Successive Potentiometric Titration of Chromium(VI) and Iron(III) with Cobalt(II) in the Presence of 1,10-Phenanthroline

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Studies are made on the effect of 1,10-phenanthroline (phen) on the redox reactions such as chromium(VI) and iron(III) with cobalt(II). In the presence of phen, the conditional redox potential of the Co(III)/Co(II) system is lower than that of the Cr(VI)/Cr(III) and the Fe(III)/Fe(II) systems. Two large potential breaks are thus observed at equivalence points when the titration of 5×10^{-4} mol dm^{-3} chromium(VI) and 1×10^{-3} mol dm^{-3} iron(III) with cobalt(II) is carried out in the presence of 8×10^{-2} mol dm^{-3} phen at pH 1, while in the absence of this ligand no potential break can be observed at equivalence points. By using these redox reactions, we propose successive potentiometric titrations of chromium(VI) and iron (III) with cobalt(II) in a single titration. The proposed method is successfully applied to the determination of chromium and iron in high carbon ferrochromium.

The applicability of the redox reaction,

$$\mathrm{M_{Ox}} + \mathrm{N_{Red}} \overset{K_{\mathrm{M-N}}}{\rightleftharpoons} \mathrm{M_{Red}} + \mathrm{N_{Ox}} \qquad (1)$$

to the titrimetric method can be evaluated in terms of the equilibrium constant $K_{\mathrm{M-N}}$ of this reaction. The presence of a suitable ligand which forms more stable complexes with $\mathrm{M_{Red}}$ than $\mathrm{M_{Ox}}$ and/or with $\mathrm{N_{Ox}}$ than $\mathrm{N_{Red}}$ shifts the equilibrium constant toward the right hand side and, thus, makes possible the direct titration of $\mathrm{M_{Ox}}$ with $\mathrm{N_{Red}}$.[1—12] Vydra and Pribil[2,3] reported the effect of 1,10-phenanthroline (phen) on the redox reaction of cobalt(II) with iron(III) and developed the potentiometric titration of cobalt(II) with iron(III) in the presence of this ligand. Recently, we have also reported potentiometrically the effect of this ligand on several redox reactions involving metal ions.[4—6] The presence of diphosphate improves the potential break at the equivalence point of chromium(VI) with iron(III), and a clear potential break is observed in the titration of copper(II) with iron(II) in the presence of diphosphate together with neocuproine.[4] The use of a ligand buffer[13] with zinc(II) in excess over EDTA is effective for the titration of vanadium(V) with iron(II).[5] In the presence of phen or 2,2′-bipyridine (bpy), a remarkable potential break is observed in the titration of vanadium(IV) with iron(III), cobalt(II) with vanadium(V) and cobalt(II) with chromium(VI).[6]

This phenomenon based on the ligand effect has a potential capacity for the development of new redox systems which are applicable to analytical chemistry. Teshima et al.[14] reported a simple and rapid flow injection procedure for the simultaneous determination of iron(III) and vanadium(V) and of iron(III) and chromium(VI) by using the effect of ligands on the redox potential of the Fe(III)/Fe(II) system with a single spectrophotometric detector. The method could be successfully applied to the determination of iron(III)–vanadium(V) and iron(III)–chromium(VI) in synthetic mixtures.

The present paper describes the effect of phen on the redox reactions of chromium(VI) and iron(III) with cobalt(II). By using these redox reactions in the presence of phen, successive potentiometric titration of chromium(VI) and iron(III) with cobalt(II) is presented. This method is successfully applied to the determination of chromium and iron in high carbon ferrochromium issued by The Japan Iron and Steel Federation.

Experimental

Reagents. All of the reagents used were of analytical grade. The water used to prepare the solutions was purified with a Milli-Q PLUS water system (Millipore).

Stock solutions of chromium(VI), cobalt(II), and iron(III) (0.1 mol dm^{-3}) were prepared and were standardized as described previously.[4—6] A phen solution (0.2 mol dm^{-3}) was prepared by dissolving 7.93 g of the reagent in 200 cm^3 of 0.5 mol dm^{-3} sulfuric acid.

Apparatus. All potentiometric titrations were performed using a Mitsubishi Chemical Model GT-07 automatic titrator equipped with a Mitsubishi Chemical Model GTPR10 combination platinum electrode (the reference electrode was a silver–silver chloride electrode) and a Model GT5TSN thermometer. A Horiba Model F-8 AT pH/mV meter was used for the pH measurements. A Tokyo Rikakikai T-80 thermostat was used to maintain a constant temperature. The titration vessel was a specially ordered five-necked flask (for micro-burette, electrode, thermometer and inlet and outlet of nitrogen gas) with a water jacket.

Procedure for Successive Titration of Chromium(VI) and Iron(III) with Cobalt(II). To a 50-cm^3 volumetric flask, 20 cm^3 of phen (0.2 mol dm^{-3}), 2.5 cm^3 chromium(VI) (1×10^{-2} mol dm^{-3}) and 5 cm^3 iron(III) (1×10^{-2} mol dm^{-3}) solutions were added. The pH of the solution was adjusted to about 1.0 by adding 5 mol dm^{-3} sulfuric acid and the solution was then diluted to the mark with water. A 20 cm^3 aliquot of the solution was taken into the titration vessel and nitrogen gas was bubbled through the solution for 30 min before the titration. The solution was then titrated with a standard cobalt(II) solution (1×10^{-2} mol dm^{-3}). Similarly the potential values were recorded automatically when the potential change was within ±2 mV min^{-1} for each addition. All titrations were performed at 50 °C under a nitrogen atmosphere.

Results and Discussion

Effect of Phen on the Redox Reaction of Chromium(VI) and Iron(III) with Cobalt(II). The equilibrium constant, $K_{\mathrm{Fe-Co}}$, of the redox reaction of iron(III) with cobalt(II),

$$\mathrm{Fe^{3+} + Co^{2+}} \overset{K_{\mathrm{Fe-Co}}}{\rightleftharpoons} \mathrm{Fe^{2+} + Co^{3+}} \quad (2)$$

can be written as

$$\log K_{\mathrm{Fe-Co}} = \log \frac{[\mathrm{Fe^{2+}}][\mathrm{Co^{3+}}]}{[\mathrm{Fe^{3+}}][\mathrm{Co^{2+}}]} = \frac{E^{\circ}_{\mathrm{Fe}} - E^{\circ}_{\mathrm{Co}}}{0.059} \quad (3)$$

E°_{Fe} and E°_{Co} as standard redox potentials of the Fe(III)/Fe(II) and Co(III)/Co(II) systems are 0.77 and 1.82 V vs. NHE, respectively. The $K_{\mathrm{Fe-Co}}$ is thus calculated to be $10^{-17.8}$; the direct titration of iron(III) with cobalt(II) is thus impossible.

If phen forms complexes with cobalt(III) and cobalt(II), the conditional redox potential of the Co(III)/Co(II) system, E'_{Co}, can be written as

$$E'_{\mathrm{Co}} = E^{\circ}_{\mathrm{Co}} + 0.059 \log \frac{\alpha_{\mathrm{Co^{II}(phen)}}}{\alpha_{\mathrm{Co^{III}(phen)}}} + 0.059 \log \frac{C_{\mathrm{Co^{III}}}}{C_{\mathrm{Co^{II}}}}, \quad (4)$$

where α denotes the side reaction coefficient taking into account the complex formation of cobalt(II) and cobalt(III) with phen, e.g., $\alpha_{\mathrm{Co^{II}(phen)}} = 1 + \Sigma\beta_{n(\mathrm{Co^{II}(phen)})}[\mathrm{phen}]^n$ with $\beta_{n(\mathrm{Co^{II}(phen)})} = [\mathrm{Co^{II}(phen)})_n]\ [\mathrm{Co^{II}}]^{-1}\ [\mathrm{phen}]^{-n}$ (n=1, 2, 3). $C_{\mathrm{Co^{II}}}$ and $C_{\mathrm{Co^{III}}}$ are the total concentrations of cobalt(II) and cobalt(III), respectively. Vydra and Pribil[2,3] have reported the standard redox potential of the system $\mathrm{Co(phen)_3}^{3+}$/$\mathrm{Co(phen)_3}^{2+}$ to be 0.37 V by the analysis of the potentiometric titration curve of cobalt(II) with iron(III) in the presence of phen at pH 2. The conditional redox potential of the Fe(III)/Fe(II) system increases in the presence of phen, because $\log\beta_3$ of the iron(II)–phen complex (21.3) is higher than that of the iron(III)–phen complex (14.1).[15] Therefore, the reduction of iron(III) to iron(II) by cobalt(II) should be favored in the presence of phen. On the other hand, the effect of phen on the redox reaction of cobalt(II) with chromium(VI) (Eq. 5) has been studied potentiometrically:[6]

$$\mathrm{Cr_2O_7^{2-} + 6Co^{2+} + 14H^+} \overset{K_{\mathrm{Cr-Co}}}{\rightleftharpoons} \mathrm{2Cr^{3+} + 6Co^{3+} + 7H_2O} \quad (5)$$

The conditional redox potential of the Co(III)/Co(II) system was sufficiently lower than that of the Cr(VI)/Cr(III) system in the presence of phen at pH range 1—2 : The potential change of the Cr(VI)/Cr(III) system was not observed under the same conditions. Thus, in the presence of phen, chromium(VI) and iron(III) should be easily reduced by cobalt(II). E°_{Cr} and E°_{Fe} as standard redox potentials of the Cr(VI)/Cr(III) and Fe(III)/Fe(II) systems are 1.33 and 0.77 V vs. NHE, respectively. The first potential break corresponds to the reduction of chromium(VI) to chromium(III)

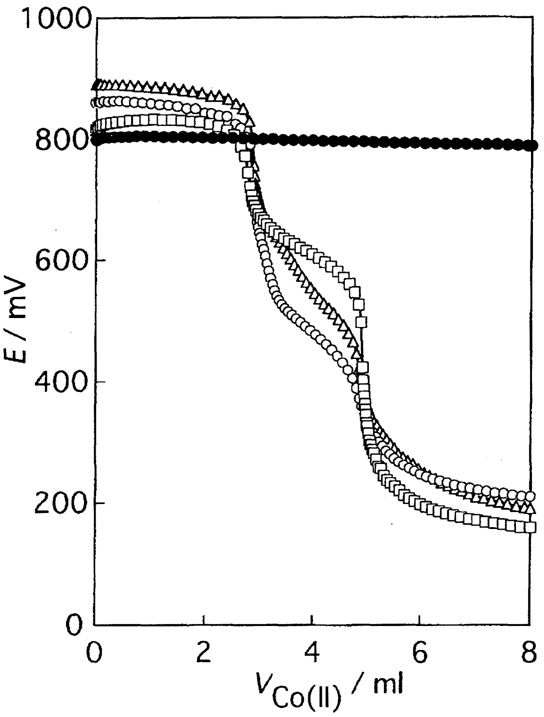

Fig. 1. Effect of phen concentration on the successive titration curves of chromium(VI) and iron(III) with cobalt(II) at pH 1. Concentration of phen (mol dm^{-3}) : (●), 0; (○), 2×10^{-2}; (△), 4×10^{-2}; (□), 8×10^{-2}.

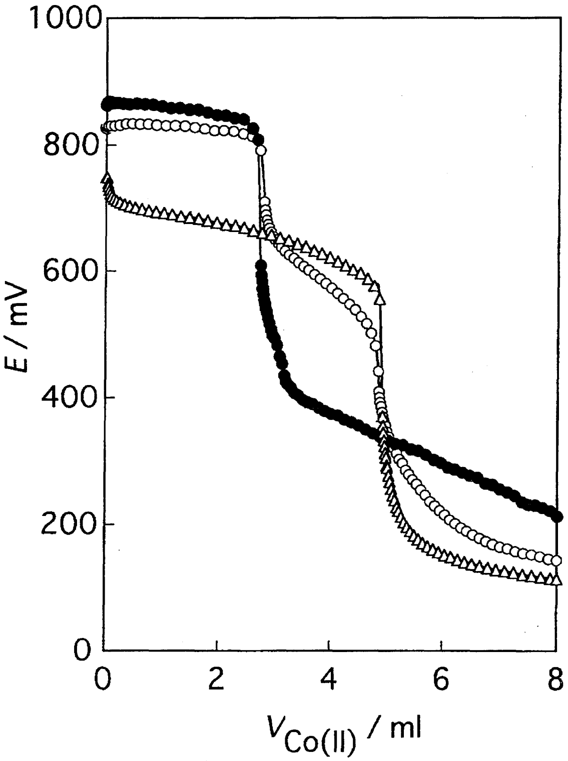

Fig. 2. Effect of pH on the successive titration curves of chromium(VI) and iron(III) with cobalt(II) in the presence of 8×10^{-2} mol dm^{-3} phen. pH : (●), 0.6; (○), 1.0; (△), 2.0.

Table 1. Successive Potentiometric Titration of Chromium(VI) and Iron(III) with Cobalt(II) in the Presence of 8×10^{-2} mol dm^{-3} phen

Added/10^{-3} mol dm^{-3}		Found/10^{-3} mol dm^{-3}		Recovery/%	
Cr(VI)	Fe(III)	Cr(VI)	Fe(III)	Cr(VI)	Fe(III)
0.300	1.000	0.301	1.000	100	100
0.500	1.000	0.500	1.003	100	100
0.700	1.000	0.696	0.993	99	99
0.500	0.500	0.499	0.494	100	99
0.500	2.000	0.511	2.036	102	102
1.000	0.500	1.012	0.496	101	99

Table 2. Effect of Diverse Ions and Compounds on Potentiometric Titration of 5×10^{-4} mol dm^{-3} Chromium(VI) and 1×10^{-3} mol dm^{-3} Iron(III) with Cobalt(II) in the Presence of phen

Ion or Salt	mol dm^{-3}	Found/10^{-3} mol dm^{-3}		Recovery/%	
		Cr(VI)	Fe(III)	Cr(VI)	Fe(III)
NaCl	5×10^{-2}	0.49	1.01	98	101
	5×10^{-3}	0.49	0.98	98	98
KNO_3	5×10^{-3}	0.53	0.98	102	98
Mg(II)	5×10^{-3}	0.49	0.99	98	99
Ca(II)	5×10^{-4}	0.49	0.99	98	99
Al(III)	5×10^{-4}	0.49	1.01	98	101
V(V)	5×10^{-4}	0.49	1.55	98	155
	5×10^{-5}	0.50	1.01	100	101
Mn(II)	5×10^{-4}	0.49	0.99	98	99
Ni(II)	5×10^{-4}	0.49	0.99	98	99
Cu(II)	5×10^{-4}	0.49	0.99	98	99
Zn(II)	5×10^{-4}	0.49	0.99	98	99
Pb(II)	5×10^{-4}	0.50	0.98	100	98

A ±3% error was considered to be tolerable.

Table 3. Determination of Chromium and Iron in High Carbon Ferrochromium a)

	Found/% b)	Content/%
Cr(VI)	56.12±0.081	56.15±0.134 c)
Fe(III)	30.85±0.095	30.68±0.226 d)

a) The digested solution was diluted 20 times with water before measurement. b) Each analytical value shows the mean of three analyses. c) Certified value. d) Phenanthroline method.

by cobalt(II) and the second one corresponds to the reduction of iron(III) to iron(II) by cobalt(II). The effect of phen on the reduction reactions of chromium(VI) and iron(III) in the same solution with cobalt(II) was examined by adding phen to the redox systems of Eqs. 2 and 5.

The effect of the phen concentration was examined over the range 0—8.0×10^{-3} mol dm^{-3} at pH 1. As is shown in Fig. 1, two potential breaks were observed at phen concentrations higher than 2.0×10^{-3} mol dm^{-3}, because the conditional redox potential of the Co(III)/Co(II) system decreased with increasing the phen concentration. As is expected, the first break corresponded to the reduction of chromium(VI) to chromium(III) and the second one corresponded to the reduction of iron(III) to iron(II). These results indicate that successive potentiometric titration of chromium(VI) and iron(III) with cobalt(II) can be possible in the presence of phen in a single titration. A 8×10^{-3} mol dm^{-3} phen concentration was selected for the procedure.

The effect of pH was examined over the range 0.6—2.0 in the presence of 8×10^{-3} mol dm^{-3} phen. The results are shown in Fig. 2. Only one potential break was observed at pH 0.6 and 2.0. The end-point of chromium(VI) disappeared at pH 2.0 because of a decrease in the conditional redox potential of the Cr(VI)/Cr(III) system. The end-point of iron(III) can not be detected at pH 0.6 because of a decrease in the conditional redox potential of the Fe(III)/Fe(II) system, i.e., complexation of iron(II) with phen should not be favored at this pH. For these reasons, the successive titration of chromium(VI) and iron(III) with cobalt(II) in the presence of phen should be performed at a pH of around 1.

Successive potentiometric titration of chromium(VI) and iron(III) in a synthetic mixture was carried out over the ranges 3×10^{-4}—1×10^{-3} mol dm^{-3} chromium(VI) and 5×10^{-4}—2×10^{-3} mol dm^{-3} iron(III), respectively, in the presence of 8×10^{-2} mol dm^{-3} phen at pH 1. Table 1 shows the analytical results of chromium(VI) and iron(III). As is seen in Table 1, the recovery of both ions was satisfactory.

Interferences. The effect of diverse ions on the titration of a mixture of 5×10^{-4} mol dm^{-3} chromium(VI) and 1×10^{-3} mol dm^{-3} iron(III) with cobalt(II) was examined in the presence of 8×10^{-2} mol dm^{-3} phen (Table 2). The following compounds and ions have no influence: NaCl (5×10^{-2} mol dm^{-3}); KNO_3 and Mg(II) (5×10^{-3} mol dm^{-3}); Ca(II), Mn(II), Ni(II), Cu(II), Zn(II), and Pb(II) (5×10^{-4} mol dm^{-3}). Vanadium(V) caused a positive interference in the successive titration of chromium(VI) and iron(III) because of the reduction of vanadium(V) to vanadium(IV) by cobalt(II) under the experimental conditions.6)

Application. The proposed method was applied to the determination of chromium and iron in high carbon ferrochromium issued by The Japan Iron and Steel Federation. Alkali fusion of this material was carried out according to JIS G 1313 (1989) procedure. The digested solution was diluted 20 times with water before measurement. The results obtained by the proposed method are given in Table 3. In order to verify the results, the conventional phenanthroline method for iron in the sample was also carried out. The analytical results are in good agreement with the certified values.

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