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Spectrophotometric studies of ternary complexes of lead and bismuth with *o*-phenanthroline and eosin

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Abstract

The reaction of lead and bismuth as metal ions with *o*-phenenthroline as a primary ligand and eosin as a secondary ligand were examined spectrophotometricalty. An absorption band characterized the solution spectra of mixed ligand complexes formed, with λ_{max} at 558 nm for lead and 552 nm for bismuth at pH 4.5 and 5.0 respectively. These association complexes obey the Beer's law over the concentration range of 1.93×10^{-6} to 9.6×10^{-6} mol/l (0.4–2.0 ppm) and 1.93×10^{-6} to 9.6×10^{-6} mol/l (0.4–2.0 ppm) with molar absorption coefficient of 1.92×10^{4} l mol^{-1} cm^{-1} and 2.05×10^{4} l mol^{-1} cm^{-1} respectively. Stability constants and diverse ion effect on these complexes were also investigated.

Keywords: Lead (II); Bismuth (II); Mixed ligand complexes; *o*-Phenanthroline; Eosin spectrophotometry

1. Introduction

Considerable work has been done on the formation of the association complexes. These complexes have various analytical applications e.g. estimation of ultra traces of metal ions [1,2] and determination of antibiotics in pharmaceutical products [3,4]. Most of the ternary complexes involve the additional extraction step [5–8], which makes the method long, difficult and expensive. Development and measurement of colour in aqueous medium itself would alleviate this difficulty leading to a rapid accurate and more precise analytical work. Ternary complexes in aqueous media are further extensions of complex formation and have not been extensively covered in the literature, however, some studies of relative systems are reported [9,10], while considerable work in this area needs to be exploited.

In this context a detailed examination of the reaction of lead (Pb) and bismuth (Bi) with *o*-phenanthroline and eosin showed that the colour reaction of metal, *o*-phenanthroline and eosin could be used to advantage for an aqueous finish. This paper describes the studies conducted on these systems. Pb and Bi were picked out for these studies as they are both hazardous to the environment and are present in industrial effluents.

2. Experimental

2.1. Reagents

All the reagents were procured from E. Merck and were of analytical grade unless stated other wise with certified purity of 99.9%

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(1) Lead (II) solution (1.5×10^{-3} M): dissolving 0.52 g of lead (II) nitrate in 1 l of doubly distilled water produced 1.5×10^{-3} M lead solution.

(2) Bismuth (II) solution (1.5×10^{-3} M): the desired concentration was prepared by dissolving 0.59 g of bismuth nitrate in 1 l of doubly distilled water with a few drops of nitric acid.

(3) *o*-Phenanthroline solution (1.5×10^{-3} M): the solution was obtained by dissolving 0.27 g of *o*-phenanthroline in a minimum amount of ethanol and diluting it to 1 l with doubly distilled water.

(4) Eosin solution (1.5×10^{-3} M): 1.04 g of disodium salt of eosin-Y was dissolved in 1 l of doubly distilled water.

(5) Gum acacia (0.1%) solution: dissolving 0.05 g of gum acacia in 50 ml of hot doubly distilled water produced the desired solution. The solution was prepared freshly daily.

(6) Buffer solution: a buffer solution of pH 4.5 was prepared by adding 164 ml of 0.1 M acetic acid in 36 ml of sodium acetate solution, while a buffer solution of pH 5.0 was prepared by adding 141 ml of 0.1 M acetic acid in 59 ml of 0.1 M sodium acetate solution.

(7) Solutions of ions: solutions of divers ions used for interference studies were prepared by dissolving the calculated amounts of each compound in doubly distilled water in order to generate 1–10 mg/ml of a particular ion. All cations were added as nitrates, whereas anions were added as their potassium salts.

2.2. Apparatus

A Shimadzu UV-120 spectrophotometer with 10 mm matched quartz cell was used for absorption measurements of the solutions.

For pH studies of the solutions, a Horiba pH meter was utilized.

2.3. Procedure

The aliquots of standard solutions containing 25–100 mg of lead (II) and 2–200 mg of bismuth (III) were introduced into two different 50 ml volumetric flasks already containing 15 ml of buffer solutions of pH 4.5 and 5.0 and 5 ml of 0.1% gum acacia. An amount of 5 ml of 1.5×10^{-3} M *o*-phenanthroline solution was then introduced in both the flasks. Contents were mixed well and 5 ml of 1.5×10^{-3} M solution of eosin was added to both the flasks at this stage and mixed thoroughly. The contents were diluted to 50 ml with doubly distilled water. The regent blank was prepared in the same way except for the metal ion.

3. Results and discussion

3.1. Absorption spectra

The visible spectrum of eosin shows an absorption band at 515 nm and there are no significant changes in colour or in absorption spectrum in the presence of *o*-phenanthroline or metal ion (Fig. 1). However, the solution containing *o*-phenanthroline and eosin undergoes a change in colour from orange-yellow to pink when mixed with lead(II) or bismuth(III) solutions in any amount. The absorption spectrum of reaction mixture against a blank solution containing the same concentration of two ligands showed an appropriate decrease in absorption at 515 nm and exhibited a new band at 558 nm for lead and at 552 nm for bismuth (Fig. 1). The later spectrum is presumably due to the formation of mixed ligand complexes of lead and bismuth. The maximum colour development for both the ternary systems was attained at pH 4.5 for lead and 5.0 for the bismuth complex (Fig. 2). It is worth mentioning that the visible spectrum of the mixture containing eosin and metal ion did not show an absorption band when the solution was scanned versus eosin (Fig. 1).

3.2. Stoichiometries of the complexes

The stoichiometries of the complexes were studied by Job's method [11]. The mole fractions of the two components were varied continuously, keeping their combined concentration constant and keeping the third component in large excess for all solutions in the series. The molar ratio of lead to *o*-phenanthroline was 1:2 and lead to eosin was 1:1 (Fig. 3), thus the overall composition of lead *o*-phenanthroline and eosin complex was found to be 1:2:1, while the composition of the bismuth complex was 1:2:1 (Fig. 4).

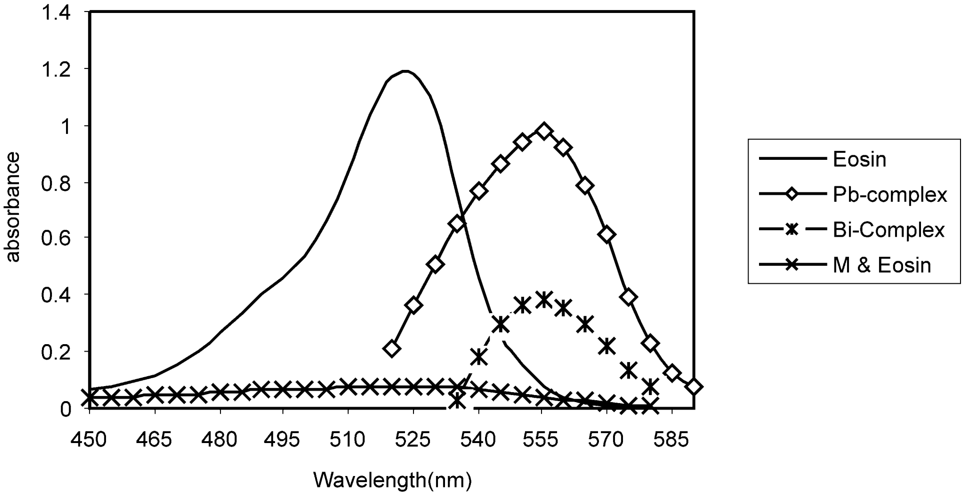

Fig. 1. Absorption spectrum of eosin, Pb(II)-complex, Bi(III)-complex and M (Pb and Bi ions) with eosin versus blank.

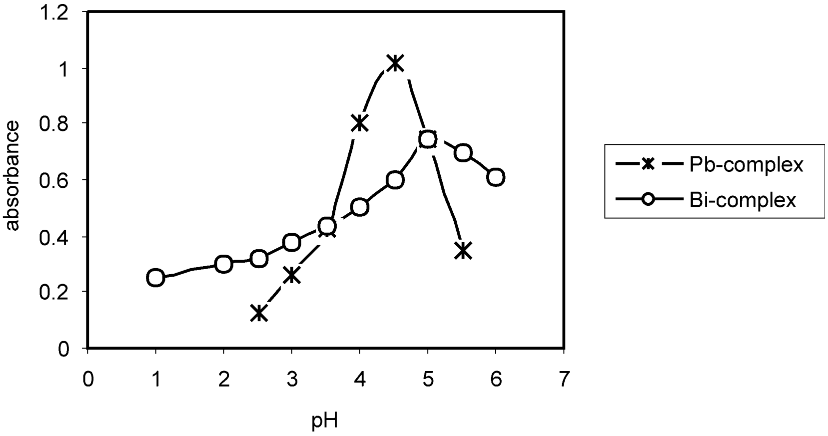

Fig. 2. Effect of pH on Pb(II) and Bi(III) complexation.

In the formation of these complexes, two molecules of *o*-phenanthroline on entering the co-ordination sphere of lead and bismuth fully satisfies primary valency, while the complex ion bears an overall positive charge of the original metal ion and this cationic complex associates with eosin anion to form the ternary complex.

3.3. Calibration graphs

The Beer's law was obeyed over the concentration range 1.93×10^{-6}–9.6×10^{-6} mol/l (0.4–2.0 ppm) for the lead complex while this range was found to be 1.93×10^{-6} to 9.6×10^{-6} mol/l (0.4–2.0 ppm) for bismuth complex (Fig. 5). These graphs were plotted by taking the concentration of eosin and *o*-phenanthroline in excess and varying the concentration of metal ion. Under the optimum conditions, the molar absorption coefficients of lead and bismuth complexes were estimated to be 1.92×10^{4} and 2.05×10^{4} l mol^{-1} cm^{-1} respectively.

3.4. Stability

The stability constants of the complexes (metal ion, *o*-phenanthroline and eosin) were determined by taking the *o*-phenenthroline in excess and applying Job's method of continuous variation [11]. The

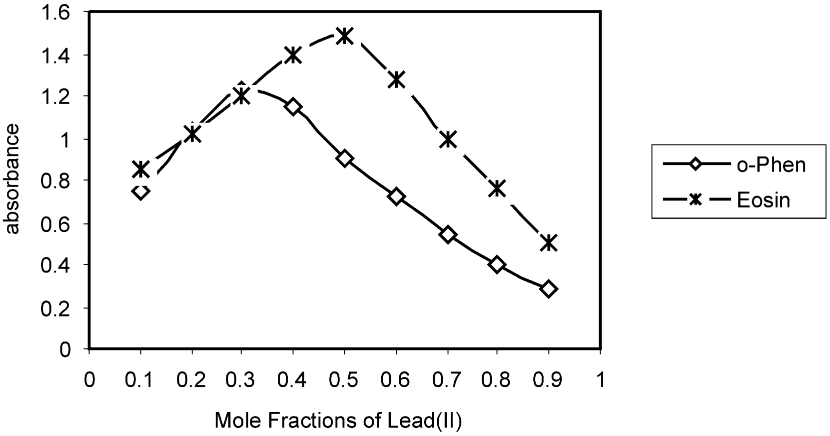

Fig. 3. Stoichiometric studies of the Pb(II)-complex.

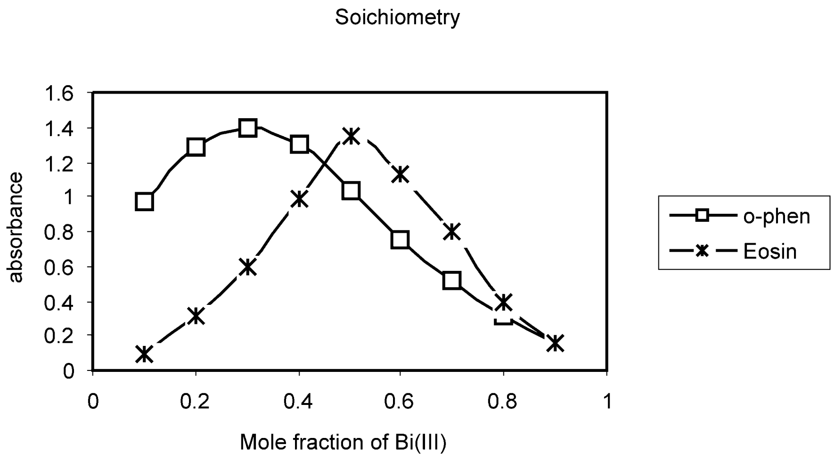

Fig. 4. Stoichiometric studies of the Bi(III)-complex.

log of stability constant (log *K*) for the lead complex was found to be 6.41 and 6.93 for bismuth complex. The magnitude of the stability constant indicates that these complexes are of dissociative nature. These complexes are very temperature sensitive and they start dissociating above 30 °C (Fig. 6), The complexes are stable up to 48 h at 25 °C (Fig. 7). Temperature studies confirm the unstable nature of the complexes.

3.5. Interference of foreign ions

Divers ion effect shows that K(I), Ca(II), Mg(II), Ba(II) and Sr(II) cations while Cl(I), Br (I), NO_3(I) anions have no significant effect on the complexation even if they are present in higher concentrations. But Al(III), Cu(II), Co(II), Ni(II) and Cr(III) cations and SO_4(II), IO_3(I) anions cause a decrease in absorbance value. CN(I) anion has a drastic effect on complexation even if present in trace amounts. Fig. 8 shows the effect of diverse ions where they are present in equimolar concentration with metal ions. Table 1 shows the concentration of foreign ions at which they start interfering. The studies were monitored by observing a change in the absorbance intensities of these complexes in the presence of such ions.

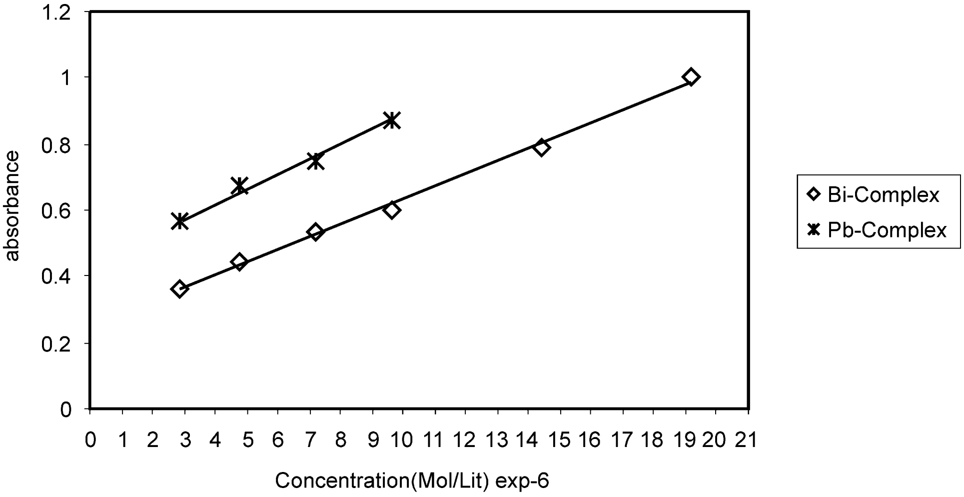

Fig. 5. Calibration graph of the metal complex.

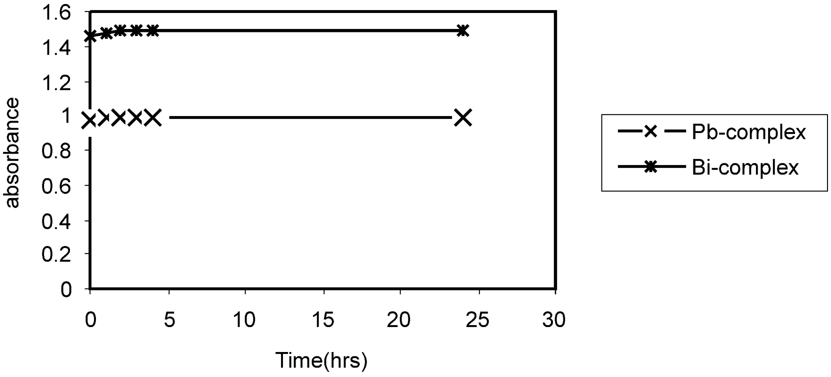

Fig. 6. Effect of time on complexation.

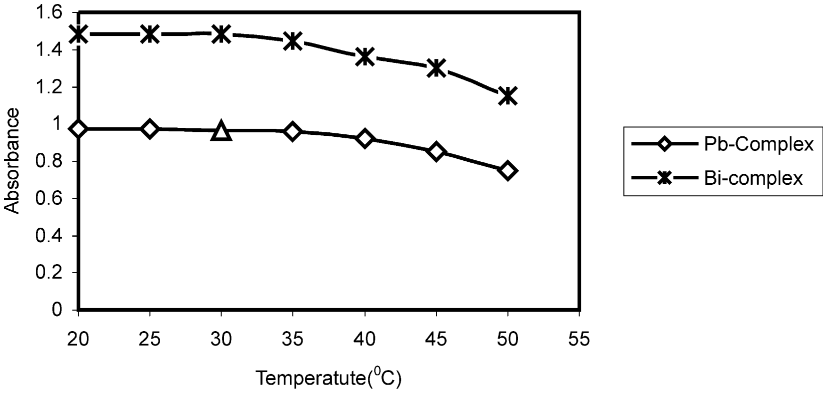

Fig. 7. Effect of temperature on complexation.

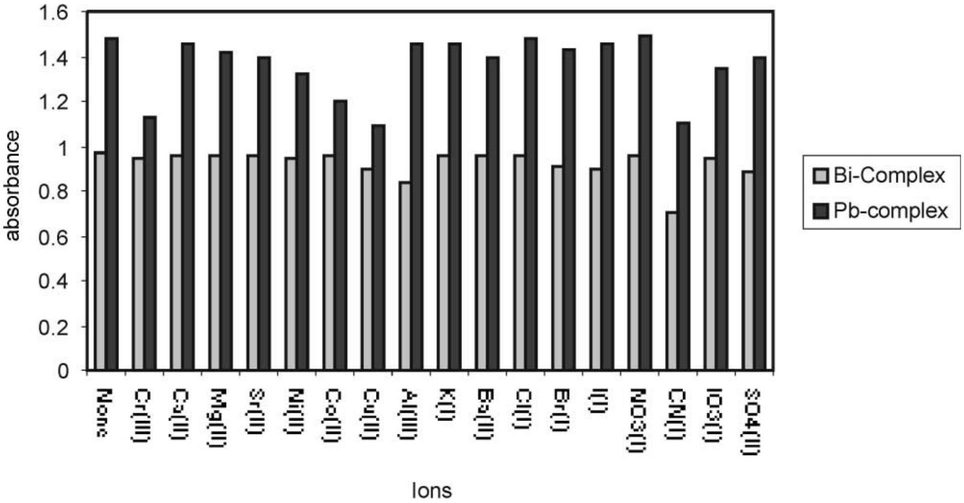

Fig. 8. Effect of diverse ions.

Table 1
Effect of different ions on complexation

Ions	Pb-complex		Bi-complex	
	Limiting concentration (M)	% Effect on absorption intensity	Limiting concentration (M)	% Effect on absorption intensity
Cr^{+3}	1.3×10^{-5}	−12	1.3×10^{-5}	−12
Ca^{+2}	3.7×10^{-4}	−3	3.7×10^{-4}	−3
Mg^{+2}	7.2×10^{-4}	−4	7.2×10^{-4}	−4
Sr^{+2}	1.3×10^{-4}	−3	1.3×10^{-4}	−3
Ni^{+2}	3.7×10^{-5}	−9	3.7×10^{-5}	−8
Co^{+2}	3.7×10^{-5}	−10	3.7×10^{-5}	−12
Cu^{+2}	3.7×10^{-6}	−7	3.7×10^{-6}	−15
Al^{+3}	3.7×10^{-6}	−5	3.7×10^{-6}	−5
K^{+1}	3.7×10^{-4}	−1	3.7×10^{-4}	−1
Ba^{+2}	1.3×10^{-4}	−2	1.3×10^{-4}	−2
Cl^{-1}	3.7×10^{-2}	−2	3.7×10^{-2}	−2
Br^{-1}	3.7×10^{-2}	−3	3.7×10^{-2}	−3
I^{-1}	3.7×10^{-3}	−4	3.7×10^{-3}	−4
NO$_3^{-1}$	3.7×10^{-1}	−1	3.7×10^{-1}	−1
IO$_3^{-1}$	3.7×10^{-5}	−4	3.7×10^{-5}	−4
SO$_4^{-2}$	3.7×10^{-5}	−8	3.7×10^{-5}	−8
CN^{-1}	1.3×10^{-7}	−18	1.3×10^{-7}	−6

4. Conclusion

The complexes of Pb(II) and Bi(III) showed their maximum absorbance at 558 and 552 nm, respectively. The maximum complexation was achieved at pH 4.5 and 5.0, respectively.

Stoichiometries of these complexes were investigated by using Job's method of continuous variation. The values calculated are given below:

Complexes	Stoichiometry		
	Metal	*o*-Phen.	Eosin
Pb(II)-complex	1	2	1
Bi(III)-complex	1	2	1

The log of stability constant of these complexes ranged from 6.41 to 6.93, indicating the dissociative nature of these complexes. Time dependent studies of these complexes show that these complexes are stable up till 24 h. These complexes are also temperature sensitive and start decomposing at 35 °C. It is evident from the stability constant and time dependent studies that these complexes are relatively unstable.

Diverse ion effect showed that cations like K(I), Ca(II), Mg(II), Ba(II), Sr(II)and anions like Cl(I), Br(I), I(I) and NO_3(I) have no significant effect on the complexation, whereas the presence of Al(III), Cu(II), Co(II), Ni(II) Cr(III) cations and SO_4(II), IO_3(II) and CN(I) anions decrease the absorbance values. CN(I) has a drastic effect on complexation and it starts interfering at very low concentration (10^{-7} M). The complexes obey the Beer's law over ppm level.

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