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NOTE

Alkali Solubilized Nickel(II)-Dimethylglyoxime as a New Redox Indicator

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Alkali solubilized nickel(II)-dimethylglyoxime has been proposed as a new redox indicator in ferricyanide oxidimetry. The determination of hydroxylamine and semicarbazide is carried out with a pooled standard deviation of 0.09 and 0.11 mg respectively.

Key Words: Nickel(II) sulphate, Dimethylglyoxime, Redox indicator, Ferricyanometry.

Potassium ferricyanide is an oxidant of choice for the determination of many organic and inorganic substances in alkaline solutions. But the ferricyanometric titrimetry seems to be limited probably due to lack of suitable indicators. Phenolphthalein was reported[2, 3] as a redox indicator in the determination of some hydrazine derivatives, that has the restrictions of indicator solution preparation as well as shelf life. The titration of iron(II) with ferricyanide at pH 4.2 or in 10 M phosphoric acid medium was reported using oxazine dyes[4] or ferroin[5] as an indicator respectively. However, the determination of the end-point needs a trained eye. The use of cacotheline as an indicator[6] in alkaline medium in the titration of ascorbic acid with ferricyanide requires the presence of inert atmosphere in addition to the tediousness associated with its preparation from brucine. Iron(III) complex of 4,7-dihydroxy-1,10-phenanthroline, of late, is slowly gaining attention in analytical titrimetry[7, 8] and spectrophotometry[9].

Attempts[10] were made for the use of iron(II)-dimethylglyoxime complex as an indicator in the titration of iron(II), sulphide and hydrosulphite with ferricyanide under pH conditions only. But it is not satisfactory in higher alkaline solutions. No attempts have been carried out so far making use of the red colour of nickel(IV)-dimethylglyoxime (nickelicoxime, shortened as 'nicoxime'), produced by the oxidation of the alkali solubilized nickel(II)-dimethylglyoxime (nickelousoxime, shortened as 'niousoxime,) by ferricyanide.

0.05 M solutions of potassium ferricyanide (BDH, AnalaR), hydroxylamine hydrochloride (E. Merck, India), semicarbazide hydrochloride (BDH, AnalaR) were prepared and standardized[11, 12]. 0.05 M-Nickel(II) sulphate (E. Merck, India), 1% dimethylglyoxime (E. Merck, India) in 8 M ammonia, 0.1% copper(II) sulphate (E. Merck, India) and 13 M ammonia (BDH, AnalaR) solutions were prepared.

The indicator solution can also be prepared by mixing 10 mL of 0.05 M nickel(II) with 10 mL of 1% DMG and 30 mL of 8 M ammoniacal solution.

Recommended Procedure

An aliquot of ferricyanide is taken in a titration vessel. To it, 0.5 mL of 0.05 M nickel(II), required volume of 13 M ammonia so as to maintain the total concentration of ammonia as 5 M in a total volume of 50 mL, 0.5 mL of 1% ammoniacal DMG and 2 drops of 0.0 1% copper(II) are added. The solution is titrated with hydroxylamine or semicarbazide solution. The end point is indicated by a change from red to colourless. The reverse visual titration with ferricyanide as titrant is also found to be feasible with the colour change from colourless to red near the end point.

Preliminary attempts in the potentiometric titration of hydroxylamine with ferricyanide indicated that the reaction is considerably slow near the equivalence point in 8 M ammoniacal medium. Based on the earlier reports[7, 13] copper(II) is anticipated to exert a catalytic function in the titration of hydroxylamine with ferricyanide. The potential break values in the presence of copper(II) (2 drops of 0.01%) and in the absence of copper(II) are found to be 305 mV and 205 mV per 0.1 mL of hydroxylamine respectively, which indicates the catalytic function of copper(II). The role played by copper(II) is believed to be restricted to enhance the attainment of equilibrium[14]. Similar trends in results are observed in the titration of semicarbazide with ferricyanide also.

The concentration ranges with respect to ammonia in the visual titrations of ferricyanide with hydroxylamine and semicarbazide are found to be 4.5 to 10 M and 4 to 10 M respectively. The visual titrimetric values are found to be in good agreement with potentiometric values which indicate negligible indicator correction. Solubilized niousoxime in ammoniacal solutions produces red coloured nicoxime on treatment with ferricyanide and nicoxime in turn oxidizes hydroxylamine or semicarbazide producing back niousoxime.

10–80 mg of hydroxylamine can be determined to an accuracy of ±0.55% with 0.09 mg as pooled standard deviation and for semicarbazide is ±0.77% with 0.11 mg as pooled standard deviation in the range of 15–140 mg. These results are given in Table-1 . The transition potential of the proposed indicator is found to be 60±5 mV. The formation of nicoxime was reported in the literature earlier[15].

The present proposed indicator, ammoniacal nickel(II)-dimethylglyoxime has definite marked advantages over other reported indicators because of simple preparation, easy availability of relatively cheaper chemicals in their pure form and pre-preparation of indicator solution is not necessary.

TABLE-1
DETERMINATION OF HYDROXYLAMINE AND SEMICARBAZIDE WITH FERRICYANIDE

Taken	Found* by author's method	Pooled standard deviation Sg, mg
Amount of Hydroxylamine, mg		
18.71	18.74	
23.39	23.26	
28.06	28.16	
37.42	37.46	0.09
46.77	46.71	
56.13	56.28	
Amount of Semicarbazide, mg		
21.54	21.52	
43.08	43.41	
64.62	64.26	
86.16	86.32	0.11
107.70	107.35	
129.24	129.52	

*Average of four determinations each.

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