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Amperometric Trace Determination of Cu(II), Ag(I), Au(III), Pd(II) and Pt(IV) with 2-Mercapto and 3-Mercaptopropanoic acids

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Amperometric determination of trace amounts of Cu(II), Ag(I), Au(III), Pd(II) and Pt(IV) is reported with the help of 2-mercaptopropanoic acid (RSH) and 3-mercaptopropanoic acid (MPSH) at d.m.e. Lowest determinable concentration ranges from 3 ppm to 20 ppm depending upon the metal ion. The fundamental reaction involved in all the cases is complexation. M:L ratio is 1 : 1 for Cu(II), Au(III), Pd(II) and Pt(IV) when any of the ligands is employed as titrant; this ratio for Cu(II), however, changes to 1 : 2 if the ligand is MPSH. If the metal ion is used as titrant, the M : L ratio is 1:2 in case of Cu(II), Au(III) and Pd(II) and 1:1 in case of Ag(I). Tolerance for diverse foreign ions has been worked out.

INTRODUCTION

2-Mercaptopropanoic acid (RSH)[1–5] and 3-mercaptopropanoic acid (MPSH)[6–9] have often been used as complexing agents and sometimes as analytical reagents[6,10] for determination of metal ions; in fact, these ligands have been exploited earlier also for the amperometric determination of a large number of metal ions in this laboratory[10–14]. The present work was undertaken with a view to extend the use of these ligands for the amperometric determination of Cu(II), Ag(I), Au(III), Pd(II) and Pt(IV) in traces at d.m.e. It is noteworthy that the complexation reaction between these ligands and Pt(IV) and MPSH and Au(III) is being reported for the first time; similarly, the stoichiometry of such reactions betwen RSH and Au(III) and MPSH and Pd(II) is being reported for the first time, though the complexation was observed by earlier workers[15,16] also.

EXPERIMENTAL

Only analytical grade chemicals and doubly distilled water were used. All the titrations were performed at d.m.e. (versus SCE) employing a manual polarograph (Toshniwal, India, Model CLO2A). $CuSO_4{\cdot}5H_2O$, $AgNO_3$, $AuCl_3$, $PdCl_2$ and H_2PtCl_6 were used as source compounds of Cu(II), Ag(I), Au(III), Pd(II) and Pt(IV) respectively. Au(III), Pd(II) and Pt(IV) were standardized amperometrically with thiomalic acid[17]. RSH and MPSH solutions were prepared afresh daily and standardized[18]. Amperometric determination of metal ion solution of any particular concentration was carried out at least thrice. Purified nitrogen was employed for deaeration. Titration voltages selected fell in the limiting region of the metal wave or the anodic wave of the ligand or both as specified in Table 1. KNO_3 salt bridge, instead of KCl salt bridge was, employed in case of Ag(I).

RESULTS AND DISCUSSION

Both RSH and MPSH are known to undergo reversible, one electron oxidation at d.m.e. in certain supporting electrolytes[10,19–21]. Similar anodic waves were obtained in our media too. All the conditions required for the amperometric determination of various metal ions as well as complete amperometric data have been included in Table 1. It may be mentioned that M:L stoichiometry of 1 : 1 obtained by the authors for the RSH complexes of Cu(II), when the ligand was used as titrant, and Ag(I) was the same as reported earlier by other workers employing techniques other than amperometry[1,21–23]; 1 : 2 stoichiometry observed for Cu(II) when the metal ion was used as titrant is understandable as the reaction was initiated in the excess of the ligand. The colour of Au(III) complex (in acetate buffer) was also the same as observed earlier by Schoeller and Allardt[16] though the stoichiometry is being reported here for the first time. 1 : 2 stoichiometry for the Pd(II) complex is also the same as that worked out by Srivastava *et al.*[1] on the basis of potentiometric study; additional 1 : 1 ratio obtained by the authors seems to be due to the fact that the relevant reaction was initiated in presence of limited amount of the ligand, which was used as titrant.

Fernando *et al.*[7] have reported formation of 1 : 2 yellow complex of Cu(II) with MPSH (same ratio and colour as observed by the authors of this communication) in the absence of oxygen, a condition very much present during amperometric titrations. Similarly, 1 : 1 stoichiometry for Ag(I) complex tallies with that reported by Fernando *et al.*[7] potentiometrically. The present authors also concluded from the nature of the amperometric curve that the Ag(I) complexes formed with RSH and MPSH were themselves reducible at d.m.e. Height of these complex waves was proportional to the concentration of Ag(I); the complex waves were also found to be diffusion controlled though the $E_{1/2}$ could not be determined as the mixture polarograms (containing metal and ligand in various ratios such as 1 : 3, 1 : 5 and 1 : 10) showed an overlapping of the anodic wave of excess ligand and cathodic wave of complexed Ag(I). Complex formation between Pd(II) and MPSH (yellow complex) has earlier been reported by Burke and Yoe[15] also though they failed to report any stoichiometry; also the spectrophotometric method worked out by them on the basis of this colour reaction has serious limitations[15]. Authors of this communication have observed two stoichiometries for the Pd(II) complex, 1 : 1 and 1 : 2, under different conditions. The higher stoichiometry obtained, when the metal ion was used as titrant seems to be due to the initiation of the reaction in presence of excess of the ligand.

Checking of Interference of Foreign Ions and Selectivity

Study of interference of foreign ions in the new amperometric methods was carried out for three concentrations of each metal species *viz.* 5.00 mM, 1.00 mM

TABLE 1 TITRATION CONDITIONS AND AMPEROMETRIC DATA

Metal	Medium	Cathodic limiting region of metal wave —E	Anodic limiting region of RSH wave —E	Titration potential —E	Titrant	M:L	Minimum concentration determined ppm	Average stand deviation
			Part A-Ligand:RSH					
Cu(II)	Acetate buffer (pH 4.99)	0.10–1.60	0.00–0.20	0.60	RSH	1 : 1	3	0.054
				0.15	Metal	1 : 2	6	0.054
Ag(I)	0.1M NaOH	No wave	0.20–0.50	0.35	Metal	1 : 1	10	0.072
Au(III)	(i) Acetate buffer (pH 4.99)	0.00–1.50	0.00–0.20	0.60	RSH	1 : 1	10	0.054
	(ii) 0.25M NH_3–NH_4Cl	0.20–1.60	0.20–0.45	1.00	RSH	1 : 1	10	0.054
				0.30	Metal	1 : 2	20	0.056
Pd(II)	0.1M KCl	0.00–1.30	0.00–0.20	0.60	RSH	1 : 1	5	0.056
				0.10	Metal	1 : 2	10	0.056
Pt(IV)	0.1M Na_2CO_3 + $NaHCO_3$	0.05–0.80	0.00–0.45	0.60	RSH	1 : 1	10	0.106
			Part B-Ligand: MPSH					
Cu(II)	0.1M K_2SO_4	0.10–1.40	0.00–0.20	0.60	MPSH	1 : 2	3	0.054
				0.60	Metal	1 : 2	6	0.054
Ag(I)	0.1M NaOH	No wave	0.20–0.50	0.30	Metal	1 : 1	10	0.072
Au(III)	(i) Acetate Buffer pH 4.99	0.00–1.50	0.00–0.20	0.60	MPSH	1 : 1	10	0.054
	(ii) 0.25M NH_3–NH_4Cl	0.20–1.60	0.20–0.45	1.00	MPSH	1 : 1	10	0.054
				0.30	Metal	1 : 2	20	0.056
Pd(II)	0.1M KCl	0.00–1.30	0.00–0.20	0.60	MPSH	1 : 1	5	0.056
				0.10	Metal	1 : 2	10	0.056
Pt(IV)	0.1M Na_2CO_3 + $NaHCO_3$	0.05–0.80	0.00–0.45	0.60	MPSH	1 : 1	10	0.108

TABLE 2 SAFE LIMIT OF THE CONCENTRATION OF FOREIGN IONS IN THE CELL SOLUTION WITH RESPECT TO THE CONCENTRATION OF THE METAL SPECIES DETERMINED. LIGAND:MPSH

Metal ion	Cu(II)		Ag(I)	Au(III)			Pd(II)	Pt(IV)	
Medium	0.1M K_2SO_4		0.1M NaOH	Acetate buffer (pH 4.99)	0.25M NH_3–NH_4Cl		0.1M KCl	0.1M Na_2CO_3 + $NaHCO_3$	
Foreign ion	X	Y	Y	X	X	Y	X	Y	X
SO_4^{2-}	b	b	b	b	b	b	b	b	b
Cl^-	b	b	b	b	b	b	b	b	b
NO_3^-	b	b	b	10t	10t	10t	b	b	b
$S_2O_3^{2-}$	1/20	1/20	1/20	a	1/15	1/10	1/10	1/2	1/10
Ox^{2-}	equal	5t	b	equal	15t	b	10t	b	b
WO_4^{2-}	1/5	1/10	b	b	1/5	1/10	2t	2t	b
Molybdate	1/5	1/5	5t	10t	1/5	a	a	a	10t
Mg(II)	b	b	b	10t	10t	a	b	b	b
Al(III)	b	b	b	10t	15t	5t	b	b	b
V(V)	1/20	a	1/10	1/5	1/5	a	1/10	a	equal
Cr(III)	b	b	5t	10t	10t	5t	b	b	b
Mn(II)	b	1/15	5t	10t	equal	a	b	1/5	1/2
Mn(VII)	a	a	a	a	a	a	a	a	a
Fe(II)	a	a	1/10	1/20	1/10	a	5t	1/2	equal
Fe(III)	1/15	a	1/10	a	a	a	10t	equal	1/10
Co(II)	1/10	1/10	1/10	10t	1/10	a	b	1/2	1/5
Ni(II)	5t	1/10	1/2	equal	1/5	1/20	b	b	a
Zn(II)	b	b	b	1/10	10t	1/10	b	b	equal
Cd(II)	1/10	1/20	1/5	a	1/10	a	equal	1/5	1/2
Pb(II)	a	a	a	a	a	a	2t	equal	a
Cu(II)	—	—	a	a	a	a	1/10	a	a
Au(III)	1/15	a	—	—	—	—	1/15	a	a
Ag(I)	—	—	—	—	—	—	—	—	—
Pd(II)	1/2	a	—	1/10	1/10	1/10	—	—	a
Pt(IV)	5t	equal	—	1/5	1/2	1/5	1/5	1/5	—
Os(VIII)	a	a	a	a	a	a	a	a	a

X = MPSH as titrant, Y = Metal ion as titrant, t = Times, a = serious interference even when the concentration of foreign ions is 1/20 of the metal.
b = Nointerference even when foreign ion is 20 times that of metal.

TABLE 3 SAFE LIMIT OF THE CONCENTRATION OF FOREIGN IONS IN THE CELL SOLUTION WITH RESPECT TO THE CONCENTRATION OF THE METAL SPECIES DETERMINED. LIGAND: RSH

Metal ion Medium	Cu(II) Acetate buffer (pH 4.99)		Ag(I) 0.1M NaOH	Au(III) Acetate buffer (pH 4.99)		0.25M NH₃–NH₄Cl	Pd(II) 0.1M KCl	Pt(IV) 0.1M Na₂CO₃ + NaHCO₃	
Foreign ion	x	y	y	x	x	y	x	y	x
SO_4^{2-}	b	b	b	b	b	b	b	b	b
Cl^-	b	b	b	b	b	b	b	b	b
NO_3^-	b	1/20	b	10t	10t	10t	b	b	b
$S_2O_3^{2-}$	a	a	1/20	a	1/10	1/10	1/5	1/2	1/10
Ox^{2-}	10t	10t	b	equal	15t	b	10t	b	b
WO_4^{2-}	b	10t	b	b	equal	equal	2t	2t	b
Molybdate	1/10	a	5t	1/10	equal	1/15	1/10	1/15	10t
Mg(II)	b	5t	b	15t	b	equal	b	b	b
Al(III)	b	b	b	10t	b	10t	b	b	b
V(V)	1/10	1/20	1/10	1/10	1/5	a	1/5	a	equal
Cr(III)	b	5t	5t	15t	15t	1/5	b	b	b
Mn(II)	b	1/20	5t	15t	10t	1/10	b	b	1/2
Mn(VII)	a	a.	a	a	a	a	a	a	a
Fe(II)	b	a	1/10	1/10	1/10	a	10t	equal	equal
Fe(III)	1/10	a	1/10	a	1/20	a	5t	1/2	1/10
Co(II)	b	b	1/10	b	1/10	a	b	equal	1/15
Ni(II)	equal	1/15	1/2	equal	equal	1/10	b	b	a
Zn(II)	b	equal	b	1/10	b	1/10	b	b	equal
Cd(II)	1/5	a	1/5	a	1/10	a	5t	5t	1/2
Pb(II)	a	a	a	a	1/20	a	2t	2t	a
Cu(II)	—	—	a	equal	a	a	1/10	a	a
Au(III)	equal	a	—	—	—	—	1/15	a	a
Ag(I)	—	—	—	—	—	—	—	—	—
Pd(II)	1/10	1/10	—	1/10	1/10	1/10	—	—	a
Pt(IV)	5t	equal	—	1/5	1/2	1/5	1/5	1/5	—
Os(VIII)	a	a	a	a	a	a	a	a	a

X = RSH as titrant, Y = metal ion as titrant, t = Times, a = serious interference even when the concentration of foreign ions is 1/20 of the metal.
b = No interference even when foreign ion is 20 times that of metal.

and 0.50 mM. Tables 2 and 3 include safe limits of foreign ions in the cell solution. Non-interfering species did not interfere even when present simultaneously in this solution. However, for these selectivity tests, the maximum concentration of each species taken was 0.25 mM to avoid supersaturation. Perusal of Table 1 reveals that the use of ligand (instead of metal) as titrant, wherever feasible, enables one to determine comparatively lower concentrations of metal solutions. Also, RSH can be termed as slightly more efficient reagent on the basis of interference studies (Tables 2 and 3).

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