.

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