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Application of Xylenol Orange as an Adsorption Indicator in the Precipitimetric Assaying of Some Anions

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Xylenol orange has been successfully employed as an adsorption indicator in the semimicro estimation of fluoride, metaborate, oxalate, sulphate and phosphate ions against lead(II) ions in the acetate buffer (pH = 4.99), hexamine buffer (pH = 6.2) and pyridine buffer (pH=6.00) media. The indicator exhibited a sharp colour change from purple to bluish violet on the surface of the precipitate at the end point.

INTRODUCTION

A survey of literature reveals that a large number of adsorption indicators have been employed in the precipitimetric titrations of some anions such as oxalate, sulphate, hexacyanoferrate (II), tungstate and molybdate using Pb (II) ions as titrant[1-4]. Xylenol orange has also been used as anadsorption indicator in the determination of halide, pseudohalide, oxalate, hexacyanoferrate(II) against Ag(I)[5], Hg(I)[6], La(III)[7] and Th(IV)[8] ions.

In the progress of our work[9-11], we report the extended application of xylenol orange as an adsorption indicator in the precipitmetric determination of fluoride, metaborate, oxalate, sulphate and phosphate ions against lead (II) ion as titrant in semimicro amount, in the presence of acetate buffer (pH=4.99), hexamine buffer (pH=6.20) and pyridine buffer (pH = 6.00). The dye (indicator) exhibited a sharp colour change from purple to bluish violet on the surface of the precipitate at the end point.

Chemicals

All the chemicals employed were of A. R. (BDH) or G. R. (E. Merck) quality. The stock solutions of sodium fluoride (NaF), sodium oxalate ($Na_2C_2O_4$), sodium sulphate (Na_2SO_4), sodium phosphate (Na_3PO_4) and lead nitrate $Pb(NO_3)_2$ were prepared in doubly distilled water and standarised by usual methods[12].

The solution of sodium metaborate ($NaBO_2$) was prepared by dissolving appropriate amount of $Na_2B_4O_7.10H_2O$ (borax) in doubly distilled water and it was warmed at 100°C for few minutes to convert orthoborate into metaborate.[13] The solution was standardised by titrating against Pb^{2+} ions precipitimetrically using dichlorofluorescein as indicator[4].

Buffer Solution

(i) Acetate buffer of pH = 4.99 was prepared by usual method[12].

(ii) Pyridine buffer of pH = 6.00 was prepared by mixing redistilled 30 ml pyridine in 120 ml doubly distilled water with addition of 6N- 2 ml HNO_3[14].

(iii) Hexamine buffer of pH = 6.20 was prepared by dissolving 3 gm of hexamine in 100 ml doubly distilled water[15].

Indiactor Solution

0.2% (w/v) solution of dye was prepared in ethanol.

Instruments

The pH measurements were made with the help of Philips digital pH meter (PP 9045 M) within an accuracy of ±0.01 using standard glass (PV 9011) and calomel (PV 9021) electrodes.

Recommended Procedure

(i) Titration of metaborate/oxalate/sulphate/phosphate ions against lead (II) ions

10.00 Ml of titre ($NaBO_2$/$Na_2C_2O_4$/Na_2SO_4/Na_3PO_4) of strength (0.1M, 0.2M, 0.01M, and 0.005M) was taken in a conical flask and the solution was neutralised by adding 0.01M HNO_3 or NH_4OH. Now requisite amount of hexamine buffer solution was added and the titration was carried out with standard solution of $Pb(NO_3)_2$ of a respective molarity. At the end point the indicator exhibited a sharp colour change from purple to bluish violet on the surface of precipitate.

(ii) Titration of fluoride ions against lead (II) ions

10.00 Ml of titre (NaF) of strength (0.1 M and 0.02M) solution was taken in a conical flask which was neutralised by adding 0.01M HNO_3 or NH_4OH. To this requisite amount of acetate buffer (pH = 4.99)/pyridine buffer (pH = 6.00) was added. Now 3-4 drops of 0.2% (w/v) indicator solution was added and the titration was carried out with standard solution of $Pb(NO_3)_2$ of respective molarity. At the end point the indicator showed a sharp colour change from yellow to bluish violet (in the presence of acetate buffer) and purple to bluish violet (in the presence of pyidine buffer) on the surface of precipitate.

The above estimations could be performed upto the dilution limit of 0.005 M in the case of oxalate, sulphate and phosphate whereas upto 0.02 M in the case of fluoride and metaborate due to their solubility. The results and statistical data are recorded in Table 1.

TABLE 1

RESULTS AND STATISTICAL DATA

Conc (M)	Titre	Titrant ml [$Pb(NO_3)_2$]	Amount taken (mg)	Mean ($\bar{X}$)	Standard deviation (σ)	Coefficient of variation	Limit of Confidence at 95%	Relative Error (%)
0.1	NaF	5.00— 5.05	18.9984	19.0934	0.09	0.45	±0.0850	+0.50
0.1	$NaBO_2$	4.95— 5.00	42.8088	42.5976	0.16	0.34	±0.1620	−0.50
0.1	$Na_2C_2O_4$	10.00—10.05	88.0000	88.2347	0.20	0.23	±0.1990	+0.27
0.1	Na_2SO_4	9.95—10.00	96.0576	95.8175	0.22	0.23	±0.2169	−0.25
0.1	Na_3PO_4	14.95—15.00	94.9714	94.8131	0.14	0.15	±0.1430	−0.17
0.02	NaF	5.00— 5.05	3.7996	3.8187	0.02	0.45	±0.0172	+0.49
0.02	$NaBO_2$	4.95— 5.00	8.5618	8.5642	0.07	0.87	±0.0743	+0.03
0.02	$Na_2C_2O_4$	9.95—10.00	17.6000	17.5530	0.05	0.29	±0.0518	−0.27
0.02	Na_2SO_4	10.00—10.05	19.2115	19.2592	0.04	0.23	±0.4350	+0.25
0.02	Na_3PO_4	14.95—15.00	18.9943	18.9626	0.03	0.15	±0.0286	−0.17
0.01	$Na_2C_2O_4$	10.00—10.05	8.8000	8.8220	0.02	0.24	±0.0216	+0.25
0.01	Na_2SO_4	9.95—10.00	9.6058	9.5817	0.02	0.23	±0.0217	−0.25
0.01	Na_3PO_4	14.95—15.00	9.4971	9.4813	0.01	0.15	±0.0143	−0.17
0.005	$Na_2C_2O_4$	10.00—10.05	4.4000	4.4102	0.02	0.36	±0.0156	+0.23
0.005	Na_2SO_4	10.00—10.10	4.8028	4.8280	0.02	0.48	±0.0229	+0.53
0.005	Na_3PO_4	15.00—15.05	4.7486	4.7549	0.01	0.16	±0.0074	+0.13

Mechanism

Mode of action : Various theories have been proposed by different workers but the mode of action of xylenol orange can be explained in the light of Mehrotra's surface compound formation theory.[16]

In the beginning of titrations, the anions ($C_2O_4^{2-}/SO_4^{2-}/PO_4^{3-}/F^-/BO_2^-$) are consumed in the formation of flocculent precipitate of $PbC_2O_4/PbSO_4/Pb_3(PO_4)_2/PbF_2/Pb(BO_2)_2$ having solubility products 4.8×10^{-10}, 1.6×10^{-8}, 7.9×10^{-43}, 3.7×10^{-8} and 1.6×10^{-11} respectively with metal ions (Pb^{2+}) by preferential precipitation than Pb-Dye compound. Near the end point when anions are almost consumed, the precipitate starts absorbing Pb^{2+} ions from surroundings and develops a positive charge on the surface, which interacts dye anions and form a bluish violet coloured xylenol orange-Pb derivative on the surface which is responsible for colour change from purple to bluish violet as yellow to bluish violet at the end point.

$$[MX]\ M^{++} + Dye^{2-} \rightarrow [M - X]\ M\text{-}Dye.$$

Near the end point
purple or yellow

At the end point
Bluish violet

$$M = Pb^{2+},\ X = C_2O_4^{2-},\ SO_4^{2-},\ PO_4^{2-},\ F^-\ \text{and}\ BO_2^-$$

The mode of action of xylenol orange has been further supported by preparative and analytical studies of Pb-xylenol orange derivative.

Preparative and Analytical Studies of Pb-dye Derivative

0.5 Gm of recrystallised xylenol orange dye was dissolved in ethanol and 8–10 ml hexamine buffer was added. Now 0.1 M $Pb(NO_3)_2$ solution was added with constant shaking. A precipitate of violet coloured Pb-Dye derivative was formed which was filtered and dried. The analytical data of compound confirmed the stoichiometry of 1 : 1 Pb-Dye derivative.

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