Amperometric Determination of Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} with 2-Mercapto-propanoic Acid

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2-Mercaptopropanoic acid (RSH) has been used as a complexing agent [1-5] and sometimes as an analytical reagent [5] for the micro determination of metal ions in the past. The present work was undertaken with a view to probe this potentiality further. Amperometric determination of Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}, with the help of 2-mercaptopropanoic acid (RSH) is reported. It is noteworthy that its use in amperometric titrations is reported for the first time.

EXPERIMENTAL

Only analytical grade chemicals and doubly distilled water were used. $FeSO_4(NH_4)_2SO_4.6H_2O$, $CoSO_4.7H2O$, $NiSO_4.7H_2O$ and $CuSO_4.5H_2O$ served as source compounds. Co^{2+} and Ni^{2+} stock solutions were standardized gravimetrically as $Co[Hg(SCN)_4]$ [6] and nickel dimethyl glyoximate [7] respectively while standard Fe^{2+} and Cu^{2+} solutions were prepared by direct weighing of the source compounds. All titrations were performed at DME *vs* SCE using a Toshniwal manual polarograph model CLO2A. RSH solution was prepared afresh daily and standardised [8]. Purified nitrogen was employed for deaeration. Titration voltages in Fe^{2+} and Co^{2+} titrations were selected in the limiting region of the anodic wave of RSH and metal solutions were employed as titrant. In case of Ni^{2+}, both type of titrations - cathodic (using RSH as titrant at -1.20 V) and anodic (using nickel solution as titrant at -0.30 V) - were carried out successfully. In case of Cu^{2+}, either RSH or metal ion could be used as the titrant. Titration voltage was set in the cathodic region of Cu^{2+} at -0.60 V.

Amperometric determination of metal solution of any particular concentration was carried out atleast thrice.

RESULTS

RSH is known to undergo one electron oxidation at DME in various supporting electrolytes [9-10]. Anodic limiting region of acid and cathodic limiting region of metal ions in different media of interest for the estimations are mentioned in Table I. All the conditions necessary for the amperometric determination of various metal ions, as well as complete amperometric data have also been given in the Table I. L-shaped amperometric curves were obtained in case of anodic titrations (Titration voltage set on the anodic wave of RSH and metal ion used as titrant) and reverse L-shaped in case of cathodic titrations (Titration voltage on the cathodic diffusion current of the metal ion and RSH used as titrant). It may be noted that the maximum error mentioned in Table I was encountered in case of most dilute metal ion solutions only.

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Table 1

Titration Conditions and Amperometric Data

Limiting Potential Region of Metal	RSH	← Titration Voltage	Type →	Max.Error %	M:L
Estimation of Fe^{2+} in 0.1 M KCl					
-1.50 to -1.80	0.00 to-0.20	-0.10 V	anodic	2	1:2
Estimation of Co^{2+} in 0.1 M Na_2CO_3 + 0.1 M $NaHCO_3$					
-1.60 to -1.80	0.00 to-0.45	-0.30 V	anodic	1	1:1
Estimation of Ni^{2+} in 0.1 M NH_3 + 0.1 M NH_4Cl					
-1.00 to -1.80	0.2 to-0.45	-1.20 V	cathodic	2	1:1
		-0.30 V	anodic	4	1:2
Estimation of Cu^{2+} in 0.1 M K_2SO_4					
-0.20 to -1.60	0.0 to-0.20	-0.60 V	cathodic	2	1:1
		-0.60 V	anodic	4	1:1

Concentration range estimated in all cases 5.0 to 0.10 mM

Table 2

Interference and Selectivity

Foreign Ions	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
Cl^-, CH_3COO^-, NO_3^-, SO_4^{2-}, Al(III)	T	T	T	T
Oxalate	10 times	10 times	T	T
Thiosulphate	i	5 times	10 times	i
Tungstate	equal	T	T	T
Molybdate	i	T	T	T
V(V)	i	equal	5 times	1/5 times
Cr(III)	T	1/5 times	T	T
Mn(II)	1/15 times	i	i	i
Mn(VII), Fe(III)	i	i	i	i
Fe^{2+}	-	i	i	i
Ni^{2+}	10 times	i	-	i
Cu^{2+}	i	i	i	-
Zn^{2+}	T	1/10 times	5times	1/5 times
Cd^{2+}	10 times	1/10 times	1/5 times	1/15 times

i serious interference even when foreign ion is 1/20 of metal conc
T no interference with 20 times metal conc

It needs to be mentioned that cathodic titrations were more successful for determining the concentration of most dilute solutions in case of Ni^{2+} and Cu^{2+}. It will also not be out of place to point out that potentiometric studies indicated the same stoichiometry as obtained by us in case of Fe^{2+}, Co^{2+} and Cu^{2+} and have already been reported [1-4]. Similarly 1:1 inner complex and 1:2 anionic complex for Ni^{2+} have been synthesized and characterised by Srivastava et al [2].

Checking of Interference of Foreign Ions and Selectivity.

Study of interference of foreign ions in the new titrimetric methods was carried out for three concentrations of each metal solution: 5.0 mM, 1.0 mM and 0.5 mM. Table 2 includes safe limits of the concentration of each foreign ion that may be present in the cell solution. It is apparent that a large number of such ions are quite well tolerated. However, for these selectivity tests, the maximum concentration of each species was limited to 0.25 mM to avoid supersaturation.

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