Amperometric Determination of Metal Ions with Thioacids - Copper, Silver, Gold, Palladium and Platinum with Thioacetic acid

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Ethane thioic acid (thioacetic acid; ETA) has sometimes been used as a complexing agent for metals [1-3], but its use as analytical reagent remains largely unexplored. The present work has been undertaken to examine this aspect of the acid. New amperometric method is reported in this paper for estimating trace amount of Cu(II), Ag(I), Au(III), Pd(II) and Pt(IV).

EXPERIMENTAL

Thioacetic acid, a Fluka - chemie sample, was distilled once and used directly for preparing solutions. Its stock solution was prepared afresh daily. $CuSO_4.5H_2O$, $AgNO_3$, $AuCl_3$, $PdCl_2.2H_2O$, and $H_2PtCl_6.xH_2O$ were employed as source compounds for the respective metal species. Stock solutions of Au(III), Pd(II) and Pt(IV) were standardised amperometrically with thiomalic acid [4]. Copper and silver solutions were prepared by direct weighing of the source salts. 0.2 M sodium acetate buffer of pH = 5 or 0.1 M $NaClO_4$ solution were used as supporting electrolyte in the titration. Only analytical grade chemicals and doubly distilled water were used.

All titrations were performed at DME vs SCE using a manual polarograph (Toshniwal Model CLO2A). Agar agar salt bridge containing KCl (KNO_3 in case of silver titrations) was used with SCE. Purified nitrogen was used for deaeration. All titrations were carried out four times.

RESULTS AND DISCUSSION

Polarographic Characteristics of Thioacetic acid

Thioacetic acid (ETA) gives a reversible, one-electron, anodic wave. The height of the diffusion currents was found to be proportional to the concentration of the depolarizer. The limiting current region is spread over a potential range of 0.00 V through -0.15 V. ; $E_{1/2}$ = -0.24 V in acetate buffer (Medium 1) and $E_{1/2}$ = -0.23 V in 0.1 M $NaClO_4$ solution (Medium 2).

Polarographic Characteristics of Metal Species

Cu(II) gives irreversible, cathodic wave in acetate buffer - medium 1 (containing 0.005% gelatin) with long limiting current region (includes -0.6 V) [5]. Au(III) gives cathodic wave in this medium (similar to the one in 2.0 M acetate buffer [6]) with limiting region from 0.0 V onwards. Though a maximum is reported at higher concentrations, our study showed no maximum at 0.1 mM or lower concentration.

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Ag(I) did not give any wave in this medium.

Pd(II) gave a well-defined, diffusion controlled, cathodic wave in 0.1 M $NaClO_4$ medium with limiting region starting fron 0.0 V. A maximum was observed when Pd(II) concentration was 0.50 mM or higher. Pt(IV) also gave similar cathodic wave from 0.0 V onwards but this showed two maxima when Pt(IV) concentration was greater than 0.15 M. However, the maxima could be suppressed with 0.005% gelatin in both cases.

Amperometric Titrations

Details of the titrimetric parameters are given in Table 1.

The concentration range of the titration given is calculated from the millimolar concentration of the solution titrated. The maximum error was nearly 3% in the most dilute solutions. Higher the concentration, better the accuracy.

The molar ratios for the different titrations observed is governed by the complexation

Table 1

Amperometric Titration Parameters

Titrant ETA; (Cathodic titration) Medium 1 = 0.2 M Acetate buffer (pH = 5); Medium 2 = 0.1 M $NaClO_4$

Metal ion	Medium	Titre. poten. V on i_1 of	M:ETA	conc. ppm	St. dev.
Cu(II)	1	-0.6 on i_1 of metal	1:1	317 - 3.2	±0.33
Dirty white turbidity at [Cu] ≥31.8; No max. suppressor added because -0.6 V is well past maximum. Current is diffusion controlled.					
Ag(I)	1	-0.8 on i_1 of metal	2:1	539 - 5.4	±0.22
Ag(I)	1	-0.1 on i_1 of both	2:1	539 - 5.4	±0.28
Colour is light brown. Reverse titration (anodic) slightly less accurate but possible at both the voltages; end point at Ag(I) : ETA as 1:1. Colour is brown in this case too.					
Au(III	1	-0.6 on i_1 of metal	1:1	984 - 9.9	±0.39
No max. suppressor added because at -0.6 V no maximum exists.					
Pd(II)	2	-0.6 on i_1 of metal	1:1	532 - 5.4	±0.25
Pd(II)	2	-0.1 on i_1 of both	1:1	532 - 5.4	±0.25
Pd(II) at concn ≥53.2 ppm is determined in presence of gelatin.					
Pt(IV)	2	-0.1 on i_1 of Both	1:3.57	975 - 4.9	±0.22
All titrations are performed in presence of 0.005 % gelatin. Conc. lower than 19.5 ppm could be determined, though less accurate, by reverse titrations, other conditions remaining the same.					

reaction. Higher stoichiometric ratio observed in the reverse (anodic) titration of Ag is because Ag is added to excess of ETA which is now taken in the titration cell. Infact, complexes of ETA with Cu(II) and Pd(II) of different stoichiometry are already reported [1,2,7]. However, complexation reactions of ETA with Ag and Au are reported for the first time here.

In case of Pt(IV), titration is not because of complexation. It is noteworthy that an attempt to titrate Pt(IV) at -0.6 V with ETA (where anodic current of ETA is absent) does not show any change in the cathodic current of the metal wave. Titration at -0.1 V is possible because of mutual compensation of the anodic current of ETA and the cathodic current of the added metal species. The titrimetric ratio (Pt(IV) : ETA) observed is the same as the reverse ratio of their diffusion currents in equimolar solutions.

Estimation of Pd(II) in Presence of Pt(IV)

Pt(IV) did not interfere in the amperometric estimation of Pd(II) with

Table 2

Safe Limit of Concentration wrt Metal Species in Molar tolerated

Ion	Cu(II)	Ag(I) cath.	Ag(I) anodic	Au(III)	Pd(II)	Pt(IV)
Oxalate	x 10	x 5	x 5	x 15	t	t
thiosul	i	x 1/20	x 1/15	i	x 1/10	i
tungstat	t	t	t	x 1/5	equal	equal
molybdat	x 1/5	x 1/5	x1/5	equal	x 5	equal
Al (III)	t	t	t	t	t	x 10
V (V)	x 1/5	x 1/5	x 1/5	x 1/5	x 5	i
Cr(III)	t	t	t	t	t	equal
Mn(II)	x 1/2	x 5	equal	equal	-	x 1/15
Mn(VII)	i	i	i	i	i	x 1/15
Fe(II)	x 1/15	i	i	x 1/5	x 5	i
Fe(III)	i	i	i	i	x 10	i
Co(II)	t	x 1/5	x 1/10	x 1/5	t	i
Ni(II)	t	x 1/5	x 1/5	equal	t	i
Zn(II)	x 15	x 5	equal	x 15	t	x 1/10
Cd(II)	i	i	i	-	-	-
Rh(III)	i	i	i	equal	x 5	i
Ir(III)	x 1/10	x 1/10	x 1/10	x 1/15	equal	i
Cu(II)	-	i	i	i	equal	i
Au[III	x 1/10	i	i	-	x 5	i

i = interferes even when foreign ion present is 1/20 times the metal.
t = no interference even when foreign ion is 20 times the metal.

ETA in medium 1 because the titration is carried out here at -0.6 V where no anodic current of ETA exists. However, Pd(II) seriously interferes in case of Pt(IV) because at -0.1 V, ETA current decreases by both Pt and Pd (anodic current is compensated by cathodic current of Pt(IV) and thio acid is used up by reaction with Pd(II)). This is very much apparent from the amperometric titration curve of equimolar mixture of the two metal ion solution. The curve shows two breaks; the first is at the Pd(II) : ETA ratio of 1:1. The Pd(II) is preferentially complexed here with ETA. Infact, Pd(II) also could be estimated at this voltage (-0.1V) on the basis of this break in equimolar mixtures in the range 5.0 to 0.05 mM. At this null point, the remaining current is slightly more than the cathodic current of Pt(IV); in all probability, some free Pd(II) formed due to dissociation of the complex may be contributing to the total cathodic current at this stage. The second break in the curve is at an approximate (and variable) ratio of 1:2.5. The reason for this break is inexplicable. The current becomes zero at a ratio of 1:3.1.

Interference Studies

Nitrate, sulphate and magnesium do not interfere in any of these titrations. Chloride interferes with silver titration. Ruthenium, palladium(II), platinum(IV) and osmium(VIII) interfere with all titrations. Tolerance limit of some other foreign ions are examined and given in Table 2.

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