Polarographic Behavior of Vanadium and Iron in Thiocyanate

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Thiocyanate has been used extensively as a complexing agent for a number of cations. Meite's[1] observation that iron (III) is reduced in a medium composed of 0.7 M KCNS, 0.02 M sulfuric acid and 0.004% gelatin with a half-wave potential >0.0 volt is contradicted by the data of the "Polarographic spectra"[2] giving $E_{1/2}$ vs. S. C. E. as −0.2 volt. The condition for the latter observation has not been defined.

Direct estimation of VO^{2+} based on the catalytic action of the ion on potassium chlorate and potassium iodide reaction has been developed recently by Shiokawa[3]. Polarographic characteristics of vanadyl ion showed that it is reducible or oxidizable depending on the nature of the complex formed with the supporting electrolyte[4]. Syrokomskiĭ and Nazareva[5] devised a new type of coulometer to effect anodic oxidation of VO^{2+} to VO^{3+} which is titrable with Mohr's salt solution.

Preliminary investigations showed that thiocyanate in presence of mineral acids is capable of reducing vanadium(V) to lower valency states. Vanadium(V) and thiocyanate solution when mixed together developed the green coloration characteristics of trivalent vanadium ion, which on raising the acidity of the solution turned blue. The intermediate green state was initially mistaken to be vanadium green, corresponding to molybdenum blue, and was found to be very stable even on prolonged exposure to air. Spectrophotometric studies revealed that it is only the mixture of vanadium(V) and vanadium(IV). This conclusion was further confirmed when the green solution was shaken with isobutyl alcohol. The solution separated into two layers; the yellow aqueous layer and blue tetravalent vanadium in the organic layer.

The present communication reports in detail a study of polarographic behavior of vanadium (IV) thus obtained and iron(III) in potassium thiocyanate. Appropriate conditions for the simultaneous determination of the two elements in presence of each other have also been described.

Experimental

Leeds and Northrup Electrochemograph Type E was used for recording the polarograms in conjunction with an external saturated calomel reference electrode connected through an agar-potassium chloride bridge to the electrolysis cell. The temperature was maintained throughout at 25±0.1°C. A Beckman zeromatic pH meter was used for measuring the pH of the solutions. The dropping mercury electrode had $m^{2/3}t^{1/6}$ value of 2.414 $mg^{2/3}/sec^{1/2}$ with open circuit.

Vanadyl sulfate solution was prepared by dissolving the reagent grade vanadium pentoxide in dilute sulfuric acid and reducing it by sulfur dioxide. Excess of sulfur dioxide was boiled off and the solution standardized against potassium permanganate. Iron solution was obtained by dissolving a weighed quantity of "A. R. ferric ammonium sulfate" in distilled water. This was

1) L. Meites, "Polarographic Technique", Interscience Publishers, New York, N. Y. (1955), p. 269.
2) L. Meites, loc. cit Front and back lining papers.
3) T. Shiokawa, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **70**, 418 (1950).
4) I. M. Kolthoff and J. J. Lingane, "Polarography", Vol. II, Interscience Publishers, New York, N. Y. (1952), p. 449.
5) V. S. Syrokomskii and T. I. Nazareva, *Zhur. Anal. Khim.*, **6**, 15 (1951).

also standardized against potassium permanganate. All other chemicals used were of reagent grade.

Results and Discussion

Characteristics of Polarographic Waves.—A number of vanadium(IV) and iron(III) polarograms were recorded at different pH values. It was observed that vanadium(IV) gets reduced at and below pH≈3. The two reduction stages of vanadium(IV) are well developed when the pH of the solution was below 2.0 but above 1.5. Further increase in acidity shifted the half-wave potentials of the first wave towards positive potentials. The wave was completely obliterated below a pH of 0.5. In less acidic solutions (between pH 2.0~3.5), the first wave was drawn out and ill defined. Iron polarograms also were well defined below pH 3.0 but the $E_{1/2}$ ($E_{1/2}=-0.17$ volt vs. S. C. E. in 1.0 M potassium thiocyanate containing 0.005% gelatin at pH 1) was not much affected by the pH of the solution (cf. Table I).

TABLE I. EFFECT OF pH ON VANADIUM AND IRON POLAROGRAMS

Solution No.	pH of solun.	$E_{1/2}$ of vanadium polarograms, volt vs. S. C. E.		$E_{1/2}$ of iron polarograms, volt vs. S. C. E.
		1st wave	2nd wave	
1	0.5	−0.20	−0.57	−0.20
2	0.8	−0.21	−0.57	−0.18
3	1.1	−0.23	−0.56	−0.18
4	1.3	−0.25	−0.56	−0.18
5	1.5	−0.27	−0.57	−0.18
6	1.8	−0.30	−0.57	−0.17
7	2.0	−0.32	−0.57	
8	2.5	Not defined	−0.57	
9	3.0	Not reducible	−0.57	−0.17
10	3.6	Not reducible		

Thiocyanate concentration had considerable effect on the half-wave potential of vanadium. While the first wave was shifted towards negative potentials with increasing thiocyanate concentration, the $E_{1/2}$ of the second wave moved to more positive potentials. The polarograms of iron were also shifted towards negative potentials by the increased concentrations of the supporting electrolyte. The shift in both the cases i. e., the first wave of vanadium and the polarograms of iron, towards negative potentials with the increasing thiocyanate concentrations may possibly be attributed to the superimposition of the anodic wave of thiocyanate. During the course of experiments it was further observed that the half-wave potential of the iron wave was dependent not only on the thiocyanate concentrations but also on the iron and thiocyanate ratio. Conjugating it with the previous observation that the $E_{1/2}$ of iron polarograms remain unaffected by the pH of the solution, it may

TABLE II. EFFECT OF SUPPORTING ELECTROLYTE'S CONCENTRATION ON VANADIUM AND IRON POLAROGRAMS

Solution No.	Thiocyanate concentration M	$E_{1/2}$ of vanadium polarograms, volt vs. S. C. E.		$E_{1/2}$ of iron polarograms, volt vs. S. C. E.
		1st wave	2nd wave	
1	5.0	−0.30	−0.49	−0.31
2	3.75	−0.28	−0.51	−0.29
3	2.50	−0.24	−0.53	−0.26
4	1.25	−0.25	−0.56	−0.20
5	1.00	−0.25	−0.56	−0.17
6	0.50	—	−0.57	−0.15
7	0.25	Washed off	−0.58	−0.15

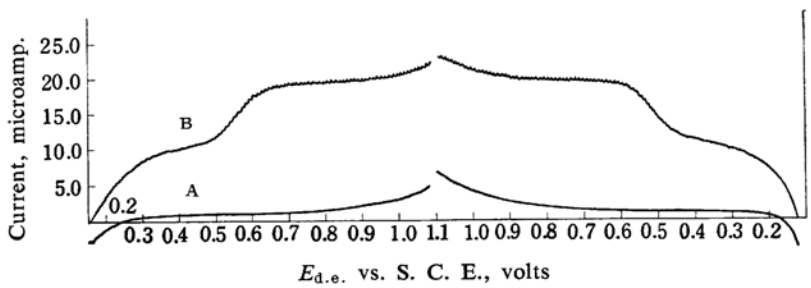

Fig. 1. Direct and reverse vanadium (2.19 mM) polarograms

Temperature 25±0.1°C
Drop time 3.33 sec.
Gelatin concn. 0.005%
Recorder damping 2.0
Recorder range 50 μA
pH of solution 1.6

Waves	Zero line	$E_{1/2}$ of 1st wave	$E_{1/2}$ of 2nd wave
A	0.0	Blank	—
B	2.5	−0.21	−0.537

be concluded that over the pH range studied a series of iron thiocyanate complexes are formed depending on the iron : thiocyanate ratio. Shifting of the second wave of vanadium towards more positive potentials with increasing thiocyanate concentrations suggest that the V(II)-NCS complex apparently has a lower dissociation constant than the V(III)-NCS complex (cf. Table II).

A study of the typical polarogram and its log plot shows that the vanadium waves are reversible (Fig. 1). The polarogram was obtained with a mixture of 2.19 mM vanadyl sulfate and 1.0 M potassium thiocyanate and 0.005% gelatin as maximum suppressor. In agreement with the general equation

$$E_{d.e.} = E_{1/2} - \frac{0.059}{n} \log \frac{i}{i_d - i}$$

the plot of $E_{d.e.}$ vs. $\log \frac{i}{i_d - i}$ is a straight line. The slope of 0.07 volt for the second wave suggests one electron transfer in reduction. As both the waves of vanadium have the same height, it was concluded that vanadium gets reduced first to vanadium(III) and finally to vanadium(II).

Iron polarograms exhibit only one reduction stage, and thus suggest the possibility of only one electron change. $E_{1/2}$ for iron reduction could not be assigned due to its dependence both on iron as well as on thiocyanate concentration but under the most restricted conditions of 2.00 mM iron and 1.0 M thiocyanate with 0.005% gelatin as maximum suppressor the $E_{1/2}$ observed was -0.17 volt vs. S. C. E.

The average $E_{1/2}$ for 2.19 mM vanadyl sulfate in 1.0 M potassium thiocyanate and 0.005% gelatin as maximum suppressor at pH 1.5 was found to be -0.21 volt, and to be -0.54 volt for the first and second wave respectively.

Under the conditions defined, a series of vanadium(IV) polarograms were run to plot the calibration curve. All the wave heights for the first wave were read from the plots at -0.45 volt and the corresponding values for the residual current were deducted to obtain the i_d for vanadium(IV) alone. The wave heights for the second stage reduction were calculated by extrapolating the plateau of the two waves.

The values of I obtained for different concentrations (cf. Table III) show that the reduction for both the waves are diffusion controlled. A linear concentration-current relationship is also followed by iron polarograms. The wave heights for iron polarograms were obtained by taking the difference of the actual and residual wave height at the same potential i. e., at -0.45 volt.

Table III. Diffusion current constant for vanadium polarograms

Solution No.	Concentration of vanadium mM	$I(I=i_d/cm^{2/3}\ t^{1/6})$ of vanadium waves	
		1st wave	2nd wave
1	0.438	1.43	1.65
2	0.876	1.42	1.65
3	1.09	1.42	1.65
4	1.31	1.42	1.65
5	1.75	1.42	1.66
6	2.19	1.42	1.65
7	2.62	1.42	1.65
8	3.5	1.42	1.66
9	3.94	1.42	1.65
10	4.38	1.42	1.65

The effect of different cations on vanadium polarograms was also studied. Cobalt and manganese do not interfere with the polarogram. Nickel and chromium(III) develop their own waves at more negative potentials but the diffusion current plateau for vanadium is not appreciably distorted. The presence of molybdenum(VI) and tungsten(VI) is detrimental as these ions deteriorate the vanadium waves, thus making the measurement of diffusion current practically impossible. Cupric ion has a typical effect of shifting the vanadium waves to more negative potentials. This results in the formation of only one wave which is probably the resultant of the waves comprising the wave heights due to Cu^{2+} and both the vanadium waves. The presence of nitrates, chlorides, bisulfates and ammonium ions has no effect on vanadium polarograms. None of these above mentioned ions except molybdenum and tungsten affect the iron polarograms. Molybdenum and tungsten completely distort the wave.

Recommended Procedure of Analysis.—The appropriate amount of unknown solution to give a final vanadium concentration above 0.4 mM and iron concentration above 0.5 mM is mixed with potassium thiocyanate. The overall potassium thiocyanate concentration is maintained at 1.0 M. The acidity of the solution is adjusted to pH 1.5 with hydrochloric acid and the mixture allowed to stand for 15 min. During this period vanadium(V) gets reduced to vanadium(IV). The appearance of violet color (being a mixture of blue due to vanadium(IV) and blood-red due to iron(III) thiocyanate) indicates the completion of the reduction. This solution when polarographed exhibits a two-step reduction, the first being the composite wave due to the reductions of iron(III) to iron(II) and vanadium(IV) to vanadium(III), and the second one being due to the degradation of vanadium(III) to vanadium(II). In order to derive the vanadium

content of the solution, the wave height of the second stage reduction is measured by extrapolating the plateaus and reading it from the calibration curve.

On subtracting the height of the first wave of vanadium as read from the calibration curve for the corresponding value of vanadium obtained previously, from that of the composite wave (the polarogram of the mixed iron and vanadium solution), the contribution due to iron alone is calculated. In the procedure adopted, wave heights of iron and vanadium polarograms are appreciable, only if the concentrations of corresponding elements are above the prescribed limit, i. e., 0.5 mM and 0.4 mM respectively.

Table IV. Simultaneous determination of iron and vanadium

Solution No.	Vanadium added mM	Vanadium recovered, mM	Iron added, mM	Iron recovered mM
1	0.438	0.438	0.4	0.42
2	0.87	0.87	0.8	0.81
3	1.31	1.33	1.2	1.21
4	1.75	1.79	1.6	1.62
5	2.19	2.21	2.0	2.0
6	2.62	2.66	2.4	2.4
7	3.16	3.16	2.8	2.82
8	3.50	3.50	3.2	3.18
9	3.94	4.10	3.6	3.6
10	4.38	4.42	4.01	4.01

Values obtained by the above procedure are reported in Table IV. It may be seen that the results are within the limits of experimental error. The method provides a convenient procedure for the simultaneous determination of iron and vanadium contents and may suitably be adopted to the analysis of vanadium steels provided copper(II), molybdenum(VI), and tangsten(VI) are sequestered.

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