Amperometric Determination of Metal Ions with 2-Mercaptopropanoic acid - Fe(III) and Fe(II) in a Mixture

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2-Mercaptopropanoic acid (RSH) has often been used as an analytical reagent for the amperometric determination of various transition metal ions because of its complexing properties [1-5]. The present Communication describes amperometric determination of Fe(III) individually and in presence of Fe(II) with this acid.

EXPERIMENTAL

Stock solution of 2-mercaptopropanoic acid was prepared afresh daily and standardised using standard chloramin T solution [6]. Hydrated samples of ferric and ferrous sulphates were employed as source compounds for the respective metal species. These salts were dissolved in 5% sulphuric acid to prepare stock solutions of metal ions and were standardised [7]. Only analytical grade chemicals and doubly distilled water were used.

All titrations were performed at DME *vs* SCE using a manual polarograph (Toshniwaal Model CLO2A). Purified nitrogen was used for deaeration. All titrations were carried out thrice.

DETERMINATION

Ferric Ions

Fe(III) gives a single reduction wave ($Fe^{3+} \rightarrow Fe^{2+}$) in 0.1 M NH_4Cl medium [8] the limiting region starting from 0.0 V. 2-Mercaptopropanoic acid is known to undergo a one-electron reversible oxidation in various supporting electrolytes [9]. In 0.1 M NH_4Cl medium, limiting region of the anodic wave of the acid is stretching from 0.00 to -0.10 V. Thus 0.0 V is on the cathodic limiting region of Fe(III) and the anodic region of the acid (RSH). Amperometric titration was carried out at this potential using RSH as the titrant. During this titration, cathodic current decreased, reached zero value. Addition of further quantities of RSH led to the appearance of anodic current. This increased linearly with further addition of RSH but slope of this line is slightly different from that of the other arm of the titration graph. Thus, the two arms of the titration curve intersected with each other on the residual current line. At this point, the molar concentration ratio of Fe^{3+} : RSH was found to be 1 : 0.68.

When RSH was titrated with Fe^{3+} solution, initial anodic current decreased, appoached zero and went on to cathodic current but the titrimetric molar ratio remained the same. This method enabled the estimation of ferric solutions in the

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concentration range of 5.00 through 0.1 mM (279.2 to 5.58 ppm).

When titration was carried out at a more negative potential (-0.60 V) where anodic current was totally absent, addition of RSH did not bring about any reduction in the cathodic current of the metal species - thus indicating that the titration was not a consequence of any chemical interaction. It is worth mentioning that the ratio of i_d/C of RSH and Fe^{3+} is 1: 0.68, thus confirming the above conclusion.

Ferric in Presence of Ferrous

In presence of ammonium sulphate, Fe(II) does not react with RSH. Fe(III) could be titrated with RSH even in presence of twenty times higher concentration Fe(II) if ammonium sulphate is present in the medium. However, higher concentration of Fe(II) introduced substantial deviation in the results. This method gives quite accurate results in the concentration range 5.00 to 0.25 mM in presence of 0.4 M ammonium sulphate.

Ferric and Ferrous in a Mixture

A satisfactory method for estimating both the iron contents in a mixture was developed. The Fe(III) content was determined by the above procedure. The Fe(II) in the mixture was oxidised with nitric acid, excess acid was removed and the total iron was estimated by the above procedure. Then by subtracting the Fe(III) value from the total iron, the concentration of Fe(II) is calculated. The results are given in Table 1.

Table 1

Amperometric Determination of Ferric and Ferrous in a Mixture

Mixture	Fe(III)	Total Fe	Fe(II)	Error%
5.0 +5.0	5.0	9.96	4.96	0.80
5.0 + 0.25	5.0	5.249	0.2490	0.800
1.0 + 5.0	1.0	5.97	4.97	0.60
1.0 + 0.25	1.00	1.248	0.248	0.800
0.5 + 5.0	0.5	5.46	4.96	0.80
0.50 + 0.25	0.50	0.746	0.246	1.60
0.25 +1.00	0.25	1.24	0.99	1.00
0.25 + 0.25	0.25	0.4959	0.245	2.0

Interference of Foreign Ions and Selectivity

Interference experiments were carried out for three concentrations (5.00, 1.00 and 0.50 mM). A large number of such ions were quite well tolerated. Mg(II), Al(III) Mn(II), Cr(III), Zn(II), Cd(II), nitrate, acetate and sulphate did not interfere even when present in twenty fold excess. The non-interfering ions did not interfere even when added to the cell solution simultaneously. Equal concentration of all these ions was maintained in the cell solution for these selectivity tests; the maximum concentration of metal taken was limited to 0.25 mM to avoid supersaturation. Oxalate did not interfere when present in concentration equal to ferric ion in cell solution. V(V),

Cr(VI), Mn(VII), Fe(II), Co(II), Ni(II), Cu(II), Mo(VI) and Hg(II) interfered at all concentrations in all the titrations.

REFERENCES

1. S.K.Srivastava, P.C.Srivastava and H.L.Nigam, *Indian J.Chem.* **10** (1972) 223

2. S.K.Srivastava, K.B.Pandey and H.L.Nigam, *Indian J.Chem.* **13** (1975) 498

3. J.Maslovska and J.Szmich, *Act.Univ.Lodz.Folia Chim.*, **3** (1984) 35

4. J.K.Nepal and S.N.Dubey, *J.Indian Chem.Soc.*, **65** (1988) 795

5. F.Baykut and A.Guron, *Istanbul Univ. Fen. Fag. Mecmuasi Seri C* **29 - 34** (1964) 153

6. R.C.Paul, S.K.Sharma, N.Kumar and Ram Parkash, *Talanta* **22** (1975) 311; O.P.Agrawal and S.P.Khatkar, *J.Electrochem. Soc. India*, **33-4** (1984) 275

7. A.I.Vogel, *A Textbook of Quatitative Inorganic Chemistry* III Ed. **ELBS Longmans, London** (1961) p 287

8. L.Meites, *Handbook of Analytical Chemistry* I Ed. **McGraw Hill, Newyork** (1963) p 5 - 59

9. R.S.Saxena, Pratap Singh and M.L.Mittal, *Indian J.Chem.* **7** (1969) 1149; Ram Parkash, R.S.Verma and Naresh Kumar, *Indian J.Chem.* **14-A** (1976) 997