AMPEROMETRIC DETERMINATION OF U(VI) AND Cd(II) WITH THIOMALIC ACID

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Thiomalic acid (TSH) has shown the promise of becoming a common analytical reagent for the amperometric determination of metal ions because of its reducing and complexing properties as well as the polarographic activity[1]. The present work was undertaken with a view to further probe this potentiality of the acid.

EXPERIMENTAL

All titrations were performed at dme vs SCE using a manual polarograph (Toshniwal, India, model CL02A). Only analytical grade chemicals and doubly distilled water were used. Purified nitrogen was used for aeration. Uranyl nitrate ($UO_2(NO_3)_2 . 6H_2O$) and cadmium sulphate ($3CdSO_4 . 8H_2O$) were taken as source compounds and their stock solutions were prepared by direct weighing [2]. TSH solutions were prepared afresh daily. Amperometric determination of any solution of a particular strength was carried out thrice.

RESULTS AND DISSCUSSION

Determination of Uranyl Uranium

Amperometric determination of uranyl uranium was carried out in acetate buffer medium of pH 4.63 (total acetate concentration = 0.2 M). TSH was found to give its usual one-electron anodic wave in this medium with the limiting region stretching from +0.05V through -0.015V. [3]. Titration of thiomalic acid with the metal species solution was carried out at 0.00V and -0.10V. U(VI) also gave a reduction wave in this medium similar to the one reported[4] in the acetate buffer of pH 5. However, it started at much more negative potential and no uranium current was observed at the titration voltages mentioned. Gradual addition of U(IV) into TSH solution resulted in an amperometric curve of upside-down L-shape and the end point corresponded to the metal-ligand molar ratio of 1:2. It is noteworthy that Cefola et al [5] have also reported this very ratio on the basis of potentiometric study of the system. The method enabled the estimation of uranium in the concentration range of $5x10^{-3}$ M through $1x10^{-4}$ M. Maximum error (less than 2%) was encountered in the case of $1x10^{-4}$ solution only. More than 50% anodic current always remained unneutralized at the end point, indicating the formation of a weak complex. This observation was also in conformity with the stability constant value reported by Cefola et al (loc.cit:).

Reverse titration, using TSH as titrant at the voltages mentioned above or at any other voltage in the limiting region of the cathodic wave of U(VI) did not yield desired result and hence, this form of titration can not be recommended.

Determination of Cd(II)

Amperometric determination of Cd(II) was accomplished in 0.5M NH_4OH-0.5M NH_4Cl medium. Cd(II) gave a reduction wave in this medium similar to one reported in 1M NH_4OH-1M NH_4Cl medium [6]. Limiting region stretched from -0.90V through -1.80V. Titration with TSH (cathodic titration) was carried out at -1.00V and -1.20V. TSH also gave its wave in this medium, but its anodic current was nil at these potentials. The titration resulted in L-shaped curve and end point corresponded to the metal ligand molar ratio of 1:1. It is noteworthy that Patil and Krishnan[7] have also isolated a Cd(II)-TSH complex pertaining to this very stoichiometry. The method enabled the estimation of Cd(II) in the concentration range of $5x10^{-3}$ M through $3.5x10^{-5}$ M with acceptable accuracy. Even $2.5x10^{-5}$ M solution could be estimated with a maximum inaccuracy of 4% only. More dilute solutions, however, could not be estimated at all.

Cd(II) could also be estimated by using it as titrant for TSH solution (anodic titration). Limiting region of anodic wave of TSH stretched from -0.20V through -0.40V and in this medium titration was carried out at -0.30V. Cathodic current of Cd(II) was not present at this potential. The titration, this time resulted in upside-down L-shaped amperometric curve, the end point again corresponded to 1:1 molar ratio. The method enabled estimation of Cd(II) solutions in the concentration range of $5x10^{-3}$ M through $2.5x10^{-4}$ M; the titration of $1x10^{-4}$ M solution resulted in an error to the maximum extent of 4%

40-80% Current remained unneutralized at the null point in case of cathodic titrations and also quite substantial current in case of anodic titrations. This indicated the formation of a weak complex. However, cathodic form of the method seems to be far more efficient than the anodic one in view of the larger range of Cd(II)concentrations covered as well as the edge that it has over the anodic form in the matter of tolerance of foreign ions (Table 1).

Checking of interference of diverse ions and specificity

Interference of diverse ions in the new titrimetric methods were also studied. Such

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TABLE 1

SAFE LIMIT OF THE CONCENTRATION OF FOREIGN IONS IN THE CELL SOLUTION WITH RESPECT TO THE CONCENTRATION OF THE METAL SPECIES

Foreign ion	Detn. of U (VI)	Detn. of Cd(II) (cathodic titration)	Detn. of Cd(II) (Anodic titration)
Cl^-	b	-	-
NO_3^-	b	b	b
SO_4^{2-}	b	b	b
CH_3COO^-	-	b	b
OX^{2-}	b	b	b
$S_2O_3^{2-}$	1/20	b	b
W(VI)	b	b	b
Mg(II)	b	b	b
Al(III)	b	b	b
Zn(II)	b	b	2 times
Ni(II)	b	1/10	1/20
Co(II)	b	a	a
Mn(II)	b	b	5 times
Cd(II)	1/5	-	-
Fe(II)	1/10	a	a
Cr(III)	b	b	5 times
V(V)	a	equal	1/20
Mo(VI)	a	a	a
Mn(VII)	a	a	a
Cu(II)	a	a	a
Hg(II)	a	a	a
Y(III)	a	-	-
La(III)	1/5	-	-
Ce(IV)	a	-	-
Nd(III)	1/20	-	-
Sm(III)	1/10	-	-
Gd(III)	1/10	-	-
Dy(III)	1/5	-	-
Ho(III)	1/10	-	-
Th(IV)	a	-	-

a - Serious interference even when the conc. of foreign ion is 1/100 of the metal.

b - No interference even when the foreign ion is 20 times that of the metal.

studies were made for three concentrations of each metal species: 5×10^{-5} M, 1×10^{-5} M and 5×10^{-4} M. Table 1 includes safe limit of the concentration of each such ion in the cell solution. These species also did not interfere even when present together in the cell. However, for these specificity tests,the maximum concentration of each species taken was 2.5×10^{-4} M to avoid supersaturation.

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