

## Na<sub>2</sub>TeO<sub>3</sub> Oxidation in presence of 1-Cyanoacetyl-3, 5-dimethyl-1H-pyrazole in aqueous Na<sub>2</sub>SO<sub>4</sub> cyclic voltammetrically

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**Abstract:** Oxidation of sodium tellurite (Na<sub>2</sub>TeO<sub>3</sub>) was studied in the absence and presence of prepared 1-Cyanoacetyl-3, 5-dimethyl-1H-pyrazole (H<sub>2</sub>CADMP) by using cyclic voltammetry in 0.1M Na<sub>2</sub>SO<sub>4</sub> electrolytic solution at 291K. Cyclic Voltammogram showed no reduction peaks that mean oxidation only is happened. Glassy carbon electrode (GCE), Ag/AgCl, and Pt wire were used as working electrode, reference electrode and counter electrode, respectively, in the conventional three electrodes cell. The oxidation stability constants and Gibbs free energies of oxidation resulting from the interaction of Na<sub>2</sub>TeO<sub>3</sub> with H<sub>2</sub>CADMP were estimated and their values were discussed.

**keywords:** Cyclic voltammetry, Oxidation, Sodium Tellurite, 1-Cyanoacetyl-3, 5-dimethyl-1H-pyrazole, stability constant, Gibbs free energy, Solvation and kinetic parameters

### 1. Introduction

The inexpensive and available sodium tellurite has hardly used as oxidizing agent. Also it is insoluble in organic solvents. The reactions being heterogeneous in nature are ineffective [1]. Extraction of anions containing oxo ions and complex anions of metals [2-5] such as MnO<sub>4</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>, [Fe(CN)<sub>6</sub>]<sup>3-</sup> and [Ce(NO<sub>3</sub>)<sub>6</sub>]<sup>2-</sup> in organic phase from aqueous phase using phase transfer catalysis is supported

In the present work, we wish to report the electrochemical behavior of the interaction of sodium tellurite with prepared H<sub>2</sub>CADMP compound. This can be studied in 0.1M Na<sub>2</sub>SO<sub>4</sub> aqueous solution as supporting electrolyte using cyclic voltammetry. The stability constants and thermodynamic parameters are discussed.

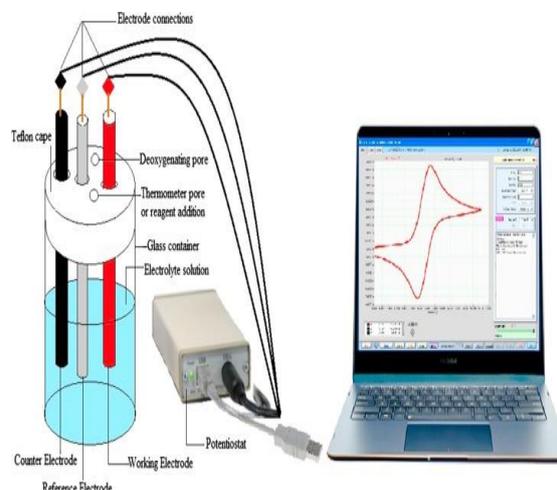
### 2. Experimental

#### 2.1. Chemicals

Sodium tellurite (Na<sub>2</sub>TeO<sub>3</sub>) was obtained from BDH Chemicals Ltd Poole England. The chemicals used are sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) from ADWIC Company, Ethyl cyanoacetate (ECA) from Alpha Chemicals, Acetyl acetone from ADWIC Company and Ethanol from PIOCHEM Company. Deionized water was used in preparing the different solutions especially freshly prepared sodium tellurite.

#### 2.2. Apparatus

Cyclic voltammetry instrument DY2000 (USA) potentiostat was used for measuring the cyclic voltammograms at different scan rates. Nitrogen gas was passed for ten minutes for each run to remove the dissolved oxygen. Three electrodes used were Ag/AgCl electrode put in saturated KCl as reference electrode, platinum wire as auxiliary electrode and glassy carbon electrode as working electrode. The glassy carbon electrode was polished well with fine Al<sub>2</sub>O<sub>3</sub> put in the wool piece. Three electrodes were immersed in a cell containing 30ml of 0.1M Na<sub>2</sub>SO<sub>4</sub>. The system was applied in the range between +1V to -1V potential window and 50mV/s scan rate at 291K

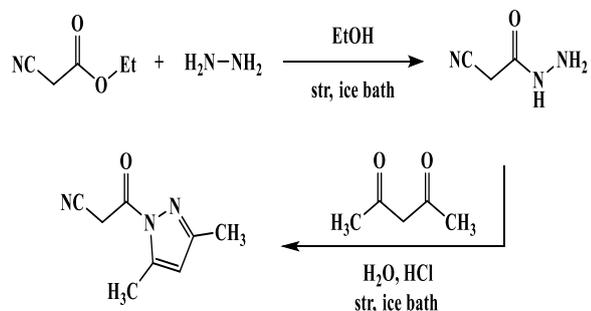


**Fig.1:** Cyclic Voltammetry system

### 2.3 Preparation of 1-Cyanoacetyl-3, 5-dimethyl-1H-pyrazole

1-Cyanoacetyl-3, 5-dimethyl-1H-pyrazole was prepared through two steps:

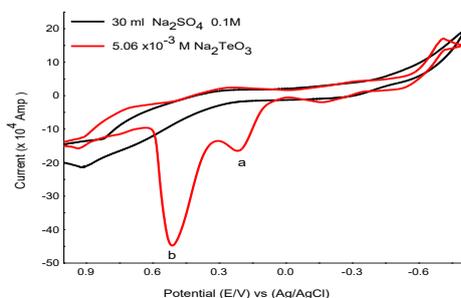
In the first step, cyanoacetic hydrazide was obtained by adding hydrazine hydrate (0.05mol) to a solution of ethyl cyanoacetate (0.05mol) in ethanol (10ml) with stirring in ice bath. The formed cyanoacetic hydrazide was filtered, washed with EtOH and dried [6, 7]. In the second step, the solution of cyanoacetic hydrazide (0.03mol) in water (10ml) containing conc HCl (1ml) was stirred in an ice bath. After 5 minutes, acetyl acetone (0.03mol) was added. The mixture was stirred for 1hr in an ice bath forming ppt. The formed 1-cyanoacetyl-3, 5-dimethyl Pyrazole was filtered, washed with H<sub>2</sub>O and dried (m.p 118°C, yield 89.8%) [7-9].



## 3. Results and discussion

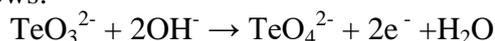
### 3.1. Cyclic voltammetry of Na<sub>2</sub>TeO<sub>3</sub> alone

The CV, cyclic voltammetry for Na<sub>2</sub>TeO<sub>3</sub> [5.06x10<sup>-3</sup> M] in 0.1M Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte was studied in the range between +1V to -1V. Two oxidation peaks were only appeared at ~ +0.2V and +0.5V respectively. No reduction peaks were detected in the used medium using a scan rate of 50mV/s, as seen in Fig. (2)



**Fig. (2):** Cyclic Voltammogram of Na<sub>2</sub>TeO<sub>3</sub> 5.06x10<sup>-3</sup>M in 30ml Na<sub>2</sub>SO<sub>4</sub> 0.1 M at 291K and scan rate 50 mV/s.

The suggested mechanism for the oxidation of Tellurite ions to Tellurate ions at ~ 0.2V is as follows:



Oxidation of tellurium, deposited on the surface of the electrode, to tellurite ions at ~ 0.5V is as follow:



Analysis of oxidation peaks was done to evaluate anodic solvation parameters and their data was given in Table (1). The reaction is an irreversible one.

**Table (1):** Anodic solvation and kinetic parameters ( $D_a$ ,  $\Gamma_a$  and  $Q_a$ ) of Na<sub>2</sub>TeO<sub>3</sub> 5.06x10<sup>-3</sup> M at 291K and scan rate 50 mV/s

$E_{p_a}$ (volt)	$(-I_{p_a}) \times 10^4$ (Amp)	$D_a \times 10^6$ (cm <sup>2</sup> /s)	$\Gamma_a \times 10^9$ (mol/cm <sup>2</sup> )	$(-Q_a)$ $\times 10^4$ (C)
(a) For the first wave				
0.191	1.46	5.79	3.876	1.47
(b) For the second wave				
0.482	2.78	20.9	7.371	2.79

### 3.2. Analysis of waves

The oxidation peaks, at ~ +0.2V and +0.5V can be analyzed by using the following equations:

#### 3.2.1. Randles-Sevcik equation

Randles-Sevcik equation (1) was used for evaluating the anodic diffusion coefficient from the anodic peak current [10-14].

$$I_{p_a} = (2.69 \times 10^5) A C n^{1.5} D_a^{0.5} v^{0.5} \quad (\text{Eq. 1})$$

Where A is the area of the electrode in cm<sup>2</sup>,  $D_a$  is the anodic diffusion coefficient in cm<sup>2</sup>/s, C is the Na<sub>2</sub>TeO<sub>3</sub> concentration in mole/cm<sup>3</sup>, n is the number of electrons and v is the scan rate in V/s.

#### 3.2.2. Anodic Quantity of electricity

The anodic quantity of electricity consumed during the anodic scan was calculated by the use of equation (2) [15, 16].

$$Q_a = n F A \Gamma_a \quad (\text{Eq. 2})$$

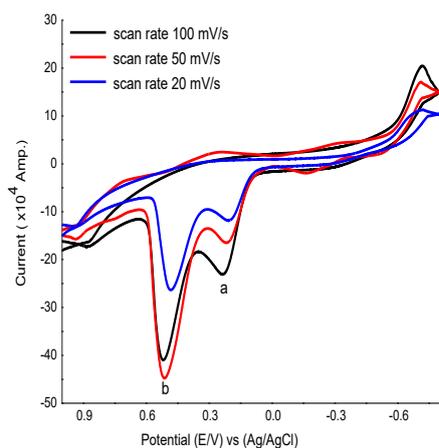
Where  $Q_a$  is anodic quantity of electricity, F is Faraday constant, equal 96485.33 C/mol and  $\Gamma_a$  is the surface coverage in mol/cm<sup>2</sup>.

The surface coverage which the area of working electrode covered by the tellurite ions was calculated using equation (3) [11, 12, 15]

$$\Gamma_a = I_{p_a} 4RT / n^2 F^2 A v \quad (\text{Eq. 3})$$

### 3.3. The scan rate effect for $5.06 \times 10^{-3}$ M $\text{Na}_2\text{TeO}_3$

Cyclic voltammetry of  $5.06 \times 10^{-3}$  M  $\text{Na}_2\text{TeO}_3$  at different scan rates (100, 50, 20 mV/s), as shown in Fig. (3), proved the diffusion control reaction as the anodic current was decreased with a decrease in scan rate while other anodic solvation parameters ( $D_a$ ,  $\Gamma_a$ ,  $Q_a$ ) were increased elucidating the diffusion ability. Calculated parameters are given in Table (2).



**Fig. (3):** Cyclic Voltammograms of  $5.06 \times 10^{-3}$  M  $\text{Na}_2\text{TeO}_3$  at 291K at different scan rates

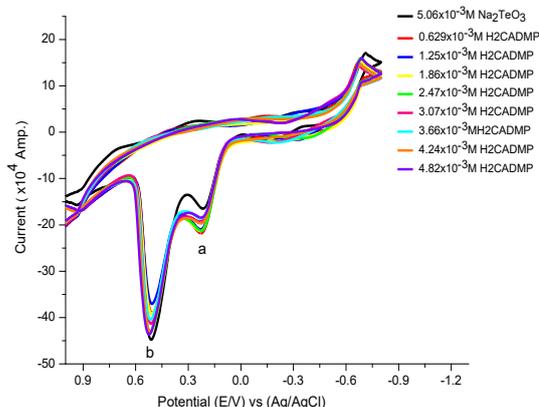
**Table (2):** Effect of different scan rate of  $5.06 \times 10^{-3}$  M  $\text{Na}_2\text{TeO}_3$  at 291K

$v$ mV/s	$E_{p_a}$ (volt)	$(-I)_{p_a}$ $\times 10^4$ (Amp)	$D_a$ $\times 10^6$ ( $\text{cm}^2/\text{s}$ )	$\Gamma_a$ $\times 10^9$ ( $\text{mol}/\text{cm}^2$ )	$(-Q)_a$ $\times 10^4$ (C)
(a) For the first wave					
100	0.201 7	1.83	4.50	2.418	0.916
50	0.190 5	1.46	5.79	3.876	1.47
20	0.175 7	0.927	5.80	6.138	2.33
(b) For the second wave					
100	0.492 6	1.98	5.3	2.6237	0.995
50	0.482	2.78	20.9	7.3706	2.79
20	0.454 4	1.48	14.8	9.8105	3.72

### 3.4. Oxidation of $\text{Na}_2\text{TeO}_3$ interacted with 1-Cyanoacetyl-3, 5-dimethyl-1H-pyrazole

On adding different concentrations of  $\text{H}_2\text{CADMP}$  to  $\text{Na}_2\text{TeO}_3$  ranging from  $0.629 \times 10^{-6}$  mol  $\text{cm}^{-3}$  to  $4.82 \times 10^{-6}$  mol  $\text{cm}^{-3}$ , we didn't observe an extra wave other than the two

oxidation peaks for tellurite ions. The positive shift in the oxidation potential and change in the anodic current were observed as shown in Fig. (4). The obtained anodic voltammetric data in presence of  $\text{H}_2\text{CADMP}$  changed from the same for  $\text{Na}_2\text{TeO}_3$  alone, as given in Table (3), indicating that there is the electrostatic interaction between  $\text{H}_2\text{CADMP}$  and  $\text{Na}_2\text{TeO}_3$ .

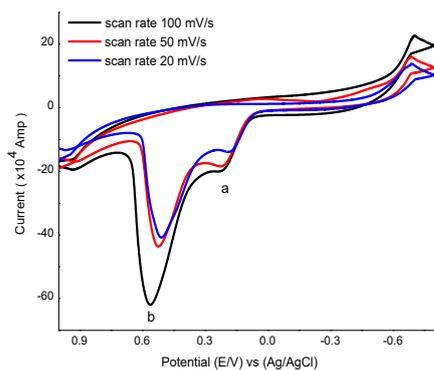


**Fig. (4):** Cyclic Voltammogram of  $5.06 \times 10^{-3}$  M  $\text{Na}_2\text{TeO}_3$  in 0.1M  $\text{Na}_2\text{SO}_4$  in different concentrations of  $\text{H}_2\text{CADMP}$  at 50mV/s and at 291K.

**Table (3):** Effect of different concentrations of  $\text{H}_2\text{CADMP}$  at 291K, scan rate 50 mV/s

[M] $\times 10^6$ mol $\text{cm}^{-3}$	$E_{p_a}$ volt	$(-I)_{p_a}$ $\times 10^4$ Amp	$D_a$ $\times 10^6$ $\text{cm}^2/\text{s}$	$\Gamma_a$ $\times 10^9$ mol/ $\text{cm}^2$	$(-Q)_a$ $\times 10^4$ C
(a) For the first wave					
0.629	0.1926	1.60	6.91	4.237	1.61
1.25	0.1965	1.79	8.64	4.736	1.80
1.86	0.1947	1.64	7.29	4.35	1.65
2.47	0.1934	1.62	7.08	4.289	1.63
3.07	0.1918	1.50	6.11	3.983	1.51
3.66	0.188	1.48	5.91	3.916	1.48
4.24	0.1851	1.42	5.46	3.765	1.43
4.82	0.1834	1.40	5.30	3.708	1.41
(b) For the second wave					
0.629	0.482	1.88	9.57	4.983	1.89
1.25	0.4784	1.67	7.56	4.431	1.68
1.86	0.4802	1.82	8.93	4.816	1.83
2.47	0.4819	2.07	11.6	5.483	2.08
3.07	0.4848	2.07	11.6	5.483	2.08
3.66	0.4872	2.10	11.9	5.547	2.10
4.24	0.4895	2.18	12.9	5.778	2.19
4.82	0.4918	2.27	13.9	6.014	2.28

Different scan rates on the oxidation of  $\text{Na}_2\text{TeO}_3$  in presence of  $\text{H}_2\text{CADMP}$  were discussed and the values, cited in Fig. (5) and Table (4), indicated the diffusion control of the oxidation process under consideration.



**Fig. (5):** Cyclic Voltammograms of  $\text{Na}_2\text{TeO}_3$   $5.06 \times 10^{-3} \text{M}$  in  $0.1 \text{M Na}_2\text{SO}_4$  with  $\text{H}_2\text{CADMP}$   $4.82 \times 10^{-3} \text{M}$  at different scan rates

The oxidation stability constant  $\beta_{\text{MX}}$  and Gibbs free energy  $\Delta G$  can be calculated by applying the following equations [17-23].

**Table (4):** Effect of different scan rate on oxidation of  $\text{Na}_2\text{TeO}_3$   $5.06 \times 10^{-3} \text{M}$  in presence of  $\text{H}_2\text{CADMP}$   $4.82 \times 10^{-3} \text{M}$

vmV/s	$E_{\text{pa}}$ (volt)	$(-I_{\text{pa}} \times 10^4)$ (Amp)	$D_{\text{a}} \times 10^6$ ( $\text{cm}^2/\text{s}$ )	$\Gamma_{\text{a}} \times 10^9$ (mol/ $\text{cm}^2$ )	$(-Q_{\text{a}} \times 10^4)$ (C)
(a) For the first wave					
100	0.1865	1.45	2.85	1.922	0.728
50	0.1834	1.40	5.30	3.708	1.41
20	0.1523	1.08	7.84	7.132	2.70
(b) For the second wave					
100	0.5212	3.65	18.0	4.8362	1.83
50	0.4918	2.27	13.9	6.0144	2.28
20	0.4755	2.38	38.1	1.5725	5.96

**Table (5):** Stability constant of the interaction between  $\text{Na}_2\text{TeO}_3$  and  $\text{H}_2\text{CADMP}$

$[\text{M}] \times 10^6$	$[\text{L}] \times 10^6$	$(E_{\text{pa}})_{\text{M}}$ volt	$(E_{\text{pa}})_{\text{C}}$ volt	$\Delta E$ volt	$\text{Log } \beta_{\text{MX}}$	$\Delta G$ KJ/mol
(a) For the first wave						
5.03	0.629	0.1905	0.1926	0.0021	0.8489	-4.7266
5.00	1.25	0.1905	0.1965	0.006	1.6835	-9.3848
4.97	1.86	0.1905	0.1947	0.0042	2.2940	-12.7885
4.94	2.47	0.1905	0.1934	0.0029	2.9041	-16.1895
4.91	3.07	0.1905	0.1918	0.0013	3.4908	-19.4599
4.88	3.66	0.1905	0.188	-0.0025	3.991	-22.2485
4.85	4.24	0.1905	0.1851	-0.0054	4.5139	-25.1637
4.82	4.82	0.1905	0.1834	-0.0071	5.0713	-28.2706
(b) For the second wave						
5.03	0.629	0.482	0.482	0	0.7752	-4.3214
5.00	1.25	0.482	0.4784	-0.0036	1.3512	-7.5323
4.97	1.86	0.482	0.4802	-0.0018	2.0863	-11.6307
4.94	2.47	0.482	0.4819	-0.0001	2.8003	-15.6106
4.91	3.07	0.482	0.4848	0.0028	3.5427	-19.7494
4.88	3.66	0.482	0.4872	0.0052	4.2575	-23.7344
4.85	4.24	0.482	0.4895	0.0075	4.9605	-27.653
4.82	4.82	0.482	0.4918	0.0098	5.6563	-31.5318

Scan rate effect on stability constant was also studied and calculated in Table (6).

$$(E_{1/2})_{\text{C}} - (E_{1/2})_{\text{M}} = 2.303(RT/nF) * (\log \beta_{\text{MX}} + j \log C_{\text{L}}) \quad (\text{Eq. 4})$$

$$\Delta G = -2.303 RT \log \beta_{\text{MX}} \quad (\text{Eq. 5})$$

Where  $(E_{1/2})_{\text{C}}$  is the half-wave potential of  $\text{Na}_2\text{TeO}_3$  in presence of  $\text{H}_2\text{CADMP}$ ,  $(E_{1/2})_{\text{M}}$  is half-wave potential of  $\text{Na}_2\text{TeO}_3$  in absence of  $\text{H}_2\text{CADMP}$ , T is the absolute temperature, R is gas constant (equal  $8.314 \text{ mol}^{-1} \text{ degree}^{-1}$ ) and  $C_{\text{L}}$  is ligand concentration. The oxidation stability constant  $\beta_{\text{MX}}$  and Gibbs free energy of oxidation  $\Delta G$  were calculated and their data cited in Table (5). Valuable oxidation parameters,  $\beta_{\text{MX}}$  and  $\Delta G$  indicate the interaction between  $\text{Na}_2\text{TeO}_3$  and  $\text{H}_2\text{CADMP}$ .

**Table (6):** Scan rate effect on stability constant of the interaction between Na<sub>2</sub>TeO<sub>3</sub> and H<sub>2</sub>CADMP

vmV/s	[M] x10 <sup>6</sup>	[L] x10 <sup>6</sup>	(E <sub>p,a</sub> )M(volt)	(E <sub>p,a</sub> ) C(volt)	ΔE (volt)	Log β <sub>MX</sub>	ΔG (KJ/mol)
For the first wave							
100	4.82	4.82	0.2017	0.1865	-0.0152	4.7909	-26.7076
50	4.82	4.82	0.1905	0.1834	-0.0071	5.0713	-28.2706
20	4.82	4.82	0.1757	0.1523	-0.0234	4.507	-25.1252
For the second wave							
100	4.82	4.82	0.4926	0.5212	0.0286	6.3070	-35.1597
50	4.82	4.82	0.482	0.4918	0.0098	5.6563	-31.5318
20	4.82	4.82	0.4544	0.4755	0.0211	6.0474	-33.7124

## Conclusion

Cyclic voltammetry of Na<sub>2</sub>TeO<sub>3</sub> was done and oxidation was discussed.

Oxidation of Na<sub>2</sub>TeO<sub>3</sub> in presence of 1-Cyanoacetyl-3, 5-dimethyl-1H-pyrazole was illustrated and examined.

Oxidation stability constant and Gibbs free energy of oxidation were evaluated and data proved the electrostatic interaction between the two reagents.

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