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

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A novel potentiometric titration of iron(II) and iron(III) is proposed. The method is based on the effect of 1,10-phenanthroline (phen) on the redox reactions of chromium(VI) and iron(III) with cobalt(II). In the presence of phen the conditional redox potential of the Co(III)/Co(II) system falls below those of the Cr(VI)/Cr(III) and Fe(III)/Fe(II) systems at pH around 1. Therefore, chromium(VI) and iron(III) can be titrated with cobalt(II) in the presence of phen, alternatively. Firstly, to a sample solution containing iron(II) and iron(III), a known amount of chromium(VI) is added in excess at pH around 1, so that iron(II) can be oxidized to iron(III) in the absence of phen. After the pretreatment, the sample solution containing the excess of chromium(VI) and iron(III) (total iron) is titrated with a standard cobalt(II) solution in the presence of phen. The concentrations of iron(II) and iron(III) can be calculated from the first and second potential breaks at the equivalence points for the titration. The relative standard deviations of this method were 0.66 and 0.81% for four determinations of 5×10^{-4} mol dm⁻³ iron(II) and 1×10^{-3} mol dm⁻³ iron(III), respectively. The proposed method was successfully applied to the determination of total iron in standard iron-ore samples (JSS No. 801-4, 814-1 and 850-4) and to the successive determination of iron(II) and iron(III) in a Mosan iron-ore sample (JSS No. 812-3).

Keywords Effect of ligand, potentiometric titration, iron(II), iron(III), chromium(VI), cobalt(II), 1,10-phenanthroline

The chemical speciation^{1,2} and simultaneous determination³ of metal ions have been increasingly needed in areas such as clinical chemistry, environmental pollution and industrial control. Iron is present as bivalent and trivalent states in the natural environment. The changes between these two forms of iron are important in various biological⁴ and geochemical⁵ processes. Thus, the development of a simultaneous method for iron(II), iron(III) and thus the total iron is still desired. The redox potential of a system involving metal ions is modified by complexation of metal ions with a suitable ligand.⁶ Vydra and Pribil^{7,8} reported on the effect of 1,10-phenanthroline (phen) on the redox reaction of cobalt(II) with iron(III) and developed a method for the potentiometric titration of cobalt(II) with iron(III) in the presence of this ligand. By using this phenomenon, we have recently proposed novel redox systems, which are applicable to potentiometric titrimetry for the determination of metal ions.⁹⁻¹³ 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).¹¹ Furthermore, we have reported on the successive potentiometric titration of chromium(VI) and iron(III) with cobalt(II) in the presence of phen.¹² We also developed a new flow-injection spectrophotometric method for the simultaneous determination of

vanadium(IV) and vanadium(V), based on the effect of phen and diphosphate on the redox potential of the Fe(III)/Fe(II) system.¹⁴ In this paper, the successive potentiometric titration of chromium(VI) and iron(III)¹² is further developed, that is, successive potentiometric titration of iron(II) and iron(III) with cobalt(II) is presented. The redox potential of the Cr(VI)/Cr(III) system is higher than that of the Fe(III)/Fe(II) system at low pH. Thus, iron(II) was oxidized to iron(III) by adding excess chromium(VI) as an oxidizing agent before the titration. Then, non-reacted chromium(VI) and total iron were titrated with cobalt(II) in the presence of phen. The present method can determine iron(II) and iron(III) in the range 3×10^{-4} – 1×10^{-3} mol dm⁻³; the relative standard deviations of this method were 0.66 and 0.81% for four determinations of 5×10^{-4} mol dm⁻³ iron(II) and 1×10^{-3} mol dm⁻³ iron(III), respectively. The method was successfully applied to the determination of total iron in standard iron-ore samples and to the successive determination of iron(II) and iron(III) in a Mosan iron-ore sample issued by The Japan Iron and Steel Federation.

Experimental

Reagents

An iron(II) standard solution (0.01 mol dm⁻³) was prepared daily by dissolving 0.098 g of iron(II) ammonium sulfate hexahydrate (Mohr's salt) in 50 cm³ of 0.01

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mol dm⁻³ sulfuric acid and stored in a nitrogen atmosphere; it was then standardized with standard potassium permanganate. A stock solution of iron(III) (0.01 mol dm⁻³) was prepared by dissolving 0.48 g of iron(III) ammonium sulfate dodecahydrate in 100 cm³ of 0.01 mol dm⁻³ sulfuric acid and standardized with EDTA. A solution of chromium(VI) (0.01 mol dm⁻³) was prepared by dissolving 0.15 g of potassium dichromate (primary standard) in 100 cm³ of 0.5 mol dm⁻³ sulfuric acid. A cobalt(II) solution (0.04 mol dm⁻³) was prepared by dissolving 4.75 g of cobalt(II) chloride hexahydrate in 500 cm³ of 0.05 mol dm⁻³ sulfuric acid and standardized with EDTA. Working solutions of metal ions were prepared by suitable dilution with 0.01 mol dm⁻³ sulfuric acid. A phen solution (0.2 mol dm⁻³) was prepared by dissolving an appropriate amount of the reagent in 0.5 mol dm⁻³ sulfuric acid. All reagents used were of analytical-reagent grade, and were used without further purification. All solutions were prepared with deionized water purified with a Milli-Q PLUS system.

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 (reference electrode is a silver-silver chloride) and a Model GT5TSN thermometer. A Horiba Model F-8 AT pH/mV meter was used for the pH measurements with a Horiba combination electrode (# 6028-10T). A Sibata control unit CU-85 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

To a 50-cm³ volumetric flask, 2.5 cm³ iron(II) (0.01 mol dm⁻³), 5 cm³ iron(III) (0.01 mol dm⁻³) and 2.5 cm³ chromium(VI) (0.01 mol dm⁻³) solutions were taken. The pH of the solution was adjusted to about 1 with 1 mol dm⁻³ sulfuric acid by checking the pH with a pH meter. Under this condition, the chromium(VI) added to the sample solution completely oxidized iron(II) to iron(III). Then, 10 cm³ of phen (0.2 mol dm⁻³) was added and the pH of the solution was readjusted to around 1. The solution was then diluted to the mark with water. A 20 cm³ aliquot of the solution was transferred to the titration vessel and nitrogen gas was bubbled through the solution for 30 min before titration. The solution was then titrated with a standard cobalt(II) solution (0.01 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. A non-reacted chromium(VI) concentration was determined from the first end-point and a total iron concentration was obtained from the second end-point. The iron(II) concentration was calculated by subtracting the non-reacted chromium(VI) concentra-

tion from the initial one.

Results and Discussion

Redox reactions of chromium(VI) and iron(III) with cobalt(II) in the presence of 1,10-phenanthroline

The conditional redox potential of the Fe(III)/Fe(II) system in the presence of phen, E'_{Fe} , can be written as

$$E'_{\text{Fe}} = E^{\circ}_{\text{Fe}} + 0.059 \log \frac{\alpha_{\text{Fe(II)(phen)}}}{\alpha_{\text{Fe(III)(phen)}}}, \quad (1)$$

where α refers to the side-reaction coefficient taking into account the complex formation of the relevant metals with phen: $\alpha_{\text{Fe(II)(phen)}} = 1 + \sum \beta_n(\text{Fe(II)(phen)})[\text{phen}]^n$ with $\beta_n(\text{Fe(II)(phen)}) = [\text{Fe(II)(phen)}_n][\text{Fe(II)}]^{-1}[\text{phen}]^{-n}$ ($n=1,2,3$) and $\alpha_{\text{Fe(III)(phen)}}$ are defined similarly. It is obvious from Eq.(1) that E'_{Fe} is higher than the standard redox potential of the Fe(III)/Fe(II) system, E°_{Fe} , in the presence of phen; that is, the oxidizing power of iron(III) increases because the formation constant, $\log \beta_3$, of the Fe(II)-phen complex ($\log \beta_3$, 21.3) is higher than that of the Fe(III)-phen ($\log \beta_3$, 14.1).¹⁵ Similarly, the conditional redox potential of the Co(III)/Co(II) system is lower than that of this system in the presence of phen. Vydra *et al.*^{7,8} reported the standard redox potential of the system $\text{Co(phen)}_3^{3+}/\text{Co(phen)}_3^{2+}$ to be 0.37 V by an analysis of the potentiometric titration curve of cobalt(II) with iron(III) in the presence of phen at pH 2. Thus, the reduction reaction of iron(III) with 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) has already been studied potentiometrically.¹¹ According to the results of the previous findings, 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 1–2. A potential change in 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). A titrimetric method for the successive determination of chromium(VI) and iron(III) with cobalt(II) was developed by using these two redox reactions.¹² The method can be adapted to the successive titration of iron(II) and iron(III) by oxidizing iron(II) to iron(III) by a known amount of chromium(VI) before titration with cobalt(II). The first end-point corresponded to the reduction of chromium(VI), which was in excess over iron(II), to chromium(III) and the second one corresponded to the reduction of iron(III) (total iron) to iron(II) by cobalt(II) in the presence of phen. Therefore, a non-reacted chromium(VI) concentration was determined from the first end-point, and the iron(II) concentration was calculated by subtracting the non-reacted chromium(VI) concentration from the initial one. The initial iron(III) concentration was calculated by subtracting the iron(II) concentration from the total iron concentration.

Fig. 1 Effect of the phen concentration on the successive titration curves of iron(II) and iron(III). Concentration of phen (mol dm^{-3}): (●), 0; (○), 2×10^{-2} ; (△), 5×10^{-2} ; (□), 8×10^{-2} . Other conditions as in the text.

Effect of variables on the successive titration of iron(II) and iron(III)

The optimum conditions for the titration of $5 \times 10^{-4} \text{ mol dm}^{-3}$ iron(II) and $1 \times 10^{-3} \text{ mol dm}^{-3}$ iron(III) with $1 \times 10^{-2} \text{ mol dm}^{-3}$ cobalt(II) were examined. All measurements were carried out at 50°C .

The effect of the phen concentration on the titration curves was examined over the range $0 - 8 \times 10^{-2} \text{ mol dm}^{-3}$ at pH around 1. The results are shown in Fig. 1. Though a potential break was not obtained in the absence of phen, two remarkable potential breaks at the equivalence points were observed at higher phen concentrations than $2 \times 10^{-2} \text{ mol dm}^{-3}$, because the conditional redox potential of the Co(III)/Co(II) system decreased with increasing the phen concentration. Therefore, successive titrations of iron(II) and iron(III) could be performed in the presence of a phen concentration beyond $2 \times 10^{-2} \text{ mol dm}^{-3}$.

The effect of the pH on the titration curves was examined over the range 0.6 – 2.0 in the presence of $2 \times 10^{-2} \text{ mol dm}^{-3}$ phen. A suspension of the precipitates was observed in the solution at pH 2.0. As shown in Fig. 2, the second end-point was not clearly detected at pH 0.6 because of a decrease in the conditional redox potential of Fe(III)/Fe(II) system; that is, complexation of iron(II) with phen should not be favored at this pH. Therefore, the successive titration of iron(II) and iron(III) with cobalt(II) in the presence of phen should be carried out at a pH around 1.

The effect of the chromium(VI) concentration as an oxidizing agent was examined over the range $5 \times 10^{-4} - 1.5 \times 10^{-3} \text{ mol dm}^{-3}$ in the presence of $2 \times 10^{-2} \text{ mol dm}^{-3}$ phen at pH around 1. Both potential breaks at the

Fig. 2 Effect of the pH on the successive titration curves of iron(II) and iron(III). pH: (●), 0.6; (○), 0.9; (△), 1.5. Other conditions as in the text.

equivalence points were observed at each chromium(VI) concentration. However, the recoveries became poorer with increasing the chromium(VI) concentrations. Therefore, a $5 \times 10^{-4} \text{ mol dm}^{-3}$ chromium(VI) concentration was chosen for the procedure.

Determination of iron(II) and iron(III) in synthetic mixtures

The successive potentiometric titration of iron(II) and iron(III) in synthetic mixtures was carried out over the ranges of $3 \times 10^{-4} - 1 \times 10^{-3} \text{ mol dm}^{-3}$ iron(II) and iron(III) in the presence of $2 \times 10^{-2} \text{ mol dm}^{-3}$ phen at pH about 1. The analytical results of iron(II) and iron(III) are given in Table 1. As can be seen in Table 1, the recoveries of both ions were satisfactory. The relative standard deviations of this method were 0.66 and 0.81% for four determinations of $5 \times 10^{-4} \text{ mol dm}^{-3}$ iron(II) and $1 \times 10^{-3} \text{ mol dm}^{-3}$ iron(III), respectively.

Interferences

The effect of foreign ions on the titration of a mixture of $5 \times 10^{-4} \text{ mol dm}^{-3}$ iron(II) and $1 \times 10^{-3} \text{ mol dm}^{-3}$ iron(III) was examined in the presence of $2 \times 10^{-2} \text{ mol dm}^{-3}$ phen. The results are summarized in Table 2; a $\pm 3\%$ error was considered to be tolerable. The following compounds and ions had no influence: NaCl , KNO_3 and Mg(II) ($5 \times 10^{-3} \text{ mol dm}^{-3}$); Ca(II) , Al(III) , Mn(II) , Ni(II) , Cu(II) , Zn(II) and Pb(II) ($5 \times 10^{-4} \text{ mol dm}^{-3}$). Vanadium(V) caused a serious positive interference in the titration, because of the reduction of vanadium(V) to vanadium(IV) by cobalt(II) under the experimental conditions.¹¹ The tolerance limit of vanadium(V) was $1 \times 10^{-5} \text{ mol dm}^{-3}$ vanadium(V). Separations of iron(II) and iron(III) from this interfering ion by solvent extrac-

Table 1 Successive potentiometric titration of iron(II) and iron(III) in synthetic mixtures

Taken/ 10^{-3} mol dm^{-3}		Found/ 10^{-3} mol dm^{-3}		Recovery, %	
Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
0.30	0.50	0.31	0.50	103	100
0.30	1.00	0.31	0.99	103	99
1.00	0.30	1.01	0.29	101	97
0.50	0.50	0.49	0.50	98	100
0.50	0.75	0.49	0.75	98	100
0.50	1.00	0.50	1.00	100	100

Table 2 Effect of diverse ions and compounds on the potentiometric titration of 5×10^{-4} mol dm^{-3} iron(II) and 1×10^{-3} mol dm^{-3} iron(III) with cobalt(II) in the presence of 2.0×10^{-2} mol dm^{-3} phen

Ion or salt	Added/mol dm^{-3}	Found/ 10^{-3} mol dm^{-3}		Recovery, %	
		Fe(II)	Fe(III)	Fe(II)	Fe(III)
NaCl	5.0×10^{-3}	0.51	1.01	102	101
KNO ₃	5.0×10^{-3}	0.50	1.02	100	102
Mg(II)	5.0×10^{-3}	0.50	0.99	100	100
Ca(II)	5.0×10^{-4}	0.49	1.00	98	100
Al(III)	5.0×10^{-4}	0.50	0.99	99	99
V(V)	5.0×10^{-5}	0.48	1.11	96	111
	1.0×10^{-5}	0.49	1.03	97	103
Mn(II)	5.0×10^{-4}	0.49	0.98	98	98
Ni(II)	5.0×10^{-4}	0.49	1.02	98	102
Cu(II)	5.0×10^{-4}	0.50	1.01	99	101
Zn(II)	5.0×10^{-4}	0.50	0.97	99	97
Pb(II)	5.0×10^{-4}	0.49	1.01	98	101

A $\pm 3\%$ error was considered to be tolerable.

tion and/or an ion-exchange procedure are necessary to avoid interference when large amounts of this ion co-exist in the sample.

Application to iron ore samples

The proposed method was applied to the determination of the total iron in standard iron-ore samples (JSS No. 801-4, 814-1 and 850-4) and to the successive determination of iron(II) and iron(III) in a Mosan iron-ore sample (JSS No. 812-3) issued by the Japan Iron and Steel Federation. Decomposition of the former and the latter samples was carried out according to the JIS M 8212 (1994) and JIS M 8213 (1995) procedures, respectively. The results obtained by the proposed method are given in Tables 3 and 4. The digested sample solutions were diluted 25 times with 0.01 mol dm^{-3} sulfuric acid before measurements. The analytical results were in good agreement with the certified values.

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Table 3 Determination of total iron in standard iron-ore samples^a

Sample	Fe in sample, % (m/m)	
	Proposed method ^b	Certified value
Indian hematite (JSS No. 801-4)	65.56 ± 0.86	66.18 ± 0.044
Peru magnetite (JSS No. 814-1)	66.62 ± 1.14	65.70 ± 0.087
Marcona pellet (JSS No. 850-4)	65.80 ± 1.43	65.67 ± 0.073

a. Issued by the Japan Iron and Steel Federation.

b. Average value for four determinations.

Table 4 Determination of iron(II) and iron(III) in a Mosan iron-ore sample^a

	Proposed method, % (m/m) ^b	Certified values, % (m/m)
Fe(II)	21.08 ± 0.54	18.83 ± 0.11
Fe(III)	39.62 ± 0.57	41.12 ± 0.074

a. Issued by the Japan Iron and Steel Federation (JSS No. 812-3).

b. Average value for four determinations.

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