Amperometrically indicated "pseudotitrations". III. Volumetric determination of cobalt(III) with ethylenediamine

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Received 12 December 1973

The principle of "pseudotitration" with amperometric indication of equivalence point and its application to the volumetric determination of Co(III) with ethylenediamine is described. The method is convenient for analysis of 90—1800 μg of cobalt in 20 ml of the sample solutions. The confidence interval has been evaluated for varying amounts of the determined component.

The substitution of ligands in the coordination sphere of the analyzed ion according to equation

$$\mathrm{Me\ X}^{p} + \mathrm{Y}^{q} \rightleftarrows \mathrm{Me\ Y}^{(p+q-r)} + \mathrm{X}^{r} \qquad (1)$$

is a type of titrimetric reaction frequently used for the analytic determination of metal ions in solution. If this reaction is not fast enough, its applicability to a direct titration is conditioned by the presence of an effective catalyst. It is the redox catalysis which, is very effective in this case:

$$\mathrm{Me\ X}^{p} + n\mathrm{e} \rightleftarrows \mathrm{Me\ X}^{(p-n)}, \qquad (2)$$

$$\mathrm{Me\ X}^{(p-n)} + \mathrm{Y}^{q} \rightleftarrows \mathrm{Me\ Y}^{(p-n+q-r)} + \mathrm{X}^{r}, \qquad (3)$$

$$\mathrm{Me\ X}^{p} + \mathrm{Me\ Y}^{(p-n+q-r)} \rightleftarrows \mathrm{Me\ X}^{(p-n)} + \mathrm{Me\ Y}^{(p+q-r)}, \qquad (4)$$

where p, q, and r stand for the charge and n is the number of exchanged electrons.

The reduced form of the determined ion is a redox catalyst if its substitution reaction with titrant (*3*) is sufficiently fast. Reaction (*4*) is usually a fast redox reaction between the titrated substance and the product of the substitution reaction of catalyst (*3*). It yields the titration product and also liberates the catalyst for further action.

On the other hand, if reaction (*4*) is not rapid enough, the oxidation of $\mathrm{Me\ Y}^{(p-n+q-r)}$ (*i.e.* of the reduced forms of final product) takes place at the indication electrode causing an anodic current which is subtracted from cathodic current of titrated substance $\mathrm{Me\ X}^{p}$

$$\mathrm{Me\ Y}^{(p-n+q-r)} - n\mathrm{e} \rightleftarrows \mathrm{Me\ Y}^{(p+q-r)}. \qquad (5)$$

Such a mechanism was described for the first time for reactions of Cr(III) by *Tanaka et al.* [1]. It is difficult, however, to distinguish between both limiting cases (*4*) or (*5*) since most likely both competition reactions may proceed simultaneously. In either case practically no titration reaction takes place in the bulk phase of solution, but the indication electrode of the amperometric indication system records the state of stoichiometric reaction after each addition [2, 3].

A very advantageous method of the application of the redox catalyst is its preparation *in situ* by means of an electrode reaction. This method is especially advantageous if the

substance Me $X^{(p-n)}$ is unstable and cannot be kept in the solution titrated under normal conditions.

In this paper the principle of "pseudotitration" involving a substitution reaction with ethylenediamine is applied to the determination of Co(III). The application of this substitution reaction to a direct determination of Co(III) by normal titration is made impossible by its slowness which is typical of the substitution reactions of Co(III).

In titrimetric analysis ethylenediamine has been used only rarely because as a bidentate ligand it is able to form successively several complexes with different metal to ligand ratio. *Bjerrum* [4] applied ethylenediamine to the titration of Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}. Bjerrum also points out that in the case of Co(III) the values of the consecutive stability constants are favourable for exclusive formation of the tris-ethylenediamine complex already at very low concentrations of ethylenediamine (for Co(III) $\log k_1 = 18.7$, $\log k_2 = 16.2$, and $\log k_3 = 13.81$ [5]).

Experimental

Analytical reagent grade chemicals were used without further purification. The complex $[Co(NH_3)_6]Cl_3$ was prepared by the known preparation method [6]. The compound was identified by means of the electronic absorption spectrum obtained with aqueous solution [7]. In the same manner a 100% purity of the prepared species was confirmed in agreement with the results of elemental analysis (determination of N and H). In order to prevent the errors caused by the changes in the titre of the $[Co(NH_3)_6]Cl_3$ solution, the analysis was always carried out with freshly prepared solutions protected from light. The titre of the ethylenediamine solution was determined by the potentiometric neutralization titration to the second stage with a standard HCl solution using a glass indication electrode. The electric bulb industry nitrogen purified by bubbling through a solution of chromium(II) salt was used to keep anaerobic conditions.

A recording OH-102 (Radelkis, Budapest) polarograph in a three-electrode arrangement was used for polarographic measurements. The dropping mercury electrode had the following characteristics: drop time 4.2 s, mercury flow rate 1.53 mg s^{-1} (in a short-circuit with reference SCE and mercury column height of 64 cm). The amperometric titrations and the recording of polarographic curves were performed in a Kalousek vessel which contained about 10—20 ml of the investigated solution. The potentiometric measurements were carried out on an OP-205 (Radelkis) pH-meter. A Zeiss Specord UV-VIS was used for spectrophotometric measurements. All experiments were made at room temperature (25°C).

Results and discussion

The titrated component $[Co(NH_3)_6]^{3+}$ gives in the 1 M-KCl solution a polarographic wave corresponding to the irreversible one-electron reduction of the complex at $E_{1/2} = -0.20$ V *vs.* SCE [8]. The product of the reaction of Co(III) with ethylenediamine (en), *i.e.* $[Co(en)_3]^{3+}$ is polarographically reduced at -0.456 V *vs.* SCE in one-electron reversible wave [9]. The "pseudotitration" is accompanied by the decrease in the wave of $[Co(NH_3)_6]^{3+}$ and simultaneous increase of the more negative wave of $[Co(en)_3]^{3+}$ (Fig. 1). The choice of the working potential for a "pseudotitration" with amperometric indication depends on the position of the current plateau of the more positive wave. The optimum value of the working potential in 2 M-KCl (in which the majority of ex-

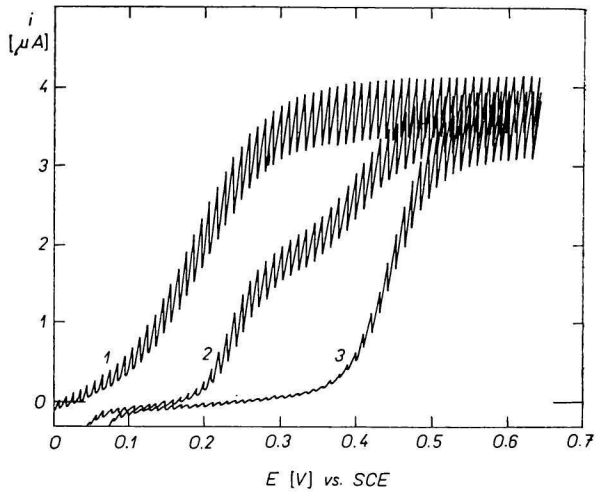

Fig. 1. Polarographic record of the course of the "pseudotitration" of $[Co(NH_3)_6]^{3+}$ with ethylenediamine.
1. 15 ml of 2 M-KCl, 2 ml of 1.00×10^{-2} M-$[Co(NH_3)_6]Cl_3$; *2.* the same as for curve *1* + 1 ml of 3.00×10^{-2} M ethylenediamine; *3.* the same as for curve *1* + 2 ml of 3.00×10^{-2} M ethylenediamine.

periments was performed) was −0.34 V *vs.* SCE. In this medium the best separation of polarographic waves was achieved. As the current plateau is relatively short, the correct choice of potential is of special importance with respect to the linearity of arms of L-shaped titration curve.

Table 1

Results of the amperometric "pseudotitration" of $[Co(NH_3)_6]^{3+}$ with ethylenediamine

Medium	Number of determinations	$[Co(NH_3)_6]^{3+}$ taken [μmol]	$[Co(NH_3)_6]^{3+}$ found (mean) [μmol]	Confidence interval [μmol]	Relative error of the mean [%]
2 M-KCl	5	3.00	3.05	±0.07	+1.67
	5	10.00	10.08	±0.18	+0.80
	5	14.04	14.16	±0.23	+0.86
	5	30.00	30.09	±0.27	+0.30
	5	60.00	59.95	±0.56	−0.08
0.5 M-KCl*	2	14.04	14.06		+0.1
1 M-KCl, 0.01 M-HCl	2	14.04	25.07		+78.5
1 M-KCl, 0.01 M-NH_4OH*	2	14.04	14.37		+2.35
1 M-KCl, 0.001 M-KOH	2	14.04	14.71		+4.76

* The separation of the waves of $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ is evidently worse than in 2 M-KCl.

The titration curves were evaluated by the method of the confidence interval according to *Dean* and *Dixon* [10].

Besides the results recorded in Table 1 many other "pseudotitrations" were carried out, but they did not give any quantitative results. The high positive errors in acidic solutions (see also Table 1) are caused by the competition of the hydrogen ions reacting with ethylenediamine (dissociation constants of the ethylenediammonium ion are $K_1 = 10^{6.98}$ and $K_2 = 10^{9.98}$ at 20°C [11]). This fact brings about a considerable decrease in the apparent stability constant of the complex $[Co(en)_3]^{3+}$. As the cobalt(III) salts hydrolyze relatively rapidly in strong alkaline solutions, the pH range recommended for the "pseudotitrations" of Co(III) with ethylenediamine is limited to neutral and weak alkaline solutions. None of the buffer solutions commonly used was suitable for this pH region because all of them impaired the separation of the waves of $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ if compared with the determination of the ion in a solution of neutral salt.

For small amounts of Co(III) it appeared to be important to remove thoroughly the oxygen dissolved, otherwise it would interfere with the measurements of the limiting current.

The thermodynamic conditions of the titration reaction

$$[Co(NH_3)_6]^{3+} + 3en \rightleftarrows [Co(en)_3]^{3+} + 6NH_3 \qquad (6)$$

are favourable, but this reaction is slow. In our investigation we revealed the slowness of reaction (*6*) spectrophotometrically. During one hour the visible spectrum of $[Co(NH_3)_6]^{3+}$ did not change appreciably in the presence of an overequivalent amount of ethylenediamine. It ensues from this fact that the electrochemically indicated state of completion of the stoichiometric reaction after addition of ethylenediamine to $[Co(NH_3)_6]^{3+}$ is the result of the reactions in the vicinity of indication electrode

$$[Co(NH_3)_6]^{3+} + e + aq \rightleftarrows Co(II)\ aq + 6NH_3, \qquad (7)$$

$$Co(II)\ aq + 3en \rightleftarrows [Co(en)_3]^{2+} + aq, \qquad (8)$$

$$[Co(en)_3]^{2+} + [Co(NH_3)_6]^{3+} + aq \overset{k_9}{\rightleftarrows} [Co(en)_3]^{3+} + Co(II)\ aq + 6NH_3, \qquad (9)$$

$$[Co(en)_3]^{2+} - e \rightleftarrows [Co(en)_3]^{3+}. \qquad (10)$$

In agreement with [12] we gathered from the spectrophotometric results that reaction (*9*) was too slow for the redox catalysis to manifest itself under the conditions used for polarographic measurements ($k_9 = 2.03 \times 10^{-2}$ l mol^{-1} s^{-1} at 25°C). Hence the cycle of the transformation of $[Co(NH_3)_6]^{3+}$ to $[Co(en)_3]^{3+}$ is closed by an reversible electrode reaction (*10*) at the indication electrode.

The described "pseudotitrimetric" method using ethylenediamine as a titrant is suitable for the determination of the Co(III) complexes which are reduced at the dropping mercury electrode at the potentials more positive than -0.2 V *vs.* SCE.

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Translated by R. Domanský