Reaction of Lead(II) with 2,6-Bis(1-hydroxy-2-naphthylazo) pyridine as a Spectrophotometric Determination of Phosphate and Citrate

ISHWAR SINGH*, ASHOK K. SHARMA, SANJIV K. YADAV and DEVENDER SINGH

Department of Chemistry
Maharishi Dayanand University, Rohtak-124 001, India
E-mail: ishsingh@rediffmail.com

A novel heterocyclic bis-azo dye, 2,6-bis(1-hydroxy-2-naph-thylazo)pyridine (PBN) has been used as a chromogenic reagent for lead(II) to give a 1 : 2 (M : L) violet-coloured complex at pH 7.0–8.5 absorbing maximum at 590 nm in a 50% aqueous ethanol medium. Sandell's sensitivity of the colour reaction is 0.0093 µg cm^{-2} with molar absorptivity of 2.22×10^4 L mol^{-1} cm^{-1}. Job's method of continuous variations showed the composition to be Pb(II)-(PBN)$_2$. Phosphate and citrate ions decompose the lead(II)-(PBN)$_2$ complex quantitatively replacing PNB molecules from the complex. Using this ligand exchange reaction, the lead(II)-(PBN)$_2$ complex has been used to determine 0.2–2.6 ppm of phosphate and 0.4–7.4 ppm of citrate spectrophotometrically.

Key Words: 2,6-Bis(1-hydroxy-2-naphthylazo)pyridine, Lead determination, Phosphate, Citrate, Spectrophotometry.

INTRODUCTION

In the present work, we describe the use of 2,6-bis(1-hydroxy-2-naph-thylazo)pyridine (PBN), a novel heterocyclic bis-azo dye, as a chromogenic reagent for the determination of lead(II). It has been found that phosphate and citrate decompose lead(II)-(PBN)$_2$ complex quantitatively, replacing the PBN molecules from the complex. The difference in absorbance between the lead(II)-(PBN)$_2$ complex before and after the addition of phosphate and citrate ions and the reagent blank was proportional to the concentration of phosphate or citrate ions present.

RESULTS AND DISCUSSION

Spectral behaviour and characteristics of lead(II)-PBN complex: Lead(II) formed a violet coloured complex with an ethanolic solution of PBN in a weakly alkaline medium. The complex had a maximum absorbance at 540 nm in the pH range 7.0–8.5. The complex precipitated out if the concentration of ethanol was less than 40%; hence all studies were carried out in 50% aqueous ethanolic solutions. Three moles of the reagent were found sufficient for full colour development. The composition as determined by Job's method of contin-

uous variations was found to be 1 : 2 (metal to ligand). Beer's law was valid up to 11.5 ppm. With the particular conditions adopted here 1.2–10.0 ppm of lead could be determined accurately. The Sandell's sensitivity of the colour reaction was 0.0093 µg cm^{-2} with a molar absorptivity of 2.22×10^4 L mol^{-1} cm^{-1} at 590 nm.

Effect of diverse ions in the determination of lead(II): The effect of diverse ions was studied by taking 4.0 µg/mL of lead(II) and varying amounts of diverse ions. It was found that nitrite, borate, chloride, sulphite, thiosulfate, thiocyanate, cyanide, thiourea, alkaline earths and platinum metals (except palladium) do not interfere at all. However, EDTA, fluoride, phosphate, citrate, tartarate and zinc(II) interfered. Phosphate and citrate avoided the colour formation of lead(II)-(PBN)$_2$ complex completely when added in stoichiometric ratios. EDTA, fluoride and tartrate, however, interfered but did not suppress the colour completely. Zinc(II) ions had a synergistic effect on the colour of lead(II) complex and attempts to mask zinc(II), however, failed.

The tolerance limits of other ions (in folds) which did not cause a deviation of ±2% in absorbance were: thiosemicarbazide (200); sulfide and oxalate (100); bromide (80), iodide (60), Hg^{2+} (20), Pd^{2+} (12), Ag$^+$ (5), Cd^{2+} (2, masked by thiosulfate), Cr^{3+} (6, masked by CN$^-$) and Mn^{2+} (3, masked by oxalate).

Stoichiometry of the reaction between lead(II)-(PBN)$_2$ complex and phosphate or citrate ions: The stoichiometry of the reaction between the lead(II)-(PBN)$_2$ complex and phosphate or citrate ions was investigated by a mole ratio study. Various aliquots of phosphate or citrate ions were added to a known amount of Pb(II)-(PBN)$_2$ complex. The decrease in absorbance recorded at 590 nm reached the maximum value at a 3 : 2 ratio in case of phosphate or at a 1 : 1 ratio for citrate ions, probably with the formation of stable Pb$_3$(PO$_4$)$_2$ species with the former, but an anionic [Pb(C$_6$H$_5$O$_7$)]$^{2-}$ species with the latter.

Determination of phosphate and citrate: The displacement reactions were studied at different pH levels as well as with varying ligand concentrations. The best results were obtained in the pH range 7.0–8.5 with a five-fold molar excess of PBN with respect to lead(II). Using the particular conditions adopted for the determination of 8.2 µg of lead(II), 0.20–2.60 µg of phosphate or 0.4–7.4 µg of citrate could be accurately determined as shown in Fig. 1.

The suppression of colour of the lead(II)-(PBN)$_2$ complex by phosphate or citrate was also studied by taking different amounts of lead(II) in the range 30–250 µg (but fixed), adding sufficient excess of the reagent and various concentrations of phosphate or citrate in a total volume of 25 mL. The results obtained had a coefficient of variation below 3.5%. For example, determination of phosphate at eight known concentrations with 250 µg of lead(II) in a total volume of 25 mL gave a coefficient of variation 1.9%, while the same was 2.5% with citrate. Presence of EDTA, fluoride, tartarate showed serious interference in the determination of phosphate and citrate. Cationic interference was also of the same order as reported for the determination of lead(II).
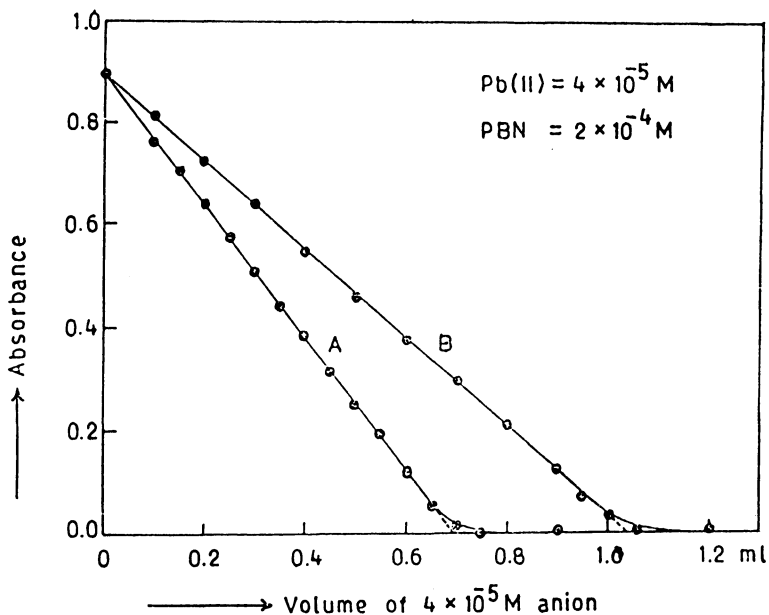
Fig. 1   Decomposition of lead(II)-PBN complex by phosphate (A) and citrate (B) ions

EXPERIMENTAL

Synthesis of 2,6-bis(1-Hydroxy-2-naphthylazo)pyridine (PBN):   Anderson and Nickless method[1, 2] was used to synthesize the bis-azo dye. 0.01 Mol of 2,6-dihydrazinopyridine was dissolved in minimum amount of dilute acetic acid. Separately, 0.02 mol of 1,2-naphthoquinone was dissolved in ethanol. The two solutions were then mixed and kept for some time to get the red precipitate. The mixture solution was made ammoniacal. A dark red solid was filtered, washed with 50% aqueous ethanol and dried over 60–70°C. The compound was recrystallized with ethanol and purity was checked by TLC. Infrared bands (cm^{-1}): $\nu(OH)$, 3500–3200; $\nu(N{=}N)$, 1580–1575; absence of naphthoquinone with $\nu(C{=}O)$, 1670 cm^{-1}.

A 1×10^{-3} M solution of PBN was prepared by dissolving 0.419 g in 1 L of pure ethanol.

Lead(II) solution, 1000 μg/mL: A stock solution of lead(II) was prepared by dissolving appropriate amount of lead nitrate (analytical grade) in double distilled water acidulated with nitric acid and was standardized by volumetric method[3]. Subsequent dilutions were made whenever necessary.

Phosphate or citrate solution, 100 μg/mL: A phosphate solution was prepared by dissolving appropriate amount (0.1432 g/L) of anhydrous potassium dihydrogen phosphate and a citrate solution by dissolving tri-sodium citrate dihydrate (0.1555 g/L) in doubly distilled water.

Borate buffer, pH 8.0: A borate buffer of pH 8.0 was prepared[4] by diluting 250 mL of a solution containing 12.369 g of boric acid and 14.911 g of potassium chloride per litre and 20 mL of 0.2 M sodium hydroxide solution to 1 L with distilled water.

A Bausch and Lomb Spectronics 2000 spectrophotometer with 10 mm matched glass cells was used for recording the spectra and a Beckman pH-meter model φ 60 was used for pH measurements.

Procedure

Determination of lead(II): To an aliquot containing 30–250 μg of lead(II) add 5 mL of 1×10^{-3} M PBN solution followed by 2 mL of borate buffer. Dilute to 25 mL keeping ethanol concentration at 50% (v/v). Measure the absorbance at 590 nm against a reagent blank prepared under similar conditions. Knowing the absorbance, lead content in any unknown solution can be deduced from the calibration curve.

Determination of phosphate and citrate: To an aliquot containing 30–250 μg of lead(II) add 5 mL of 1×10^{-3} M PBN solution followed by an aliquot containing 5.0–65.0 μg of phosphate ions or 10–185 μg of citrate ions. Add 2 mL of borate buffer and dilute to 25 mL, keeping ethanol concentration at 50%. Measure the absorbance against a reagent blank [5 mL of 1×10^{-3} M PBN + 2 mL of borate buffer diluted to 25 mL keeping 50% (v/v) ethanol concentration]. The difference between the absorbance of the complex before and after the addition of phosphate or citrate and the reagent blank was proportional to the concentration of phosphate or citrate ions present.

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