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Analysis of Some Binary Transition Metal Ion Mixtures Using Iron(II) as a Reductant in Phosphoric Acid Medium

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Simple, accurate and convenient titrimetric methods have been doveloped for the analysis of some synthetic binary transition metal ion mixtures [Ce(IV) + Mo(VI); Cr(VI) + Mo(VI); V(V) + Mo(VI); V(V) +V(IV); V(V) + Ce(IV) and V(V) + Cr(VI)] using iron(II) as a reductant in phosphoric acid medium. The method consists in titrating a metal ion mixture with iron(II) first in 6-7 M phosphoric acid medium using N-phenyl anthranilic acid (NPA) or ferroin as a redox indicator for Ce(IV), Cr(VI) or V(V) and then in 11-12 M phosphoric acid medium using resorufin as an indicator for Mo(VI) and V(VI). From the two titer values the amounts of metal ions present in mixtures can be computed. To explain the suitability of the redox indicators in the titrations, present workers have measured their transition potentials of the indicators used and compared them with the redox potentials of the metal ion systems.

Key Words: Titrimetic, Phosphoric Acid, Iron(II), Resorufin.

INTRODUCTION

Redox methods for the determination of transition metal ions are available in literature[1-4]. But, only a few procedures have been reported for the estimation of the metal ions present in their mixtures. These methods generally utilize reagents like sulphur dioxide[5], tin(II) chloride[6,7], cadmium reductor, chromium(II) sulphate[8], zinc in acid medium[9] and iron(II) in phosphoric acid medium[10], *etc*. These methods suffer from several disadvantages. For example, the sulphur dioxide method is tedious, time consuming and needs inert atmosphere. The preparation and preservation of tin(II) and chromium(II) is difficult, because, these reagents need special apparatus for their storage under inert atmosphere. The methods involving metal amalgams and zinc in acid medium require elevated temperatures. Reduction methods involving iron(II) in phosphoric acid medium requires inert atmosphere to prevent the aerial oxidation of the dyes employed to detect the end-point.

Recently, we have investigated the use of resorufin (RSF) as an advantageous redox indicator for the determination of transition metal ions employing iron(II) as a reductant in phosphoric acid medium[4]. The present paper describes the use of iron(II) as a reductant in phosphoric acid medium, for the analysis of some binary metal ion mixtures employing N-phenylanthranilic acid (NPA), ferroin and resorufin (RSF) as redox indicators. These are: [cerium(IV) + molybdenum(VI)]; [chromium(VI) + molybdenum(VI)]; [vanadium(V) + molybdenum(VI)]; [vanadium(V) +vanadium(IV)]; [vanadium(V) + cerium(IV)] and [vanadium(V) + chromium(VI)]. The methods now developed do not suffer from any of the disadvantages associated with the earlier methods.

EXPERIMENTAL

Preparation of solutions: 0.1 M solutions of molybdenum(VI), cerium(IV) and vanadium(V) have been prepared and standardized as described in literature[2]. 0.05 M solutions of vanadium(IV) and iron(II) have been prepared and standardized[10,11]. A 0.035 M solution of chromium(VI) has been prepared from AR grade potassium dichromate. A 0.1 % (w/v) solution of N-phenylanthranilic acid (NPA), a 0.025 M solution of ferroin and a 0.05 % (w/v) solution of resorufin (RSF) have been prepared and employed as redox indicators in this investigations. Synthetic binary transion-metal ion mixtures mentioned above have been prepared such that the total concentration of the metal ions did not exceed 0.045 M for molybdenum(VI), cerium(IV), vanadium(IV), 0.025 M for vanadium(V) and 0.018 M for chromium(VI), when the solution is diluted to 50 mL.

Recommended procedure: To a 10 mL aliquot of a metal ion mixture taken in a titration vessel, sufficient amount of orthophosphoric acid is added such that the concentration of the acid is about 6-7 M near the end-point. After passing purified carbon dioxide gas for *ca.* 1-3 min to expel any dissolved oxygen, 3 drops of NPA or ferroin (in case of cerium(IV) containing mixtures) are added, then it is titrated against a 0.05M iron(II) solution, while the reaction mixture is stirred by means of a magnetic stirrer to the disappearance of the dark pink colour in the case of NPA or appearance of pink/red colour in the case of ferroin. The volume of iron(II) consumed is noted as volume-I. Under these conditions Ce(IV), Cr(VI) and V(V) are quantitatively reduced by iron(II) to Ce(III), Cr(III) and V(IV), respectively. Then, the concentration of phosphoric acid is raised to about 11-12 M, 5-6 drops of RSF indicator are added and the titration continued with same iron(II) solution to the sharp colour transition from red to blue-green. The total volume of iron(II) consumed is noted as titre-II. The difference in titre-II and titre-I is then computed as volume-II. This stage corresponds to the reduction Mo(VI) and V(IV) [along with V(IV) produced from V(V) during the first stage of reduction] by iron(II) to Mo(V) and V(III), respectively. From the two volumes [volume-I and volume-II] the amounts of metal ions present in the reaction mixture may be computed based on the following relations shown against each metal ion mixture in Table-1.

TABLE-1
RELATION BETWEEN THE AMOUNT OF A METAL ION AND VOLUME OF IRON(II) VOLUME-I / VOLUME-II] CONSUMED

Metal ion mixture	Iron(II) consumed as Volume-I corresponds to the	Iron(II) consumed as Volume-II corresponds to the
Ce(IV) + Mo (VI)	Amount of Ce(IV)	Amount of Mo(VI)
Cr(VI) + Mo(VI)	Amount of Cr(VI)	Amount of Mo(VI)
V(V) + Mo(VI)	Amount of V(V)	Sum of Mo(VI) andV(V)
V(V) + V(IV)	Amount of V(V)	Sum of V(V) and V(IV)
V(V) + Cr(VI)	Sum of V(V) and Cr(VI)	Amount of V(V)
V(V) + Ce(IV)	Sum of V(V) and Ce(IV)	Amount of V(V)

RESULTS AND DISCUSSION

The amount of each metal ion present in a synthetic binary metal ion mixture computed has been shown in the Table-2.

The accuracy of the method is ± 0.6 %. The precision of the method has been expressed in the form of relative standard deviation. The colour transition of the indicators are sharp and reversible.

From the recommended procedure described above, it may be seen that the detection of the end-point for some reductimetric determinations (using NPA or ferroin as indicators) is possible even in a low phosphoric acid medium of 6-7 M; while in some other determinations it is possible at a high phosphoric acid of about 12 M (with RSF as redox indicator).

The difference in the observed redox behaviour of the metal ions may be explained based on the redox potentials of the metal ions observed at different phosphoric acid concentrations.

Rao and Sagi[13] reported that the formal redox potential of iron (III)/iron(II) system decreases from about 0.684 V to about 0.388 V as the phosphoric acid concentration increases from about 1.0 M to 12.0 M; its potential in 6-7 M phosphoric acid being about 0.432V. Rao and co-workers also reported that the formal potentials of Ce(IV)/Ce(III)[14], Cr(VI)/Cr(III)[15] and that of V(V)/V(IV)[10] are in the range of 1.10-1.25 V, while those of Mo(VI)/

TABLE-2
DETERMINATION OF A METAL ION
PRESENT IN A METAL ION MIXTURE
(Amount of total metal ion present in 50 mL, has been computed)

(A) Ce(IV) + Mo(VI) mixture					
Amount of Cerium(IV) (mg)			Amount of Molybdenum(VI) (mg)		
Standard method[12]	Present method*	RSD (%)	Standard method[12]	Present method*	RSD (%)
32.50	32.63	0.270	239.85	238.77	0.275
29.25	29.11	0.293	215.86	217.09	0.302
26.00	25.86	0.325	191.88	193.03	0.312
(B) Cr(VI) + Mo(VI) mixture					
Amount of Chromium(VI) (mg)			Amount of Molybdenum(VI) (mg)		
Standard method[10]	Present method*	RSD (%)	Standard method[10]	Present method*	RSD (%)
336.28	337.96	0.227	201.47	200.32	0.321
322.27	320.82	0.295	211.06	210.02	0.297
294.25	295.48	0.305	230.25	231.28	0.225
(C) V(V) + Mo(VI) mixture					
Amount of Vanadium(V) (mg)			Amount of Molybdenum(VI) (mg)		
Standard method[12]	Present method*	RSD (%)	Standard method[12]	Present method*	RSD (%)
48.39	48.63	0.320	249.44	250.48	0.250
56.03	55.77	0.271	220.66	219.66	0.281
29.85	60.08	0.221	206.27	207.32	0.326
(D) V(V) + V(IV) mixture					
Amount of Vanadium(V) (mg)			Amount of Vanadium(IV) (mg)		
Standard method[12]	Present method*	RSD (%)	Standard method[12]	Present method*	RSD (%)
62.40	62.63	0.275	104.43	103.90	0.325
54.76	54.51	0.296	119.71	120.28	0.282
52.21	51.95	0.321	124.80	125.29	0.251
(E) V(V) + Cr(VI) mixture					
Amount of Vanadium(V) (mg)			Amount of Chromium(VI) (mg)		
Standard method[10]	Present method*	RSD (%)	Standard method[10]	Present method*	RSD (%)
61.13	61.35	0.251	27.30	27.16	0.310
58.58	58.34	0.301	28.60	28.73	0.285
53.48	53.21	0.320	31.20	31.33	0.220
(F) V(V) + Ce(IV) mixture					
Amount of Vanadium(V) (mg)			Amount of Cerium(IV) (mg)		
Standard method[12]	Present method*	RSD (%)	Standard method[12]	Present method*	RSD (%)
63.67	63.92	0.206	280.24	281.66	0.317
57.31	57.06	0.321	315.27	313.82	0.265
50.94	50.69	0.352	350.30	348.90	0.215

*Average of six determinations.

Mo(V)[14] and V(IV)/V(III)[10] are in the range of 0.550 V-0.500 V in 6-7 M phosphoric acid medium. However, the potential of the latter two metal ion couples [Mo(VI)/Mo(V) and V(IV)/V(III)] are found to increase to about to 0.700-0.750 V with increase in phosphoric acid concentration upto 11-12 M.

When a binary metal ion mixture is titrated against iron(II) in 6-7 M phosphoric acid medium, obviously, the metal ions[Ce(IV), Cr(VI) and V(V)] having higher potential range have been reduced first. NPA and ferroin [with cerium(IV)] functioned as suitable redox indicators in these determinations.

Present authors have measured the transition potentials of the indicators in the determinations adopting the method of Belcher *et al.*[17] and found them to be in the range of 0.750 V to 0.850 V.

In the second stage of the procedure, however, when the titrations have been carried out in a high phosphoric acid medium of about 11-12 M, the remaining two metal ions Mo(VI) & V(IV), as expected from their observed formal potentials have been reduced by iron(II). RSF has been found to function satisfactorily as a redox indicator in these determinations. The transition potential of the indicator RSF has been measured in these determinations and they are found to be in the range of 0.540 - 0.600 V.

As per theoretical expectations the transition potential of the indicators have been found to be intermediate between the redox potentials of the oxidant and reductant systems; thus explaining the suitability of these indicators in the determinations.

As reported in our earlier communication, RSF which is deep red in colour in the reaction medium is reduced to its blue-green semiquinone form by iron(II) at the end-point in one electron reduction step[4].

The advantages associated with the use of RSF over the other indicators[10] used earlier in these investigations are as follows. No inert atmosphere need be maintained during the titrations as in the case of thiazine dyes used earlier. The colour transition of the indicator, being from red to blue-green, can be easily detected. Unlike, other redox indicators, RSF solutions are quite stable even in the presence of powerful oxidants like chromium(VI) and cerium(IV).

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