HOT AMPEROMETRIC TITRATION-DETERMINATION OF SMALL AMOUNTS OF VANADIUM AND ZIRCONIUM

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3-3' bis (N-N' dicarboxy methyl aminomethyl) o-cresol sulphothalein-popularly known as xylenol orange has been refered to as a spectrophotometric reagent [1-3]. The polarographic reduction of some sulphothalein dyes prompted us to make use of xylenol orange (Abbrev as XO) as an amperometric reagent.

The present paper deals with the result of amperometric titration of titled metal ions with XO. The detailed polarography of XO and the effect of various experimental factors have been reprted [4].

EXPERIMENTAL

The chemicals used were of analar quality. Vanadium and zirconium solutions were prepared by dissolving calculated quantities of the ammonium meta vandate and zirconyl nitrate. The solutions were standardized [5]. A fresh solution of xylenol orange was prepared whenever required. Britton-Robinson buffer was prepared as usual.

The polarogrphy of XO have been studied on polarograph CLO-2B Toshniwal digital type. The capillary characteristic was $m^{2/3} t^{1/6} = 2.13\ mg^{2/3} sec^{-1/2}$ at 40 cm effective height of mercury column. Toshniwal digital pH meter (model CL-46) was used for pH measurements. A temprature control device has been designed for aforesaid studies at higher temperature.

RESULTS

Polarography of Xylenol Orange

Polarograms of XO in Britton Robinson buffer were taken at different pH and at different concentration. It gives single reduction wave at pH $\leq$ 4.0 and two step reduction wave at pH $\geq$ 4.2. A logarithmic analysis for each wave at different pH values indicates that the first step is reversible while second is irreversible. The half wave potential for each of the steps is found to shift towards negative value, with pH. However, the observed limiting current is more or less pH independent. The dependence of the limiting current on the height of mercury column ($h^{1/2}$) at pH 5.5 shows linear dependence for log i-log h plot (correllation coefficient, r = 0.988).

TABLE 1

AN AMPEROMETRIC DETERMINATION USING XYLENOL ORANGE AS TITRANT

Plateau potential = -1.25 V vs Hg pool, pH = 5.5
Temperature = 75°C

Conc. of metal mM	Amount Taken mg	Amount Found mg	% Error	S.D. σ	C.V.
	Vanadium				
0.5	0.2547	0.2522	- 0.98	0.0012	0.47
1.0	0.5094	0.5108	+ 0.27	0.0030	0.58
1.5	0.7641	0.7680	+ 0.51	0.0048	0.62
2.0	1.0188	1.0132	- 0.55	0.0042	0.38
2.5	1.2735	1.2710	- 0.26	0.0017	0.13
4	1.7829	1.7782	- 0.26	0.0098	0.55
5	2.5470	2.5514	+ 0.17	0.0084	0.33
	Zirconium				
0.5	0.4561	0.4538	- 0.50	0.0028	0.61
1.0	0.9122	0.9178	+ 0.61	0.0020	0.21
1.5	1.3683	1.3609	- 0.54	0.0071	0.52
2.0	1.8244	1.8204	- 0.22	0.0092	0.50
2.5	2.2805	2.2858	+ 0.23	0.0064	0.28
4	3.1927	3.1872	- 0.17	0.0092	0.28
5	4.5610	4.5512	- 0.21	0.0104	0.22

values calculated from a set of six titrations in each case

Limiting current is found to be proportional to the concentration of XO in the range of 2.5×10^{-4} M to 1.5×10^{-3} M at pH 5.5. The $E_{1/2}$ values are -0.62V and -1.23 V vs. Hg pool for the two waves respectively. A slight positive shift in $E_{1/2}$ was observed at higher temperature. Reproducible data were obtained at 75°C using 0.5 M dye solution.

Procedure of Amperometric Titration

For titrations, sets of solution containing known amount of zirconium and vanadium in 10 ml of Britton Robinson buffer at pH 5.5 (μ = 0.5 were prepared. The metal solution was taken into titration cell and kept in thermostat adjusted for 75°C; plateau potentional on the wave of XO i.e -1.25 V vs Hg pool was applied. Standard solution of XO was added drop by drop from microburette and current change was noted. Plots of currents vs volume revealed reverse L shaped curve indicating stiochiometry of 1:1 in each case. The results of determination have been tabulated in Table 1.

Effect of Experimental Factors

(a) Temperature: Amperometric titrations performed at room temperature (nearly 25°C) are not giving

reproducible results. This might be due to lower degree of dissociation and higher degree of irreversibility at low temperature. The results are satisfactory with the increase of temperature. The optimum temperature choosen for these titration is 75°C as reproducible results were obtained for replicate set of titrations.

(b)Effect of time: The solution of dye is fairly stable for a few days. On ageing semi-XO forms, which may hinder to give true values of amperometric current. A freshly prepared solutions of XO is prefered for the amperometric titrations and all measurement should be taken within 2 hrs.

(c) Effect of divers ions: The known amount of foreign ions was added to a known amount of metal ions and titration was carried out to examine for any interference. The titrations of zirconium or vanadium, were not in any way hampered by the presence of different amount of foreign ions viz. K^+ (195 mg), Na^+(138 mg), Ca^{2+} (75 mg), Mg^{2+} (73 mg), Ba^{2+}(69 mg), Pb (58.5 mg), Te (20 mg), Tl (20 mg), respectively. Moreover, 100 fold excess of the ions like Cl^- , ClO_4^- , NO_3^-,CH_3COO^-, I^- , SO_4^{2-} had no efffect. However, it is observed that the ions Ti^{4+}, Co^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} and Lanthanides interfere seriously in this titrimetric procedure.

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