The Titrimetric Determination of Potassium Hexacyanoferrate(III) with Vanadium(II) Sulphate

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Vanadium(II) generally undergoes one or two electron changes with oxidising agents.[1-3] In a recent communication[4] from these laboratories a three-electron change was noted in response to hypochlorite and hypobromite. Potassium hexacyanoferrate(III) also instantaneously oxidises vanadium(II) to vanadium (V) in an alkaline medium; this reaction has been found to be suitable for the titrimetric determination of hexacyanoferrate(III). In an acidic medium, however, vanadium(II) undergoes a two-electron change with potassium hexacyanoferrate(III); it has also been marked successfully by the potentiometric titration method.

Experimental and Results

Reagents. All the chemicals used were of BDH, AR, or E. Merck quality.

Vanadium(II) Sulphate Solution. An approximately 0.05 M solution was prepared and standardised as described in earlier communications.[3,4]

Potassium Hexacyanoferrate(III) Solution. An approximately 0.1 M solution was prepared and standardised iodometrically.

Indicator Solutions. *Diphenyl Dianisidine-o, o'-dicarboxylic Acid (Redoxal).* A 0.05% solution was prepared as described by Frumina and Mustafin.[5]

Barium Diphenylamine Sulphonate. A 0.2% solution (oxidized form) was used.

Methylene Blue. A 0.2% aqueous solution.

Apparatus. The apparatus used was the same as that described in an earlier communication.[3]

Procedure for the Determination of Hexacyanoferrate(III) with Vanadium(II). *(1) Visually ($V^{II} \rightarrow V^{V}$ Change).* Five to ten millilitres of a potassium hexacyanoferrate(III) solution was placed in a titration vessel, and then 15 to 30 ml of a 10 M sodium hydroxide solution and 2 to 3 drops of the indicator solution (diphenyl dianisidine-*o, o'*-dicarboxylic acid, barium diphenylamine sulphonate, or methylene blue) were added. Carbon dioxide was bubbled in for about 10 min, and the solution was titrated slowly with a vanadium(II) sulphate solution until a sharp colour change was obtained. An indicator correction of 0.1 ml was applied when methylene blue was used, whereas in other cases it was almost negligible. The indicators were found to be reversible. A few results are recorded in Table 1.

(2) Potentiometrically ($V^{II} \rightarrow V^{V}$ Change). The same procedure was followed with the difference that the titrations were carried out potentiometrically using platinum and calomel electrodes. The potentials were measured after the addition of vanadium (II) sulphate in small increments.

(3) Potentiometrically ($V^{II} \rightarrow V^{IV}$ Change). Five millilitres of a potassium hexacyanoferrate(III) solution was placed in the titration flask, 10 ml

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Table 1. Visual and Potentiometric titration of hexacyanoferrate(III) with vanadium(II)

Change undergone by vanadium	Hexacyanoferrate(III), mmol					
	Visuallya)			Potentiometrically		
	Found by the procedure described	Found iodometrically	% Error	Found by the procedure described	Found iodometrically	% Error
$V^{II} \rightarrow V^{V}$	0.3580	0.3590	−0.27	0.5165	0.5165	0.0
	0.7160	0.7180	−0.28	1.0360	1.0330	+0.29
	0.7750	0.7790	−0.51	—	—	—
	1.0390	1.0330	+0.58	—	—	—
	1.0326	1.0330	−0.04	—	—	—
$V^{II} \rightarrow V^{IV}$	—	—	—	0.5020	0.5025	−0.10
	—	—	—	0.5816	0.5799	+0.29

a) Indicators used include diphenyl dianisidine-*o*, *o*′-dicarboxylic acid (Redoxal), methylene blue or barium diphenyl amine sulphonate.

of concentrated hydrochloric acid was added, and then carbon dioxide was bubbled for about 10 min. The potentials were then measured as above. The reverse titration, *i. e.*, the addition of potassium hexacyanoferrate(III) to a vanadium(II) solution, was also found to be successful. However, a tungsten electrode was employed in this titration to avoid the catalytic oxidation of vanadium(II) by platimum. A few results are given in Table 1.

The two electron change could not, however, be marked successfully using visual indicators, such as methylene blue, Lauth's violet, safranine, ferroin, diphenylamine and *o*-dianisidine, which are generally used in titration with potassium hexacyanoferrate(III) in an acidic medium. A green colour develops during the course of the titration, but the solution finally changes to violet near the end. The violet colour also develops in the absence of the visual indicators. This probably masks the colour of the indicators, but the colour change is not very sharp and nearly corresponds to a two-electron change, *i. e.*, V^{II} to V^{IV}.

Diphenyldianisidine-*o*, *o*′-dicarboxylic acid and methylene blue, employed in an alkaline medium in the present communication to mark a three-electron change, *i. e.*, V^{II} to V^{V}, give equally sharp end points. Barium diphenylamine sulphonate is, however, less sensitive and the red colour which it develops with potassium hexacyanoferrate(III) has a tendency to fade out. In this case, the indicator has to be added near the end also.

This method can also be employed successfully in the presence of hexacyanoferrate(II) ions. Other ions, such as iron(III), cerium(IV), chromium(VI), vanadium(V) and manganese(VII), which are reduced by a vanadium(II) solution, interfere and must be absent. From the results in Table 1, it can be seen that, in the concentration range from 0.3590 to 1.0330 mmol of hexacyanoferrate(III), the accuracy of the methods described is ±0.6%.

As compared to other titrimetric procedures using chromium(II),6) titanium(III),7) or tin(II)7) salts described in the literature, the present method offers some distinct advantages. In the case of chromium(II) sulphate, an excess of the reductant has to be used, whereas with titanium(III) and tin(II) salts a high concentration of hydrochloric acid (70—130 m*l* of concentrated hydrochloric acid for every 130 m*l* of the solution) is rather necessary. Recently Basinska and Rychcik8) have described the use of 3,3′-dimethylnaphtidine and *o*-dianisidine as indicators at 6 M acidity in the titration against tin(II) chloride. Titrations of hexacyanoferrate(III) with any of the reductants in the alkaline medium have not yet been reported in the literature.

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