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BIAMPEROMETRIC ESTIMATION OF SOME REDUCTANTS USING CHLORAMINE-T.

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CHLORAMINE T is found to be an excellent oxidant and has been widely employed to estimate more than two hundred compounds. A wide spectrum of techniques like titrimetry using indicators[1,2], potentiometry[3-5], conductometry[6], polarography[7], amperometry[8], spectrophotometry[9] etc have been employed in the determination of various reductants.

The present paper envisages the possibility of employing biamperometric technique to determine reductants like iodide, ferrous, ferrocyanide, ascorbic acid, nitrite, thiocyanate, oxine, thiourea, aminoacids etc by chloramine-T. This technique scores over the other electroanalytical techniques, namely polarography, amperometry and potentiometry by virtue of its simplicity, rapid equilibrium attainment and is temperature independent.

Reagents:

Chloramine-T solution. The solution of Chloramine T (AR) (0.05M) was prepared in double distilled water, stored in amber colored bottles and was standardised by usual methods[10].

In a 100 ml beaker, an aliquot of the reductant was taken and 10–20 ml of 2N HCl or the buffer was added and then suitably diluted with distilled water. In the titration of oxine a pinch of solid KI was added as a catalyst. A suitable voltage (0.6 or 1.00 V) was applied depending on the system employed. The solution was stirred continuously and the initial current was noted.

Chloramine-T is reported to be a powerful oxidising agent in acid medium ($E^\circ = 1.14$ V) than in neutral ($E^\circ = 0.832$) and basic [$E^\circ = 0.499$ V] media[11]. It also gives well-defined reductive wave at a positive potential in an acidic solution[12]. This is found to be due to the reduction of the non-ionised species of N-Chloro-p. toluene sulfonamide and a dichloramine T produced by disproportionation reaction of chloramine T. The possibility of utilising this behaviour of chloramine-T at platinum electrode is exploited in this investigation. A potential of 0.6 V is applied as the polarising potential. In certain instances a voltage of 1.0 volt has to be applied, because of low initial current in the system.

When the polarising potential is 0.6 V, the current either remains constant or slightly decreases after the end point. This is probably due to the following reaction.

CAT in acidic medium gives

$$RNCl^- + H^+ \rightarrow RNHCl \ (R = CH_3C_6H_4SO_2)$$

$$2RNHCl \rightarrow RNCl_2 + RNH_2$$

The free acid dichloramine-T predominate in strongly acidic medium. After the end point the two species RNHCl and RNCl$^-$ can form a redox couple as, $RNHCl + H^+ + 2\ e \rightarrow RNH_2 + Cl^-$

$$RNCl^- + Cl^- \rightarrow RNCl_2 + 2e$$
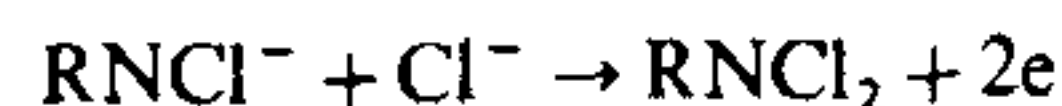
Hence even though chloramine T is irreversible the redox couple formed by the two species of chloramine T accounts for the increase in current. A polarising potential of 0.6 V is not sufficient to oxidise the above mentioned species. Hence in that case the current remains constant due to the irreversible nature of chloramine T.

The stoichiometry of the reductants with respect to the oxidant was reported by the earlier workers in

Table 1 *Estimation of inorganic compounds*

Reductant	Applied Voltage (V)	Taken (mg)	Found (mg)	% Error
Fe^{2+}	0.6	7.65	7.60	−0.7
		21.30	21.38	+0.4
		39.21	39.10	−0.3
[Fe(CN)$_6$]$^{4-}$	0.6	8.92	8.88	−0.5
		26.20	26.28	+0.3
		42.00	41.90	−0.2
KI	0.6	6.52	6.55	+0.5
		16.60	16.56	−0.2
		36.21	36.10	−0.3
NO$_2^-$	1.0	13.81	13.90	+0.7
		30.24	30.09	−0.5
CNS$^-$	1.0	9.72	9.80	+0.8
		29.56	29.41	−0.5

Table 2 *Estimation of organic compounds.*

Reductant	Applied Voltage (V)	Taken (mg)	Found (mg)	% Error
Ascorbic acid	1 0	9 89	9.85	−0.4
		20 48	20 51	+0 2
		35 23	35.24	+0.03
Thiourea	1 0	7 60	7 65	+0.7
		20.20	20.08	−0.6
		31 82	32.00	+0.6
Oxine	1.0	7.30	7.36	+0.8
		22.02	22.20	+0 8
Semicarbazide hydrochloride	1 0	11.15	11 22	+0.6
		30.56	30.32	−0.8
Thiosemi carbazide hydrochloride	1.0	12.88	12.96	+0.6
		35 62	35.39	−0.7

Table 3 *Estimation of amino acids*

Amino Acids	Applied Voltage (V)	Taken (mg)	Found (mg)	% Error
Glycine	0.6	7.50	7.54	+0.5
		16 82	16.74	−0.5
		31.24	31.04	−0 6
Alanine	0.6	8.92	8.90	−0.2
		17.50	17.57	+0.4
		38.71	38.90	+0.5
Valine	0.6	11.75	11.67	−0.7
		28.50	28.65	+0.5
Hippuric acid	0 6	8.96	8.90	−0.7
		19.80	19.89	+0.5
Methionine	1.0	14.92	15.00	+0.5
		30.20	30.00	−0.7
Phenylalanine	1.0	16.52	16.41	−0.7
		33.80	34.00	+0.6
Lysine	1.0	7.40	7.45	+0.7
		28.85	28.70	−0.5
Tryptophan	1.0	10.21	10.28	+0.7
		30 68	30.46	−0.7
Cystine	1.0	12.70	12.60	−0.8
		33.65	33.85	+0.6

potentiometry[13]. It was found that the same stoichiometry holds good in dead stop tritrimetry at the same experimental conditions.

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GEOLOGIC MAPPING OF THE KOYNA REGION IN THE DECCAN TRAPS BY THE MAGNETOTELLURIC METHOD

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ABOUT 200,000 square miles of the western peninsula of India are covered with Deccan Traps. The Koyna region (figure 1) has become of intense interest because of the devastating earthquake[1] of 10 December 1967. The earthquake is directly attributed to the loading effect due to the Koyna dam either by load failure or lubrication along some pre-existing fault. The earthquake locus is placed at a depth of 30 km. Some minor precursory tremors[1] were located at a depth of about 4 kms. The area is non seismic but unfortunately it is also aseismic. Other geophysical methods have failed to yield information either on the thickness of the traps or the thickness of the Mesozoic sediments which overlie the basement. Boreholes to depths of 2500 m exist in the surrounding areas of the Deccan Traps but in the Koyna region no such deep boreholes have been drilled due to the excessive thickness of the hard basaltic rocks and consequently the data on these