Potentiometric Studies with Manganese(III) Compounds in Solution: Determination of Thiocyanates in Metal salts and complexes

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The nature of species present in Mn(III) solution in pyrophosphate and acetate medium were elucidated spectrophotometrically. Quantitative oxidation of thiocyanate ions in metal salts and complexes were investigated using Mn(III) in different media. Number of equivalents of oxidant reacting with thiocyanate in pyrophosphate medium was pH dependent. Oxidation of thiocyanate ion by manganese(III) acetate in aqueous acetic acid was a three electron transfer process. Aquo manganic ion in aqueous sulphuric acid reacted rapidly with thiocyanate yielding 5:1 stoichiometry. This study brought out clearly the change in the redox behaviour of Mn(III)-Mn(II) couple in different coordinating environment.

Manganese(III) was first suggested by Ubbelohde as an oxidising titrant, but the solution was unstable [1]. The more stable pyrophosphate complex was studied by Waters and Kolthoff [2] and Belcher and West [3]. A number of kinetic and analytical studies using manganese (III) in pyrophosphate, sulphate and perchlorate media have been reported [4-6]. Quite recently, we have used anodically generated manganese(III) in aqueous sulphuric acid and aqueous acetic acid media for oxidation of thiocyanates [7], amino acid [8], semicarbazides [9], thiosemicarbazides [10,11]. Oxidation of aroyl and aryloxyacetyl hydrazines [12] and pyridoxine [13] by Mn(III) have also been investigated. This paper describes the potentiometric assay of thiocyanates in metal salts and complexes by manganese (III) pyrophosphate (MPy) in the pH ranges 1-3, by manganese (III) acetate (MAc) in aqueous acetic acid and by manganese (III) sulphate (MSu) in aqueous sulphuric acid.

Thiocyanates find a number of industrial applications - in photography, printing, textile, dyeing, medicines, freezing mixtures, in the manufacture of synthetic dyestuffs, sulphocyanides, thioureas and mustard oil and as reagents in analytical chemistry [14]. There are a number of

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methods of analysis of thiocyanates. But there is still a place for new procedures that could be used under different set of conditions.

EXPERIMENTAL

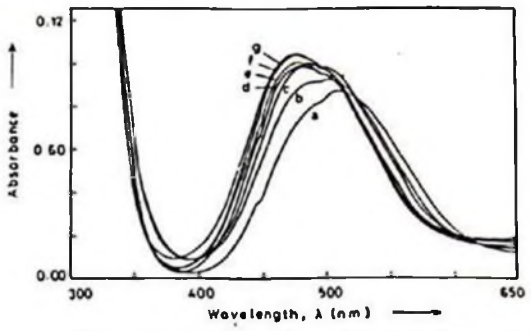
Apparatus

A Digisun (India) model D1-101 digital potentiometer equipped with platinum - calomel electrode assembly was used for the potentiometric study throughout this work. The absorption spectra of the manganese(III) solutions were recorded using a Hitachi 220 Ultraviolet - visible spectrophotometer with 1 cm quartz cells.

Reagents

Manganese (III) pyrophosphate (MPy) was prepared by the method of Belcher and West [3]. A 0.1 mol dm^{-3} solution of MPy was stable for over a month at pH 4-6. The stock solution in the present study was of pH 5 and approximately 0.05 mol dm^{-3} in Mn(III). The pH could be lowered by adding calculated amount of phosphoric/sulphuric acid or increased by adding calculated amount of pyrophosphate solution. Below pH 4, the solution was less stable; neverthless, it could be conveniently employed for analytical and kinetic studies.

The absorption maximum for MPy occured at 500 nm at pH 5. But on change of pH, there was a significant shift in λ_{max} and change in molar absorption coefficient (Fig.1).



Absorption spectra of Manganese (III) Pyrophosphate (0.01 mol dm^{-3}) different pH

pH = a (0.31), b (1.85), c (2.80), d (3.90), e (5.16 to 5.23) f (6.26), g (8.09)

Fig. 1

Manganese (III) acetate in aqueous acetic acid (MAc) was prepared by the electrolytic method as described previously [11]. It has been observed that a 0.01 mol dm^{-3} solution of manganese (III) acetate was stable in aqueous acetic acid (75% v/v) for about 48 hours. Acetic acid is a strong donor solvent. So, higher concentration of acetic acid would help enhance the stability of Mn(III) [11]. The spectra of freshly prepared MAc obtained at different concentrations of acetic acid and sodium acetate showed that a manganic complex, $Mn(OAc)^{4-}$ was formed in the presence of higher concentration of acetate, (enhanced absorption at 420 nm - fig.2). Possibly the water ligand is replaced by acetate ion [16] in higher acetate concentration.

Manganese (III) sulphate (MSu) was prepared by the anodic oxidation of an 0.2 mol dm^{-3} solution of manganese (II) sulphate in an electrochemical cell with lead electrodes [10] . Electrolytically generated MSu showed the absorption maxima at 490 nm. The molar

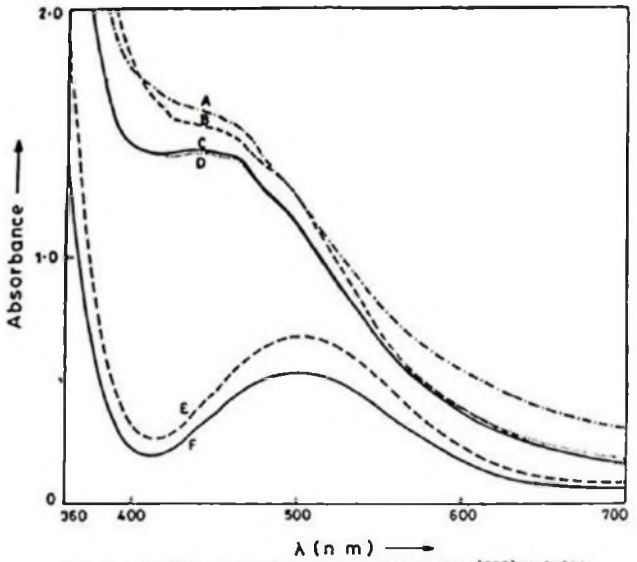


Fig. 2 - Visible absorption spectra of manganese(III)acetate: [(A) 0.05 mol dm^{-3} manganese(II)acetate, $5.0x10^{-3}$ mol dm^{-3} manganese(III)acetate in 100% HOAc
(B) 0.05 mol dm^{-3} manganese(II)acetate, $5.0x10^{-3}$ mol dm^{-3} manganese(III) acetate, 0.6 mol dm^{-3} KOAc in 80% (v/v) HOAc.
(C) 0.05 mol dm^{-3} manganese(II)acetate, $5.0x10^{-3}$ mol dm^{-3} manganese(III)acetate, 0.6 mol dm^{-3} KOAc in 100% HOAc.
(D) 0.05 mol dm^{-3} manganese(II)acetate, $5.0x10^{-3}$ mol dm^{-3} manganese(III)acetate, 0.3 mol dm^{-3} KOAc in 100% HOAc.
(E) 0.2 mol dm^{-3} manganese(III)sulphate in the mixture H_2SO_4 (2.5 mol dm^{-3}) + HOAc (50% v/v).
(F) 0.2 mol dm^{-3} manganese(III) sulphate with 5.0 mol dm^{-3}, H_2SO_4]

adsorption coefficient, ε at 490 nm varied as a function of H^+ concentration (ranged from 131 to 111 dm^3 mol^{-1} cm^{-1} at H^+ concentration of 1.28-2.98 mol dm^{-3}). The high value of ε has been attributed to the presence of hydrolysed species $MnOH_2^+$ [17]. Only a small fraction of Mn(II) could be converted to Mn(III) owing to the low solubility of the latter [10]. However it is desirable that Mn(III) is always associated with a large excess of Mn(II) to suppress the disproportionation reaction [6]:

$$2\ Mn(III) \Longleftrightarrow Mn(II) + Mn(IV) \quad ....(1)$$

Potassium thiocyanate (Qualigens, special quality) was dried at 150° C and its purity was checked by the argentometric method. The metal thiocyanates - NaNCS, $Pb(NCS)_2$, $Ba(NCS)_2$, $Zn(NCS)_2$ $Ni(NCS)_2.0.5H_2O$ and the complexes $K_2Zn(NCS)_4.4H_2O$, $K_4Ni(NCS)_6.4H_2O$ and $HgCo(NCS)_4$ were prepared by standard methods reported elsewhere [15]. Compositions of these were checked by elemental analysis. Standard solution of these compounds (0.01 mol dm^{-3}) were prepared in triply distilled water.

Procedure

All the three Mn(III) solutions were studied for the determination of thiocynate. But since the reaction was slow, invariably back titration procedures were followed. Titration of excess Mn(III) by different titrants and by different end point detection techniques have been examined. Back titration of excess of unreacted CNS^- (by Volhard's method) was also attempted. It was noted that flushing the reaction mixture with inert gases (N_2 or CO_2) made no noticeable change in results. The different methods used can be listed as the following 5 procedures.

Method A (Back titration with ferrous solution)

A known excess of the oxidant (10.0 cm^3 of 0.02 mol dm^{-3} MPy solution), syrupy phosphoric acid (15.0 cm^3 to bring down the pH of the solution to <1) and a known amount of the reductant (5.0 cm^3 of

0.005 mol dm^{-3} thiocyanate solution) were taken in a 100 cm^3 beaker in which were placed a platinum electrode and a saturated calomel reference electrode (SCE). The reaction mixture was kept stirred for at least 10 minutes using magnetic stirrer. The potential was noted. The excess oxidant, Mn(III), was back titrated potentiometrically with a standard 0.01 mol dm^{-3} solution of Fe(II). The plot of potential *vs* volume of the titrant was a well-defined curve of sigmoid form. Potential jump at the end point was large. The potential jump at the equivalence point ranged from 200 to 300 mV per 0.1 cm^3 of 0.01 mol dm^{-3} titrant. A blank titration was performed potentiometrically with the same volume of the MPy against the Fe(II) solution under similar conditions. This method was applied in solution of pH nearly 1. The number of electrons involved in the reaction could be calculated using the equation

$$n = \frac{(v_3 - v_2)\ X}{v_1\ Y}$$

where v_1 is the volume of thiocyanate solution, v_2 and v_3 are the volumes of the titrant (ferrous solution) added upto the end point in the back titration and the blank titration respectively, X and Y are the molarities of ferrous and thiocyanate solution respectively.

The above potentiometric method could not be employed at higher pH values. At pH >2, the rate of the main reaction became slow and the potential drop at the end point was not significant. Therefore alternative methods were made use of.

Method B (Oxidant excess condition - iodimetry)

A known volume of the oxidant (10.0 cm^3 of a 0.01 mol dm^{-3} MPy solution) was taken in a beaker. Calculated amount of phosphoric acid or sodium pyrophosphate was added to bring the pH to nearly 2. pH value was checked with a pH meter. A known amount of the reductant (10.0 cm^3 of a 0.005 mol dm^{-3} thiocyanate solution) was added to it. The reaction mixture was allowed to stand for 30 minutes under stirred condition. 5 ml of 2% of potassium iodide solution was added and the liberated iodine was titrated to a starch end point with 0.1 mol dm^{-3} sodium thiosulphate solution.

Method C (Reductant excess condition using Volhard's method)

A known volume of the oxidant solution (10.0 cm^3 of a, 0.005 mol dm^{-3} Mpy solution) was taken in a beaker. Calculated quantity of phosphoric acid or sodium pyrophosphate solution was added as needed to bring the pH to nearly 2. pH value was checked using a pH meter. A known excess of the reductant solution (10.0 cm^3 of a 0.01 mol dm^{-3} solution of thiocyanate) was added. The reaction mixture was allowed to stand for at least 30 minutes under stirred condition using a magnetic stirrer. The reaction mixture was then taken in a

microburette and titrated against a standard solution (a 0.005 mol dm^{-3}) of silver nitrate containing dil. HNO_3, using ferric alum indicator.

Method D (Oxidant MAc; back titrant hydroquinone)

Direct potentiometric titration of thiocyanate with MAc in aqueous acetic acid were moderately fast in the begining but became very slow in the vicinity of the end point. pH was not suitable for back titration with ferrous solution. Hence back titration with hydroquinone was employed. To a known amount of the reductant (5.0 cm^3 of 0.005 mol dm^{-3} thiocyanate) was added a known excess of the oxidant (25.0 cm^3 of 0.01 mol dm^{-3} MAc solution) both in aqueous acetic acid (90% v/v). The reaction mixture was allowed to stand for about 30 minutes and then titrated potentiometrically with 0.01 mol dm^{-3} hydroquinone in aqueous acetic acid (90% v/v). The titrations gave well-defined curves of sigmoid form. There was a large potential jump (200-300 mV per 0.1 cm^3 of the titrant added) at the end point. The effect of acetic acid concentration on the stoichiometry of the oxidation process was examined by titrating in media with varying acetic acid concentration (60-90% v/v).

Method E (Oxidant MSu; back titrant hydrazinium sulphate)

To a known amount of the reductant (5.0 cm^3 of 0.005 mol dm^{-3} thiocyanate solution) was added a known excess of the oxidant (25.0 cm^3 of 0.01 mol dm^{-3} MSu solution) maintaining the overall acid concentration constant. The reaction mixture was titrated potentiometrically against hydrazinium sulphate solution.

RESULTS AND DISCUSSION

With MPy

MPy has been titrated with thiocyanates at different pH values using methods A, B and C. The stoichiometry of redox reaction of MPy with thiocyanate is found to be pH dependent. At pH 1 the stoichiometry settles down to a reproducible value of 5:1 and above pH 2 it conforms to 1:1 (Table 1).

Table 1

Stoichiometry of Thiocyanate oxidation by Manganese(III) pyrophosphate at various pH

Stoichiometry =
Number of electrons participating / NCS oxidised =
Mol of Mn(III) consumed / mol of NCS reacted

pH	Method used		stoichiometry
1.0	Potentiometry	(Method A)	4.98
1.2	Potentiometry	-do-	2.66
2.05	Iodimetry	(Method B)	1.59
2.35	Iodimetry	-do-	1.20
2.70	Iodimetry	-do-	0.80
2.70	Volhard's	(Method C)	1.01

The 1:1 stoichiometry may be represented by the reaction

$$2\ Mn(III) + 2\ NCS^- \longrightarrow 2\ Mn(II) + NCS\text{-}SCN \quad ....(2)$$

The covalent dimer, $(NCS)_2$ was extracted with chloroform. Passing dry chlorine through this produced turbid suspension due to the formation of NCSCl [18], thereby confirming the oxidation product. In the pH range 2-3, a lower stoichiometric value was obtained. At pH 2.7, the value was 1:0.8 by the method B but 1:1 as obtained by method C (Table 1). The fractional value occured in method B because $(NCS)_2$ could oxidise KI to I_2 which in turn could take up proportionate excess of sodium thiosulphate. On reaching pH 3, the reaction slowed down drastically and such condition was not amenable for the analytical study but more suited for the kinetic investigations [19]. At pH <1 however, the reaction took place rapidly and a reproducible 5:1 stoichometry was established between the oxidant and the reductant. This formed the basis for the volumetric determination of thiocyanates (Table 2).

CN^- was detected in the reaction mixture by the spot test as follows [20]. A quantitative filter paper was impregnated with ammoniacal solution containing 0.1g

Table 2

Potentiometric titrations of thiocyanates (simple and complex) with Mn(III) pyrophosphate in pyrophosphate media employing Fe(II) as back titrant (Method A)

$Mn(III) = 0.02$ mol dm^{-3}; $Fe(II) = 0.01$ mol dm^{-3}; pH 1
n calculated = 5.0 per NCS group

Compound	Range studied (mg)	n found ±SD*	Max Error %
KNCS	0.53 - 8.01	4.98 ±0.01	0.31
NaNCS	0.42 - 6.32	5.00 ±0.01	0.54
NH_4NCS	0.44 - 6.71	5.10 ±0.21	0.60
$Ni(NCS)_2.0.5H_2O$	0.34 - 5.29	9.99 ±0.04	0.60
$Zn(NCS)_2$	0.44 - 6.60	10.06 ±0.02	0.21
$Cd(NCS)_2$	0.52 - 7.88	9.96 ±0.07	0.72
$Ba(NCS)_2.2H_2O$	0.58 - 8.75	10.08 ±0.08	0.25
$Pb(NCS)_2$	0.64 - 9.69	10.08 ±0.00	0.10
$K_4[Ni(NCS)_6].4H_2O$	0.57 - 8.58	30.03 ±0.09	0.40
$K_2[Zn(NCS)_4].4H_2O$	0.36 - 5.51	20.05 ±0.05	0.35
$Hg[Co(NCS)_4]$	0.36 - 5.46	19.99 ±0.05	0.20

*SD = standard deviation for six determinations

of copper sulphate per 100 cm^3 and dried. Hydrogen sulphide was blown onto the paper so that it acquires a uniform brown colour. A drop of the test solution formed white ring due to the formation of colourless cuprocyanide.

Further oxidation of CN^- to $(CN)_2$ was ruled out. It was found that KCN solution was not oxidised by MPy. Barium chloride test showed the presence of SO_4^{2-} in the reaction product. It is established that thiocyanates are oxidised by other oxidants using either 6 electrons or 8 electrons and have been explained [21] by the schemes:

$$NCS^- + 4H_2O - 6e \longrightarrow CN^- + SO_4^{2-} + 8H^+ \quad ...(3) \text{ ref [21a]}$$

$$NCS^- + 5H_2O - 8e \longrightarrow CNO^- + SO_4^{2-} + 10H^+ \quad ...(4) \text{ ref [21b]}$$

Table 3

Potentiometric Titration of Thiocyanates and Metal Complexes with Manganese(III)acetate (Method D employed)

Mn(III) - 0.01 mol dm^{-3}; Medium - Aq.acetic acid;
Back titrant - hydroquinone (0.01 mol dm^{-3}
Electrons participating in the redox reaction (n)
Calculated value of no. of electrons consumed per NCS group 3.0

Compound	Range studied (mg)	% HAc v/v	n (found) ±SD*	Max error %
KNCS	0.47-7.60	90	2.98 ±0.02	0.67
		80	2.91 0.09	2.40
		70	2.89 0.03	1.04
		60	2.92 0.02	0.62
NaNCS	0.45-6.81	90	2.95 0.03	0.88
NH_4NCS	0.43-6.48	90	2.95 0.03	0.88
$Ni(NCS)_2 0.5H_2O$	0.38-5.72	90	6.08 0.04	0.85
$Zn(NCS)_2$	0.38-5.78	90	6.09 0.05	1.05
$Cd(NCS)_2$	0.46-7.03	90	6.03 0.04	0.88
$Ba(NCS)_2.2H_2O$	0.58-8.75	90	5.96 0.05	1.00
$Pb(NCS)_2$	0.63-9.45	90	5.92 0.05	0.91
$K_4[Ni(NCS)_6]4H_2O$	0.45-6.86	90	18.01 0.14	1.02
$K_2[Zn(NCS)_4]4H_2O$	0.38-5.71	90	12.09 0.10	0.94
$Hg[Co(NCS)_4]$	0.37-5.61	90	12.00 0.07	0.83

SD* Standard deviation for six determinations

Therefore it seems logical that stoichiometry of 5 electrons observed in the oxidation of NCS^- by MPy at pH 1, may probably be due to the competing reactions (2) and (3) and guided by the proportion in which they occur.

With MAc

Based on earlier study [21b], standard solutions of hydroquinone were used as back titrant in these titrations (method D cited above). The results of potentiometric titrations are shown in Table 3.

All the thiocyanates were oxidised quantitatively involving 3 electrons per NCS^- ion. Sulphate and cyanide were not detected in the reaction mixture. So the observed 3:1 stoichiometry can not be due to the competing reactions (2) and (3). Therefore the following scheme was proposed:

$$2\ NCS^- + 2\ H_2O\ -\ 6e\ \rightarrow\ 2\ OCS + N_2 + 4\ H^+ \quad .(5)$$

The carbonoxy sulphide (OCS) could not be identified in the product, but the evidence for its formation comes from the observation recorded in the literature [22]. The thiocyanates of divalent metal ions and the complexes listed in the table were also oxidised with 3 electron change per NCS ligand in the molecule. Common anions like CH_3COO^-, ClO_4^-, NO_3^-, F^- and Cl^- did not interfere in these reactions.

With MSu

MSu reacted with hydrazinium sulphate instantaneously in 1:1 molar ratio as shown in the Table 4.

Table 4

Potentiometric titration of Hydrazinium sulphate with Mn(III) sulphate in sulphuric-acetic acid medium

Mn(III) 0.01 mol dm^{-3}; Temp 298 ± 2 K
Hydrazinium sulphate was taken in the range 1.30 -32.55 mg
Calculated value of number of ions participating (n) is 1.0

H_2SO_4 (mol dm^{-3})	n found ± SD	Max Error %
1.25	1.00 ± 0.01	1.17
1.50	0.99 ± 0.01	1.21
1.75	0.99 ± 0.03	1.52
2.00	1.01 ± 0.01	0.99
2.25	0.98 ± 0.00	0.59
2.50	0.99 ± 0.18	1.43
3.50	1.00 ± 0.01	0.90
5.00	0.98 ± 0.013	1.54

*SD = standard deviation for six determinations

The reaction is represented by equation (6)

$$2\ Mn^{3+} + 2\ H_2NNH_2 \longrightarrow 2\ Mn^{2+} + N_2 + 2\ NH_4^+ \quad \ldots\ (6)$$

Hydrazinium sulphate was introduced as a back titrant in this system (Method E). In the titration of thiocyanates with MSu, the overall acid concentration was varied between 1-5 mol dm^{-3} and the

titrations were carried out as above. Titrations were also repeated by taking mixture of H_2SO_4-HOAc of overall concentration 2.5 mol dm^{-3} and 20-60% (v/v) respectively (Table 5).

Common anions such as HSO_4^-, $P_2O_7^{4-}$, ClO_4^- NO_3^- and F^- did not interfere in the reaction. But Br-, I- and thiourea interfered even while present in trace amounts. Chloride does not interfere. Typical set of results in presence of Cl^- are shown in Table 6.

Table 5

Potentiometric Titration of thiocyanates (simple and complex) with Manganese(III) sulphate in aqueous sulphuric acid media

Mn(III) -0.01 mol dm^{-3}; Back titrant - 0.01 mol dm^{-3} Hydrazinium sulphate; Temp 27 ± 2 ° C
Electrons participating in the redox reaction (n); Calculated value of no.electrons consumed per NCS group 5

Compound	Range (mg)	Medium H_2SO_4(M)	HAc %	n found ±SD*	Max Error %
KNCS	0.41 onwards	1.25	-	4.96 ±0.04	1.19
		1.50	-	4.94 ±0.03	0.81
		2.00	-	5.04 ±0.03	0.79
		2.50	-	5.06 ±0.04	1.14
		3.00	-	5.07 ±0.03	0.80
		5.00	-	5.08 ±0.03	0.79
		2.50	20	4.94	-
		2.50	30	4.91	-
		2.50	40	4.86	-
		2.50	50	4.64	-
		2.50	60	4.21	-
NaNCS	0.39 - 5.95	2.50	-	4.97 ±0.03	0.90
NH_4NCS	0.40 - 6.01	2.50	-	5.06 ±0.04	0.75
$Ni(NCS)_2.0.5H_2O$	0.36 - 5.51	2.50	-	9.97 ±0.07	0.83
$Zn(NCS)_2$	0.40 - 6.05	2.50	-	9.95 ±0.06	1.00
$Cd)NCS)_2$	0.47 - 7.19	2.50	-	9.97 ±0.06	0.63
$Ba(NCS)_2.2H_2O$	0.55 - 8.36	2.50	-	9.98 ±0.04	0.55
$Pb(NCS)_2$	0.59 - 8.96	2.50	-	10.10 +±.08	0.82
$K_4[Ni(NCS)_6].4H_2O$	0.54 - 8.10	2.50	-	29.70 +0.19	0.81
$K_2[Zn(NCS)_4].4H_2O$	0.34 - 5.17	2.50	-	19.81 +0.11	0.69
$Hg[Co(NCS)_4]$	0.41 - 6.27	2.50	-	20.05 +0.16	0.98

* SD = Standard Deviation for six determinations

Table 6

Potentiometric Determination of Potassium thiocyanate by Mn(III) sulphate in sulphuric acid

Mn(III) = 0.01 mol dm-3; H_2SO_4 2.5 mol dm^{-3}; Temperature 27 ± 2° C
Hydrazinium sulphate as back titrant 0.01 mol dm^{-3}

KNCS taken mg	< KNCS found (mg) > Argentometry	potentiometry	% recovery ±SD
In absence of chloride			
0.918	0.914	0.927	100.98 ±0.57
2.296	2.282	2.293	99.87 ±0.78
2.755	2.736	2.743	99.56 ±0.34
3.584	3.602	3.585	100.03 ±0.63
5.325	5.298	5.325	100.00 ±0.39
9.498	9.536	9.498	100.00 ±0.30
In presence of 10.0 cm^3 of 0.50 mol dm^{-3} of Cl^-			
2.530		2.531	100.03 ±0.33
4.560		4.556	99.92 ±0.28
6.840		6.843	100.05 ±0.33
9.120		9.120	100.00 ±0.28

*SD = standard Deviation for six determinations

All the thiocyanates listed in this communication were oxidised at pH 1 by MPy quantitatively involving five electron change per NCS^- ion. The results were reproducible and the maximum error was less than ± 1.0%.

The thiocynates of divalent metals - $Pb(NCS)_2$, $Ba(NCS)_2.2H_20$, $Zn(NCS)_2$ and $Ni(NCS)_2.0.5H_20$ - participated in the redox reactions by donating 10 electrons each, thereby indicating the number of ligands per molecule as two. The complexes $HgCo(NCS)_4$, $K_4Zn(NCS)_4.4H_20$ and $K_4Ni(NCS)_6.4H_20$ were also involved in the redox reaction by exchange of five electrons per NCS^- group in the molecule.

It was found that number of electrons involved in the redox reaction in H_2SO_4-HOAc mixture was found to decrease with increase in % HOAc, but the values were non-stoichiometric. It may be pertinent to refer back to Manganese(III) oxidation of thiosemicarbazide in H_2SO_4-HOAc medium [10] which yielded varying stoichiometries depending on percentage composition of HOAc, thereby showing the selectivity of Mn(III) as an oxidising agent, i.e. it react differently under different reaction conditions.

An interesting point emerges from this study. In acidic pH, MPy can be considered as a chelate ring complex anion having the formula $Mn(H_2P_2O_7)^{3-}_3$. The redox potential of Mn(III)-Mn(II) system in pyrophosphate media was 1.2V. MAc in aqueous acetic acid involved undecomposed complexes -$Mn(OAc)_3$ or $Mn(OAc)_4^-$ as evident from the absorption spectra and the observed lower redox potential value of 1.16 V, accordingly the reaction was slightly sluggish. In the case of MSu in aqueous sulphuric acid the reactive species identified were the ionic form of trivalent manganese, Mn^{3+} aq. or $MnOH^{2+}$ aq. and the formal redox potential for this system was higher, namely 1.52 V and as such the reaction in sulphate media was more drastic.

CONCLUSION

It could be inferred that a change in the coordination environment of the redox system, Mn(III)-Mn(II), has brought about a significant variation in its redox behaviour in respect of stoichiometry, reactivity, selectivity and overall mechanism of the related reactions.

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