

Haematoxylin as an Adsorption Indicator in Titrimetric Determination of Some Anions & Cations

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Haematoxylin dye has been successfully used as an adsorption indicator in the determination of sulphate, against lead ions in pH range 3.70-4.40, oxalate against calcium ions in pH range 5.80-6.50 and lead against fluoride ions in pH range 2.90-4.00. A marked colour change from yellow to bluish violet is observed at the end point.

A large number of adsorption indicators have been used¹⁻³ in the precipitometric titrations of some anions such as sulphate, oxalate, hexacyanoferrate(II) and molybdate. Haematoxylin has been employed as adsorption indicator in the determination of oxalate and hexacyanoferrate(II) against lead ions by Dubey⁴ and in the determination of iodide/chloride in their binary mixture argentometrically by Agarwal⁵.

We report in this note the efficacy of haematoxylin as an adsorption indicator in the titrimetric determination of sulphate against lead ions, oxalate against calcium ions and lead against fluoride ions.

All the reagents employed were of AR(BDH) or GR (E. Merck) grade. The stock solutions of sodium fluoride, lead nitrate, anhydrous sodium oxalate, sodium sulphate and calcium nitrate tetrahydrate were prepared in doubly distilled water and standardised by usual methods⁶.

Haematoxylin (BDH, 0.4 g) was dissolved in ethanol and volume made upto 100 ml to get 0.4% indicator solution. The indicator solution could not be preserved for more than a week.

The pH measurements were made with a Philips digital pH-meter (PP 9045 M) (accuracy ± 0.01 units) using standard glass (PV 9011) and calomel (PV 9021) electrodes.

Titration of sulphate/oxalate ions against lead/ calcium ions

Sodium sulphate/oxalate solutions (0.1 M, 0.02 M, 0.01 M and 0.005 M, 10 ml each) were taken and their pHs (3.70 to 4.40 in the case of sulphate and 5.80 to 6.50 for oxalate) were adjusted by adding requisite amounts of 0.01 M HNO₃. To this were added 3-4 drops of indicator solution and the titration was carried out by adding slowly with vigorous shaking,

standard Pb(NO₃)₂/Ca(NO₃)₂ solution of appropriate strength corresponding to the strengths of solution titrated. Insoluble PbSO₄/CaC₂O₄ separated out as flocculent precipitates on adding the titrant solution. Haematoxylin underwent sharp colour change from light yellow to bluish violet at the end point.

Titration of lead ions against fluoride ions

The pH of the lead nitrate solution (10 ml) was adjusted to 2.9 to 4.0 by the addition of 0.01 M HNO₃ and to this were added 3-4 drops of indicator solution, and the titration was carried out against standard sodium fluoride solution. The flocculation of lead(II) fluoride precipitate started near the equivalence point. At the end point colour change from yellow to bluish violet occurred on the surface of the precipitates.

During the above titrations the pH of the solutions were recorded and it was observed that there was no significant change in pH.

In these titrations, the flocculation starts just before the equivalence point and is completed as soon as the end point is reached which is marked by a colour change from yellow to bluish violet which is, however, less marked in dilute solutions (0.01 M in the case of sulphate and 0.005 M for oxalate). In the titration of Pb²⁺ against F⁻ the colour change is also not so sharp for dilute solutions (0.02 M of lead). Thorough shaking is most essential.

The above estimations can be carried out with in an accuracy of $\pm 0.02\%$ in dilute solutions of 0.005 M in the case of SO₄²⁻/C₂O₄²⁻ and of 0.02 M in the case of fluoride.

In the initial stage of the titration in the presence of excess SO₄²⁻, C₂O₄²⁻ ions, the flocculent precipitates of PbSO₄ or CaC₂O₄ formed adsorb SO₄²⁻/C₂O₄²⁻ ions. Near the equivalence point when SO₄²⁻/C₂O₄²⁻ ions are almost consumed, the precipitates start accumulating Pb²⁺/Ca²⁺ from the surroundings. At the end point, the surface of the precipitate accumulates sufficient Pb²⁺/Ca²⁺ ions which react with the indicator anions giving a different coloured compound (bluish violet) on the surface. Formation of Pb/Ca-haematoxylin complexes are responsible for the colour change in accordance with the surface compound theory of Mehrotra *et al.*⁷. This has been further substantiated by the isolation of Pb-haematoxylin derivative in the pH range 4-6 which has been found to have 1:1 (Pb-dye) stoichiometry. (Found: Pb, 37.24. Calc.: Pb, 36.90%).

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