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Effect of 2,2′-Bipyridine and 1,10-Phenanthroline on the Redox Reaction of Metal Ions and Its Application to Potentiometric Titrations of Vanadium(IV) and Cobalt(II)

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The effect of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) on the redox reactions of vanadium(IV) with iron(III), cobalt(II) with vanadium(V), and cobalt(II) with chromium(VI) was studied potentiometrically. In the presence of bpy or phen, the formal potential of the Fe(III)/Fe(II) system is higher than that of the V(V)/V(IV) system in the pH range 3—6. A large potential break was thus observed at the equivalence point when the titration of 1×10^{-3} mol dm^{-3} vanadium(IV) with iron(III) was carried out in the presence of 2×10^{-2} mol dm^{-3} bpy or phen at pH 5, while the potentiometric determination of vanadium(IV) with iron(III) was impossible in the absence of these ligands. On the other hand, the oxidation reactions of cobalt(II) to cobalt(III) by vanadium(V) or chromium(VI) took place easily in the presence of bpy or phen at a pH around 1. Using these reactions, we propose a titrimetric procedure for the determination of 1×10^{-3} mol dm^{-3} cobalt(II). A visual end point detection with Variamine Blue B (*N*-(4-methoxyphenyl)-1,4-phenylenediamine) as a redox indicator was presented for the titration of 1×10^{-3} mol dm^{-3} cobalt(II) with chromium(VI) in the presence of 2.5×10^{-2} mol dm^{-3} phen.

The redox potential of a system involving metal ions is modified by complexation of metal ions with a suitable ligand.[1)] Although this phenomenon has a potential capacity for the development of new redox systems which are applicable to potentiometric titration, there are comparatively few such studies;[2—9)] the effect of the ligand was not evaluated by quantitative considerations in full detail in these studies. Recently, we showed that a redox reaction of metal ions,

$$\mathrm{M_{Ox}+N_{Red}} \overset{K_{\mathrm{M-N}}}{\rightleftarrows} \mathrm{M_{Red}+N_{Ox}}, \tag{1}$$

should be favored in the presence of a proper ligand which forms more stable complexes with $\mathrm{M_{Red}}$ than $\mathrm{M_{Ox}}$ and/or with $\mathrm{N_{Ox}}$ than $\mathrm{N_{Red}}$. Thus, the presence of such a ligand makes possible the direct titration of $\mathrm{N_{Red}}$ with $\mathrm{M_{Ox}}$, which is not feasible otherwise.[10,11)] On the basis of the ligand effect, new methods have been developed for the potentiometric titration of chromium(VI) and copper(II) with iron(II) in the presence of diphosphate and/or neocuproine.[10)] We have also studied potentiometrically the effects of citrate, diphosphate, and ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (EDTA) on the redox reaction of vanadium(V) with iron(II) and developed a method for the potentiometric titration of vanadium(V) with iron(II) in the presence of such complexing agents.[11)] The use of a ligand buffer[12)] with zinc(II) in excess over EDTA was found to be effective for improving the end-point detection in this titration.

Development of new types of spectrophotometric determinations of metal ions[13—18)] and complexing agents[19,20)] as well as potentiometric determinations is also possible by using novel redox systems based on the ligand effect. Flow injection analysis (FIA) is a suitable technique for this purpose because of its simplicity, high accuracy, and versatility.[21)] The authors have developed a simultaneous FIA determination of vanadium(IV) and vanadium(V) based on the redox reactions of vanadium(IV) with iron(III) and vanadium(V) with iron(II) in the presence of 1,10-phenanthroline (phen) and diphosphate, respectively.[16,17)] A reverse FIA (r-FIA) method have been presented for the determination of complexing agents such as EDTA, nitrilotriacetic acid (NTA), citrate, and diphosphate based on the redox reaction of copper(II) with iron(II) in the presence of neocuproine.[20)] By using this r-FIA method, a new procedure for the estimation of complexing capacity with some metal ions has been developed.[20)] In this manner, it is worthwhile to develop the novel redox systems from the viewpoint of analytical chemistry.

The present paper describes the effect of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) on the redox reactions of vanadium(IV) with iron(III), cobalt(II) with vanadium(V), and cobalt(II) with chromium(VI). By using these redox reactions in the presence of bpy or phen, direct titrations of vanadium(IV) with iron(III) and cobalt(II) with vanadium(V) or chromium(VI) are presented.

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 iron(II), iron(III), vanadium(IV), and vanadium(V) (1×10^{-2} mol dm^{-3}) were prepared and were standardized as described previously.[10,11] A cobalt(II) solution (1×10^{-2} mol dm^{-3}) was prepared by dissolving 2.37 g of cobalt(II) chloride hexahydrate in 1 dm^3 of 5×10^{-2} mol dm^{-3} sulfuric acid and was standardized by EDTA. A stock solution of chromium(VI) was prepared by appropriate amounts of potassium dichromate (a primary standard) in 5×10^{-2} mol dm^{-3} sulfuric acid. Bpy and phen solutions (0.25 mol dm^{-3}) were prepared by dissolving the reagents in 0.1 mol dm^{-3} sulfuric acid, respectively.

Apparatus. All potentiometric titrations were performed using a Mitsubishi Chemical Model GT-05 automatic titrator installed 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 Taiyo Kagaku Kogyo C-630 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 the Titration of Vanadium(IV). To a 50-cm^3 volumetric flask, 25 cm^3 of acetate buffer (1 mol dm^{-3}, pH 5), 5 cm^3 of bpy or phen (0.2 mol dm^{-3}), and 5 cm^3 of vanadium(IV) (1×10^{-2} mol dm^{-3}) solutions were added 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. The solution was then titrated with a standard iron(III) solution (1×10^{-2} mol dm^{-3}). The redox reaction may be taken as completed when the potential changed within ±2 mV min^{-1} for each addition; the potential values were recorded automatically. All titrations were performed at 50 °C under a nitrogen atmosphere.

Procedure for the Titration of Cobalt(II). To a 50-cm^3 volumetric flask, 8 cm^3 of bpy or 5 cm^3 of phen (0.25 mol dm^{-3}), and 5 cm^3 of cobalt(II) (1×10^{-2} mol dm^{-3}) solutions were added. The pH of the solution was adjusted to about 1 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. The solution was then titrated with a standard vanadium(V) (1×10^{-2} mol dm^{-3}) or chromium(VI) solution ($1/3\times10^{-2}$ mol dm^{-3}) and the potential values were recorded automatically for each addition. Similarly the redox reaction may be taken as completed when the potential changed within ±2 mV min^{-1} for each addition. All titrations were performed at 25 °C under a nitrogen atmosphere.

Results and Discussion

Effect of bpy and phen on the Redox Reaction of Vanadium(IV) with Iron(III).

A redox reaction of vanadium(IV) with iron(III),

$$\mathrm{Fe^{3+}+VO^{2+}+H_2O \overset{K_{Fe-V}}{\rightleftharpoons} Fe^{2+}+VO_2{}^{+}+2H^{+}}, \tag{2}$$

should be favored by increasing the pH of the solution because the conditional standard potential of the V(V)/V(IV) couple, $E'_{\mathrm{V(H)}}$, decreases with increasing pH:

$$E'_{\mathrm{V(H)}} = E^{\circ}_{\mathrm{V}} - 0.12\ \mathrm{pH}, \tag{3}$$

where E°_{V} is the standard redox potential of the system. On the other hand, the conditional standard potential of the Fe(III)/Fe(II) couple, E'_{Fe}, in the presence of a ligand L (L=bpy, phen) can be written as

$$E'_{\mathrm{Fe}} = E^{\circ}_{\mathrm{Fe}} + 0.059\log\frac{\alpha_{\mathrm{Fe(II)(L)}}}{\alpha_{\mathrm{Fe(III)(L)}}} + 0.059\log\frac{C_{\mathrm{Fe(III)}}}{C_{\mathrm{Fe(II)}}}, \tag{4}$$

where α denotes the side reaction coefficient taking into account the complex formation of iron(II) and iron(III) with L.[17] $C_{\mathrm{Fe(III)}}$ and $C_{\mathrm{Fe(II)}}$ are the total concentrations of iron(III) and iron(II), respectively. The potential of the Fe(III)/Fe(II) couple increases in the presence of bpy or phen because $\log\beta_3$ values of the iron(II)–bpy and –phen complexes are higher than those of the iron(III)–bpy and –phen complexes,[22] i.e., the second term of Eq. 4 is positive. Thus, the conditional equilibrium constant, $K'_{\mathrm{Fe-V}}$, of the redox reaction (Eq. 2) becomes larger and the direct potentiometric titration of vanadium(IV) with iron(III) may be possible in the presence of bpy or phen.

In order to determine the suitable pH range for the titration of vanadium(IV) with iron(III) in the presence of bpy or phen, the formal potentials of equimolar mixtures of the Fe(III)/Fe(II) and the V(V)/V(IV) couples were measured at various pH values. The results are shown in Fig. 1. The potential of the Fe(III)/Fe(II) couple was sufficiently higher than that of the V(V)/V(IV) couple in the pH range 3—6 in the presence of bpy or phen: The potentiometric titration should be carried out in this pH range.

The effect of the bpy concentration was examined over the range 0—2×10^{-2} mol dm^{-3} at pH 5. In the absence of bpy a potential break at the equivalence point was not observed even at pH 5. At more than 1×10^{-2} mol dm^{-3} bpy concentration, sufficient potential break was observed. The potential change in the vicinity of the equivalence point was ca. 49 mV per 0.01 cm^3 of iron(III) solution in the presence of

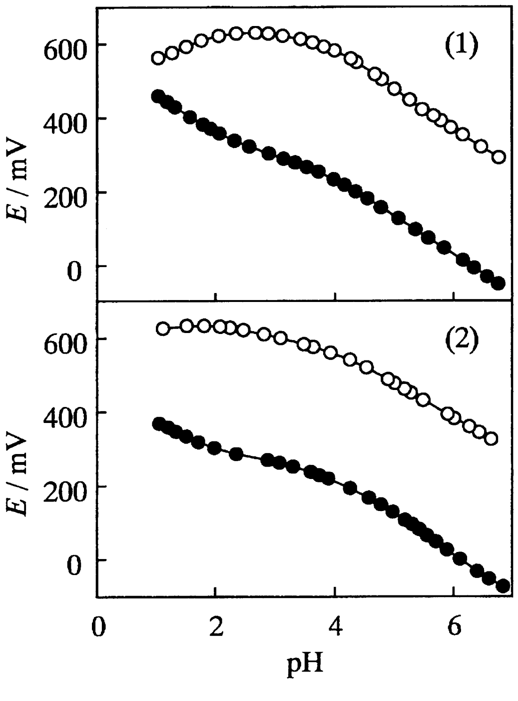

Fig. 1. Effect of pH on the formal potentials of the Fe(III)/Fe(II) (○) and V(V)/V(IV) (●) systems in the presence of 2×10^{-2} mol dm^{-3} (1) bpy and (2) phen. [Fe(III)]=[Fe(II)]= 5×10^{-4} mol dm^{-3}. [V(V)]=[V(IV)]=5×10^{-4} mol dm^{-3}.

2×10^{-2} mol dm^{-3} bpy. The effect of the phen concentration was also examined over the range 0—2×10^{-2} mol dm^{-3} at pH 5. The results are shown in Fig. 2. As expected, sufficient potential break was observed at more than 1×10^{-2} mol dm^{-3} phen concentration in a similar manner to the case of bpy.

The effect of diverse ions on the titration of 1×10^{-3} mol dm^{-3} of vanadium(IV) in the presence of 2×10^{-2} mol dm^{-3} phen was examined. The following compounds and ions have no influence: Sodium chloride, potassium sulfate, sodium nitrate, Na(I), K(I), and Mg(II) (0.15 mol dm^{-3}); Al(III), V(V), Cr(III), Mn(II), Ni(II), Cu(II), Zn(II), W(VI), and Pb(II) (1×10^{-3} mol dm^{-3}). Chromium(VI) caused a negative interference in the titration of vanadium(IV), probably because of the oxidation of a part of vanadium(IV) to vanadium(V) by chromium(VI). Cobalt(II) gave rise to a positive interference because of the reduction of iron(III) to iron(II) by cobalt(II) in the presence of phen.[3] However the presence of 1×10^{-5} mol dm^{-3} chromium(VI) and cobalt(II) did not interfere with the titration.

Effect of bpy and phen on the Redox Reaction of Cobalt(II) with Vanadium(V) and with Chromium(VI). The equilibrium constant, $K_{\mathrm{V-Co}}$, of the redox reaction of cobalt(II) with vanadium(V),

$$\mathrm{VO_2}^+ + \mathrm{Co}^{2+} + 2\mathrm{H}^+ \overset{K_{\mathrm{V-Co}}}{\rightleftharpoons} \mathrm{VO}^{2+} + \mathrm{Co}^{3+} + \mathrm{H_2O}, \qquad (5)$$

can be written as

$$\log K_{\mathrm{V-Co}} = \log \frac{[\mathrm{VO}^{2+}][\mathrm{Co}^{3+}]}{[\mathrm{VO_2}^+][\mathrm{Co}^{2+}][\mathrm{H}^+]^2} = \frac{E^\circ_{\mathrm{V}} - E^\circ_{\mathrm{Co}}}{0.059}, \qquad (6)$$

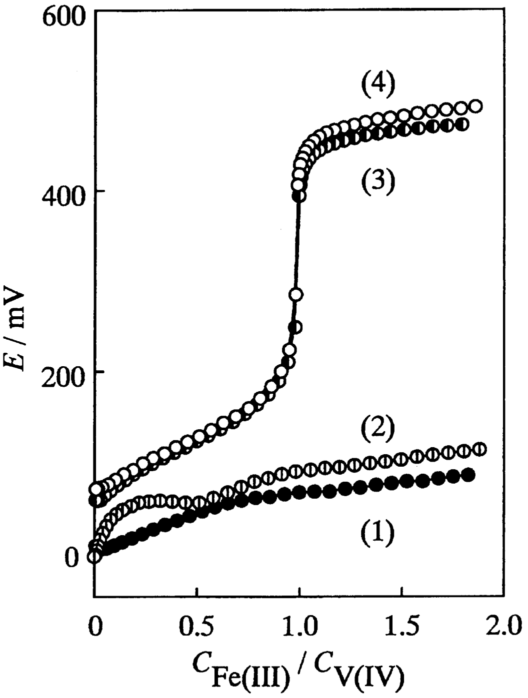

Fig. 2. Effect of phen concentration on the titration curves of vanadium(IV) with iron(III) at pH 5. Concentration of phen (mol dm^{-3}): (1), 0; (2), 2×10^{-3}; (3), 1×10^{-2}; (4), 2×10^{-2}.

where E°_{V} (1.00 vs. NHE) and E°_{Co} (1.81 vs. NHE) are the standard redox potentials of the V(V)/V(IV) and Co(III)/Co(II) systems, respectively. As the potential of V(V)/V(IV) system is dependent on the hydrogen ion concentration (Eq. 3), the conditional equilibrium constant, $K'_{\mathrm{V-Co}}$, is thus given by

$$\log K'_{\mathrm{V-Co}} = \frac{E'_{\mathrm{V(H)}} - E^\circ_{\mathrm{Co}}}{0.059}. \qquad (7)$$

Although the $K'_{\mathrm{V-Co}}$ value increases with decreasing pH according to Eq. 7, the $K'_{\mathrm{V-Co}}$ is calculated to be $10^{-13.7}$ even at pH=0; the direct titration of cobalt(II) with vanadium(V) is thus impossible.

If phen forms complexes with cobalt(III) and cobalt(II), the redox potential of the Co(III)/Co(II)system can be written as

$$E'_{\mathrm{Co}} = E^\circ_{\mathrm{Co}} + 0.059 \log \frac{\alpha_{\mathrm{Co(II)(phen)}}}{\alpha_{\mathrm{Co(III)(phen)}}} + 0.059 \log \frac{C_{\mathrm{Co(III)}}}{C_{\mathrm{Co(II)}}}, \qquad (8)$$

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 $\beta_{n(\mathrm{Co(II)(phen)})} = [\mathrm{Co(II)(phen)}_n][\mathrm{Co}]^{-1}[\mathrm{phen}]^{-n}$ (n=1, 2, 3). $C_{\mathrm{Co(III)}}$ and $C_{\mathrm{Co(II)}}$ are the total concentrations of cobalt(III) and cobalt(II), respectively. Vydra and Pribil[4] have found a value of 0.37 V for the system $\mathrm{Co(phen)_3}^{3+}/\mathrm{Co(phen)_3}^{2+}$ by the analysis of the potentiometric titration curve of cobalt(II) with iron(III) at pH 2. It is clear from the result that the $\alpha_{\mathrm{Co(III)(phen)}}$ value is larger than the $\alpha_{\mathrm{Co(II)(phen)}}$ value. Therefore, the oxidation reaction of cobalt(II) to cobalt(III) by vanadium(V) should be favored in the presence of phen. In the redox system of Eq. 5 bpy as well as phen were added to the system, and the effects of these ligands were studied potentiometrically.

The effect of bpy on the titration curves of cobalt(II) with vanadium(V) was examined at pH 1. A remarkable potential break at the equivalence point was observed in the presence of 4×10^{-2} mol dm^{-3} bpy, although the potential break was not obtained without bpy. Similarly a sufficient potential break appeared due to the presence of phen. The potential change in the vicinity of the equivalence point was ca. 48 mV per 0.01 cm^3 of vanadium(V) solution in the presence of 2.5×10^{-2} mol dm^{-3} phen at pH 1.

The effect of pH on the titration curves of cobalt(II) with vanadium(V) was examined over the range 0.7—1.5 in the presence of 2.5×10^{-2} mol dm^{-3} phen. The potential after the equivalence point decreased with increasing the pH of the solution because of a decrease in the conditional potential of the V(V)/V(IV) system. The potentiometric determination of cobalt(II) with vanadium(V) in the presence of phen should be performed in the pH range of 0.7—1.0.

The equilibrium constant, $K_{\mathrm{Cr-Co}}$, of redox reaction of cobalt(II) with chromium(VI),

$$\mathrm{Cr_2O_7^{2-}} + 6\mathrm{Co}^{2+} + 14\mathrm{H}^+ \overset{K_{\mathrm{Cr-Co}}}{\rightleftharpoons} 2\mathrm{Cr}^{3+} + 6\mathrm{Co}^{3+} + 7\mathrm{H_2O}, \qquad (9)$$

can be written as

$$\log K_{\mathrm{Cr-Co}} = \log \frac{[\mathrm{Cr}^{3+}]^2[\mathrm{Co}^{3+}]^6}{[\mathrm{Cr_2O_7}^{2-}][\mathrm{Co}^{2+}]^6[\mathrm{H}^+]^{14}} = \frac{E^\circ_{\mathrm{Cr}} - E^\circ_{\mathrm{Co}}}{0.059} \times 6, \tag{10}$$

where E°_{Cr} (1.33 vs. NHE) and E°_{Co} (1.81 vs. NHE) are the standard redox potentials of the Cr(VI)/Cr(III) and Co(III)/Co(II) systems, respectively. The conditional potential of the Cr(VI)/Cr(III) system, $E'_{\mathrm{Cr(H)}}$, increases with decreasing pH of the solution as represented by

$$\mathrm{Cr_2O_7}^{2-} + 14\mathrm{H}^+ + 6\mathrm{e} \rightleftharpoons 2\mathrm{Cr}^{3+} + 7\mathrm{H_2O}, \tag{11}$$

with

$$E'_{\mathrm{Cr(H)}} = E^\circ_{\mathrm{Cr}} - 0.14\ \mathrm{pH}. \tag{12}$$

Therefore, the conditional equilibrium constant, $K'_{\mathrm{Cr-Co}}$, increases with decreasing pH as

$$\log K'_{\mathrm{Cr-Co}} = \frac{E'_{\mathrm{Cr(H)}} - E^\circ_{\mathrm{Co}}}{0.059} \times 6. \tag{13}$$

According to the Eqs. 12 and 13, however, the $K'_{\mathrm{Cr-Co}}$ is calculated to be $10^{-48.8}$ at pH=0; the direct titration of cobalt(II) with chromium(VI) is impossible even if the titration is carried out in a strong acidic medium. Similarly to the titration of cobalt(II) with vanadium(V), bpy or phen was added to the redox system of Eq. 9, and the effects of these ligands were examined.

The effect of the bpy concentration was examined over the range 0—4.0×10^{-2} mol dm^{-3} at pH 1. As is shown in Fig. 3, the conditional potential of the Co(III)/Co(II) system decreased with increasing the bpy concentration. Remarkable potential breaks at the equivalence point were observed in the presence of bpy at concentrations higher than 2.5×10^{-2} mol dm^{-3}. The effect of the phen concentration was also examined over the range 0—2.5×10^{-2} mol dm^{-3} at pH 1. Sufficient potential breaks were observed in the presence of phen at concentrations higher than 1.0×10^{-2} mol dm^{-3}. The value of 0.37 V for the conditional potential of the Co(III)/Co(II) system in the presence of phen was found from the potential value at a half equivalence point, and the value was in fair agreement with that reported by Vydra and Pribil.[4]

The effect of the pH was examined over the range 1.0—3.0 in the presence of 2.5×10^{-2} mol dm^{-3} phen. The results are shown in Fig. 4. The potential after the equivalence point decreased with increasing the pH of the solution because of a decrease in the conditional potential of the Cr(VI)/Cr(III) system. Because the end point appeared beyond the equivalence point at pH 3, the titration of cobalt(II) with chromium(VI) in the presence of phen should be performed in the pH range 1.0—2.0.

In addition, a visual end point detection was examined for the titration of 1.0×10^{-3} mol dm^{-3} cobalt(II) with chromium(VI) in the presence of 2.5×10^{-2} mol dm^{-3} phen. The use of Methylene Blue, Variamine Blue B, diphenylamine, and 4-diphenylaminesulfonate as redox indicators having a color change potential of about 0.5—0.9 V was attempted in this titration. The results are summarized in Table 1. When Variamine Blue B was used as an indicator, the color change from yellow to violet was observed in the vicinity of the equivalence point.

The effect of diverse ions on the titration of 1.0×10^{-3}

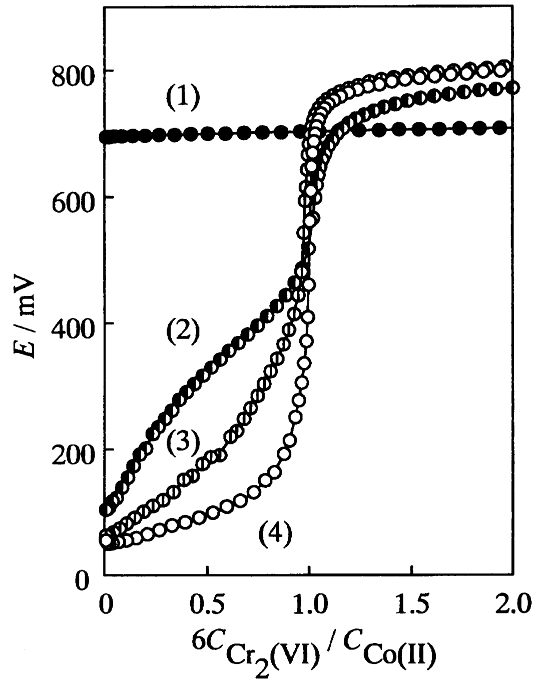

Fig. 3. Effect of bpy concentration on the titration curves of cobalt(II) with chromium(VI) at pH 1. Concentration of bpy (mol dm^{-3}): (1), 0; (2), 1×10^{-2}; (3), 2.5×10^{-2}; (4), 4×10^{-2}.

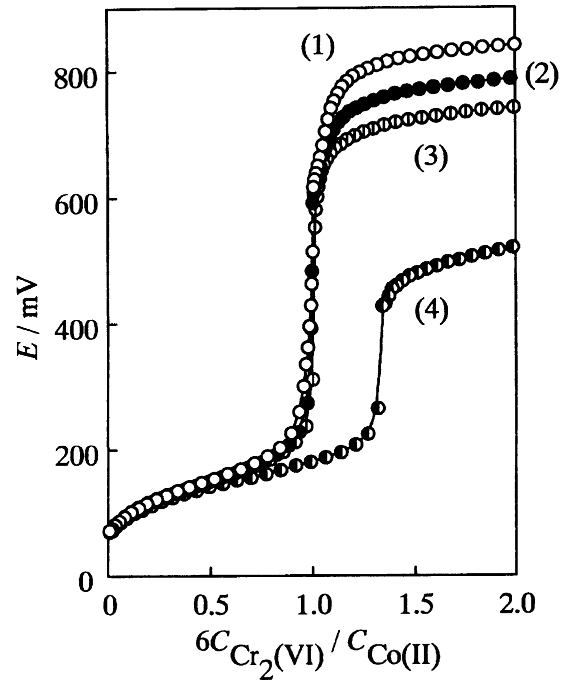

Fig. 4. Effect of pH on the titration curves of cobalt(II) with chromium(VI) in the presence of 2.5×10^{-2} mol dm^{-3} phen. pH: (1), 1.0; (2), 1.5; (3), 2.0; (4), 3.0.

Table 1. Visual End Point Detection Using a Redox Indicator on the Titration of Cobalt(II) with Chromium(VI) in the Presence of 2.5×10^{-2} mol dm^{-3} phen

Redox indicator	E°_{ind}/V (pH=0)	Volume added at end point[a)]/cm^3
Methylene Blue	0.53	<2.02
Variamine Blue B	0.71	ca. 2.02 (Yellow→Violet)
Diphenylamine	0.76	>2.02
4-Diphenylaminesulfonate	0.85	>2.02

a) The volume at the equivalence point is 2.02 cm^3.

Table 2. Effect of Diverse Ions on the Titration of 1.00×10^{-3} mol dm^{-3} Cobalt(II) with Chromium(VI) in the Presence of 2.5×10^{-2} mol dm^{-3} phen

Ion or salt	Concentration added mol dm^{-3}	Co(II) found mol dm^{-3}	Ion or salt	Concentration added mol dm^{-3}	Co(II) found mol dm^{-3}
NaCl	0.2	1.01	Mn(II)	1×10^{-3}	0.99
K_2SO_4	0.2	1.00	Fe(III)	1×10^{-4}	0.92
Mg(II)	0.2	1.00		1×10^{-5}	0.99
Ca(II)	0.2	1.00	Ni(II)	1×10^{-3}	0.99
Al(III)	2×10^{-4}	1.44	Cu(II)	1×10^{-3}	0.50
	1×10^{-5}	1.00		1×10^{-5}	0.99
V(IV)	1×10^{-3}	1.13	Zn(II)	1×10^{-3}	1.00
	1×10^{-4}	1.02	W(VI)	1×10^{-3}	0.99
Cr(III)	1×10^{-3}	1.31	Pb(II)	1×10^{-3}	0.98
	1×10^{-4}	1.00			

mol dm^{-3} cobalt(II) with chromium(VI) in the presence of 2.5×10^{-2} mol dm^{-3} phen was examined (Table 2). The following compounds and ions have no influence: sodium chloride, potassium sulfate, Na(I), K(I), Mg(II), and Ca(II) (0.2 mol dm^{-3}); Mn(II), Ni(II), Zn(II), W(VI), and Pb(II) (1×10^{-3} mol dm^{-3}). Vanadium(IV) caused a positive interference in the titration of cobalt(II) because of the oxidation of vanadium(IV) to vanadium(V) by chromium(VI) as titrant. Iron(III) gave rise to a negative interference because of the reason described above.

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