

Cyclic Voltammetry of Aqueous CdSO₄- N-(benzol [d] thiazol-2-yl)-3-(2-hydroxybenzylidene) hydrazinyl)-3-oxopropanamide (H₂BTHB) System at 291.15 K in 50% DMSO-H₂O (V/V)

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Abstract: The electrochemical behavior of cadmium ions on glassy carbon electrodes in two-step processes involves reduction at -0.95V and oxidation at -0.6 VVs. Ag/AgCl electrodes has been reported. The cyclic voltammetry data for cadmium ions using potassium chloride as supporting electrolyte in 50 % Demso-H₂O (V/V) shows enhanced currents in the absence and presence of ligand N-(benzol [d] thiazol-2-yl)-3-(2-hydroxybenzylidene) hydrazinyl)-3-oxopropanamide(H₂BTHB). Different cyclic voltammetry solvation data were obtained for cadmium ions in the absence and presence of (H₂BTHB).The obtained cyclic voltammetry and thermodynamic data prove the complexation reaction between the cadmium ions and the used ligand.

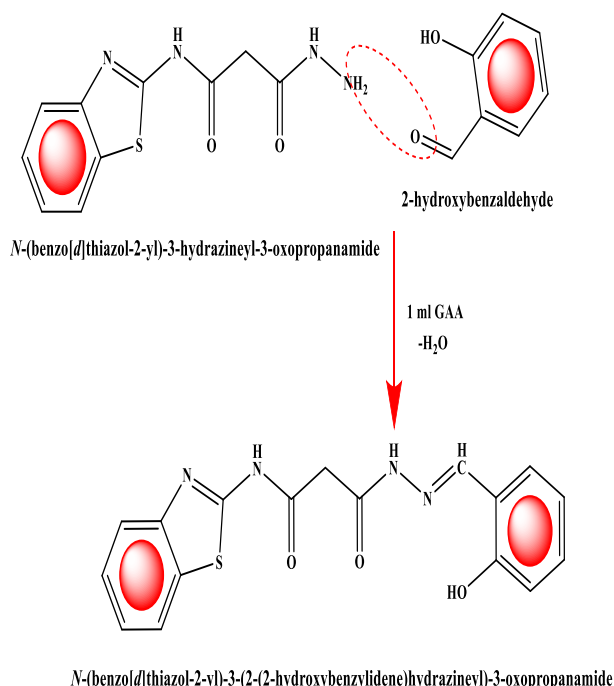
keywords: Cyclic voltammetry, Redox reaction, Electron rate constant, Thermodynamic, kinetic parameters

1.Introduction

Electrochemical redox reactions of cadmium ions in different solutions like the neutral one were studied depending on the applied potential and scan rate cyclic voltammetrically. The effect of scan rate on peak current for different peaks observed in the reduction and oxidation were studied by some authors [1, 2]. Extensive analysis could be performed using cyclic voltammetry technique (CV) for further different possible reactions with cadmium ions. The information of slope of the line was obtained by plotting anodic (*i*_{pa}) and cathodic (*i*_{pc}) peak currents with scan rate. Also, the estimation of true anodic surface coverage (Γ_a) and cathodic surface coverage (Γ_c) can be done for obtaining valuable information about the behavior at the working electrode. The present work confirms the redox mechanism and adds insights on the reduction and oxidation of cadmium ions in CdSO₄ in 0.1 M KCl at 291.15 K. Further the present work studied the interaction of cadmium ions with the used ligand (H₂BTHB).

2. Materials and methods

The preparation of the ligand [3] (H₂BTHB) was shown in Scheme 1:



Scheme 1. The outline synthesis of H₂BTHB ligand Chemicals:

Electrodes:

Three electrode systems were used jointed to DY2000 potentiostat. A commercial glassy carbon electrode was used as a working electrode. The platinum wire auxiliary electrode was used and Ag/AgCl electrode

filled with saturated KCl was used as a saturated reference electrode [4-7].

The chemicals used like potassium chloride are provided from Sigma Aldrich Company, CdSO₄ is provided from Al Gomheria Pharmaceutical Company.

Electrolytes:

Experiments of cyclic voltammetry measurements were done by using 0.1 M KCl in a 50% DMSO-H₂O mixture which was prepared by dissolving KCl in 50% DMSO by volume DMSO/H₂O.

CdSO₄ was dissolved in dist. water. The prepared ligand was dissolved in DMSO. The cell used is a four-neck vessel having a capacity of 100 ml. All glassware was washed with prill soap and then rinsed with de-ionized water.

3. Results and Discussion

Cyclic voltammetry of CdSO₄:

The cyclic voltammograms for different concentrations of CdSO₄ were produced in 0.1M KCl at 291.15K. The resulted data are given in Figure (1), in the range of -1.4V to 0.2V beginning with 0.2 V showing the reduction process firstly then followed by the oxidation process. The range of CdSO₄ concentrations used is from 8.2 x10⁻⁷ to 3.13 x10⁻⁶ mole/cm³. One reduction wave appears at -0.95 V and one oxidation wave at -0.6 V. The electrochemical behavior of CdSO₄ in 0.1M KCl using glassy carbon electrode, two different waves one reduction and the other one is oxidation [8-12].

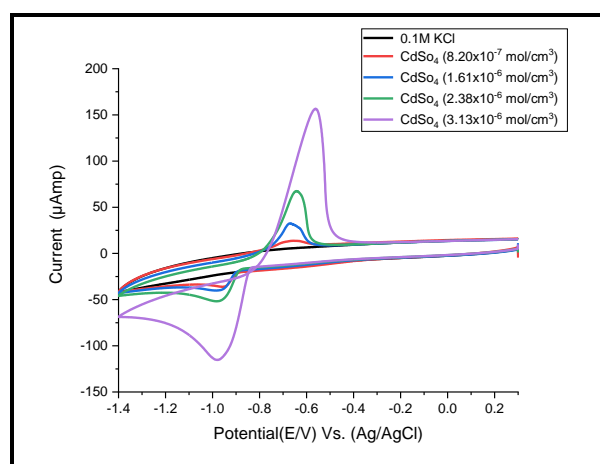


Fig.1. Cyclic voltammogram of different concentrations of CdSO₄

Estimation of the cyclic voltammetry data:

The different equations applied for the redox reaction of CdSO₄ are [13-21]:

$$i_p = 0.4463 n^{3/2} F^{3/2} D^{1/2} AC / CRT)^{1/2} v^{1/2} \quad (1)$$

$$D^{1/2} = (\text{slope}, I_{pvs} v^{1/2}) \times (RT)^{1/2} / 0.4465 n^{3/2} F^{1/2} AC \quad (2)$$

$$\Delta E_p = E_{pa} - E_{pc} = 2.303 RT/nF \quad (3)$$

$$\gamma = (D_a/D_c)^{1/2} \quad (4)$$

Where k_s is the rate constant for electron transfer, v is the rate constant, D_c is the cathodic diffusion coefficient and D_a is the anodic diffusion coefficient. T is the absolute temperature. F is Faraday's constant, n is the electron numbers and A is the surface area of the working electrode. The heterogeneous electron rate constant from solution to working electrode material was evaluated by applying equation (5) [22- 29].

$$k_s = 2.18 * [D_c \alpha_{na} F v / RT]^{1/2} * \exp [\alpha^2 nF (E_{p,c} - E_{p,a}) / RT] \quad (5)$$

The surface coverage of the working electrode was increased by the increase in metal ions concentration.

The cathodic quantity of electricity Q_a can be evaluated by the use of equations [30-33]:

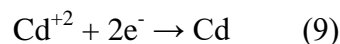
$$Q_c = n \Gamma_c A F \quad (6)$$

$$Q_a = n \Gamma_a A F \quad (7)$$

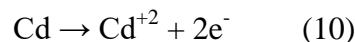
The above parameters can be evaluated for CdSO₄ in 50% (DMSO-H₂O) 0.1M KCl following equations (1-7) and the resulted values are presented in Table (1).

The redox mechanism for CdSO₄ can be presented as follow:

For the reduction process and opposite [38]:



For the oxidation:



The first mechanism is corresponding to the reduction of cadmium ions and the second mechanism is corresponding to the oxidation one.

We noticed the following from Table (1):

1 - ΔE_p is small. Lie in the range of reversible processes.

2 - i_{pa} , i_{pc} are increased by the increase of CdSO₄ concentrations indicating the large increase in the anodic process than the cathodic

one favoring the easier anodic process to happen.

3 - The cathodic D_c and anodic D_a diffusion coefficients are largely increased by the increase in $CdSO_4$ concentrations indicating reversible reaction.

4 - k_s are increased by the increase in $CdSO_4$ concentrations which facilitates the transfer of electrons.

5 - Cathodic surface coverage Γ_c and anodic surface coverage Γ_a is increased by the increase in the concentration of cadmium sulphate favoring more diffusion.

6 - The cathodic quantity of electricity Q_c and the anodic quantity of electricity Q_a is largely increased by the increase in the cadmium ion concentrations supporting also the diffusion mechanism.

Effect of scan rate on $CdSO_4$:

The effect of scan rate on $CdSO_4$ [3.13×10^{-6} mol/cm³] was studied and the resulting shown in Table (2) prove the increase of most data was observed by the decrease of scan rate, indicating the diffusion-controlled reaction. Also, Figure (2) shows the effect of scan rate on the redox reaction of chosen concentration of $CdSO_4$ at 291.15K.

Table (1) Thermodynamic and kinetic parameters of $CdSO_4$ in absence of H_2BTHB at 291.15K and 0.1scan rate

$M \times 10^6$ (mol/cm ³)	(-)Ep,a(Volt)	()Ep,c(v)	ΔEp (volt)	(-) $i_{p,a} \times 10^{-6}$ (Amp)	$i_{p,c} \times 10^{-6}$ (Amp)	$i_{p,a}/i_{p,c}$ (Amp)	(-)E°
0.82	0.694	0.954	0.26	2.56	14.5	0.177	0.824
1.61	0.671	0.969	0.298	27.6	19.8	1.394	0.82
2.38	0.65	0.97	0.32	64.3	33.5	1.918	0.81
3.13	0.565	0.975	0.41	139	96.8	1.437	0.77
$D_a \times 10^{-6}$ (Cm ² /s)	$D_c \times 10^{-6}$ (Cm ² /s)	α_{na}	$k_s \times 10^1$ (Cm/sec)	$\Gamma_c \times 10^{-9}$ (mol/cm ²)	(+) $Q_c \times 10^{-6}$	$\Gamma_a \times 10^9$ (mol/cm ²)	(-) $Q_a \times 10^6$
0.171	5.46	1.491	0.193	1.227	7.43	0.217	1.32
5.116	2.63	1.109	0.243	1.676	10.2	2.337	14.2
12.784	3.47	0.917	0.39	2.843	17.2	5.454	33
34.698	16.8	0.542	3.79	8.204	49.2	11.79	71.5

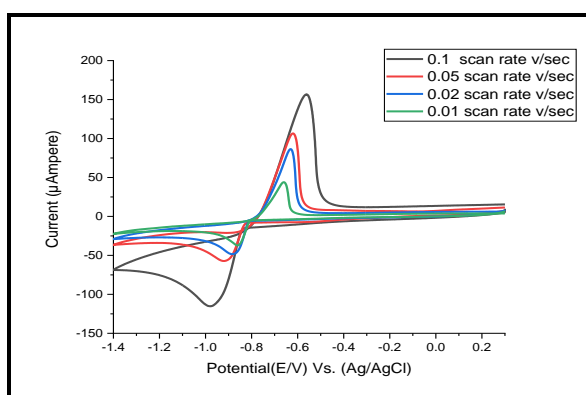


Fig.2. Cyclic voltammogram of $CdSO_4$ at different scan rates at 291.15 K

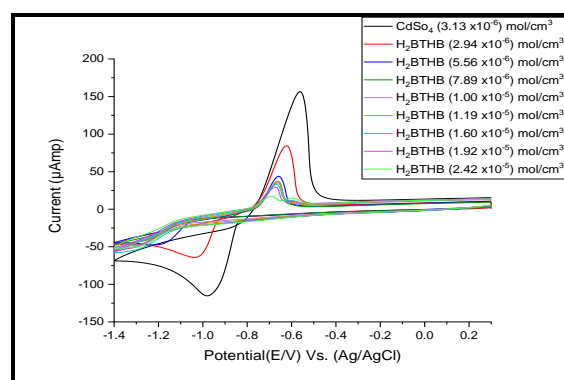


Fig.3. Cyclic voltammogram of $CdSO_4$ in presence of different concentrations of ligand

Table 2 Cyclic voltammetry parameters of $CdSO_4$ [3.13×10^{-6} mol/cm³] at different scan rates in absence of H_2BTHB at 291.15K

(V/sec)	(-)Ep,a(volt)	()Ep,c(volt)	ΔEp (volt)	(-) $i_{p,a} \times 10^{-5}$ (Amp)	$i_{p,c} \times 10^{-5}$ (Amp)	$i_{p,a}/i_{p,c}$ (Amp)	(-)E°
0.1	0.564	0.976	0.412	15.9	9.72	1.637	0.77
0.05	0.623	0.917	0.294	12.2	4.88	2.505	0.77
0.02	0.632	0.882	0.25	8.71	4.19	2.079	0.757
0.01	0.661	0.86	0.199	4.74	3.19	1.489	0.7605
$D_a \times 10^{-5}$ (cm ² /s)	$D_c \times 10^5$ (cm ² /s)	α_{na}	$k_s \times 10^1$ (cm/s ec)	$\Gamma_c \times 10^{-8}$ (mol/cm ²)	(+) $Q_c \times 10^{-4}$	$\Gamma_a \times 10^{-8}$ (mol/cm ²)	(-) $Q_a \times 10^{-4}$
4.54	1.695	0.536	3.94	0.824	0.499	1.349	0.82
5.37	0.856	0.837	0.249	0.828	0.502	2.075	1.26
6.80	1.571	1.037	0.101	1.774	1.08	3.691	2.24
4.04	1.819	1.539	0.0346	2.701	1.64	4.023	2.44

fferent concentrations of the ligand H₂BTHB were added to 3.13 x10⁻⁶ mol/cm³ CdSO₄, within (-1.4 V to 0.2 V) potential range as shown in Figure (3) and the resulted data are given in Table (3). We also noticed the following remarks from Table (3):

1 - Shift of E_{pa}, E_{pc} favoring interaction between CdSO₄ and H₂BTHB.

2 - ΔE_p is increased by the increase of ligand H₂BTHB concentrations favoring complex reaction.

3 - i_{pa} /i_{pc} are decreased in their values than in absence of the ligand favoring interaction between the metal ions and ligand.

4 - D_a and D_c are decreased than that in absence of ligand favoring complex reaction.

5 - α_{na} is slightly decreased by increase of ligand concentration due to the attraction of H₂BTHB with CdSO₄.

6- k_s are increased by the increase in H₂BTHB concentrations which facilitate the electron transfer.

7 -Γ_c and Γ_a are slightly increased by the increase in H₂BTHB favoring interaction between the ligand and metal.

8 - Slight increase of Q_c and Q_a for CdSO₄ and H₂BTHB than CdSO₄ alone.

Table 3 Kinetic and solvation parameters of CdSO₄ in presence of H₂BTHB at 291.15K and 0.1 scan rate

M x10 ⁻⁶ (mol/cm ³)	L x10 ⁻⁶ (mol/cm ³)	(-)E _{p,a} (volt)	(-)E _{p,c} (volt)	ΔE _p (volt)	(-)I _{p,a} x10 ⁵ (Amp)	I _{p,c} x10 ⁻⁵ (Amp)	I _{p,a} /I _{p,c} (Amp)	(-)E°
2.94	2.94	0.694	0.954	0.26	0.256	1.45	0.177	0.824
2.78	5.56	0.671	0.969	0.298	2.76	1.98	1.394	0.82
2.63	7.89	0.65	0.97	0.32	6.43	3.35	1.918	0.81
2.50	10.0	0.565	0.975	0.41	13.9	9.68	1.437	0.77
2.38	11.9	0.624	1.033	0.409	7.18	5.13	1.399	0.828
2.13	16.0	0.66	1.205	0.545	3.68	3.34	1.099	0.932
1.92	19.2	0.664	1.257	0.593	3.15	2.74	1.149	0.96
1.61	24.2	0.665	1.26	0.595	2.85	2.52	1.129	0.962
D _a x10 ⁻⁶ (cm ² /s)	D _c x10 ⁻⁶ (cm ² /s)	α _{na}	k _s x10 ¹ (Cm/sec)	Γ _c x10 ⁻⁹ (mol/cm ²)	(+) Q _c x10 ⁻⁵	Γ _a x10 ⁻⁹ (mol/cm ²)	(-) Q _a x10 ⁻⁵	
0.171	5.46	1.491	0.193	1.226	0.74	0.217	0.13	
5.116	2.63	1.109	0.243	1.676	1.02	2.337	1.42	
12.78	3.47	0.917	0.389	2.843	1.72	5.454	3.30	
34.69	16.8	0.542	3.79	8.204	4.97	11.79	7.15	
10.44	5.33	0.712	2.40	4.349	2.64	6.087	3.69	
3.073	2.54	0.507	19.7	2.836	1.72	3.119	1.89	
2.505	1.89	0.782	53.8	2.32	1.41	2.668	1.62	
2.272	1.78	0.712	51.8	2.138	1.30	2.414	1.46	

Effect of different scan rates on CdSO₄- H₂BTHB complex at 291.15K:

Effect of different scan rates was studied for the interaction of Cd⁺² with H₂BTHB and the resulted data are shown in Figure (4). Most of the data given in Table (4) are decreased with the decrease in scan rate Γ_c, Γ_a, Q_c and Q_a

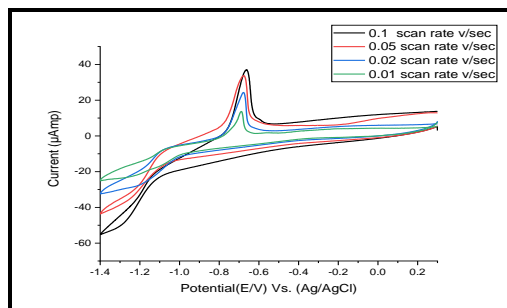


Fig.4. Cyclic voltammogram of CdSO₄ at different scan rates in presence of H₂BTHB and at 291.15 K

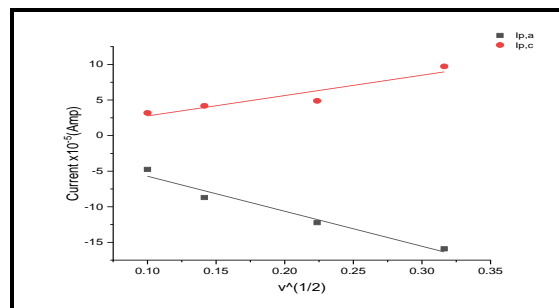


Fig.5. Relation (I_p Vs. v^{1/2}) for CdSO₄ at final adding in different scan rates at 291.15 K in absence of H₂BTHB

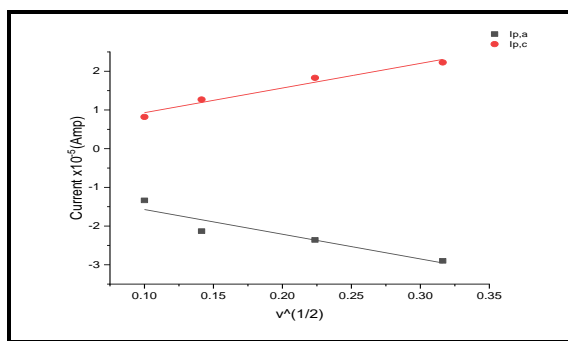


Fig.6. Relation (i_p Vs. $v^{1/2}$) for $CdSO_4$ at final adding by the molar ratio (1:1) in presence of H_2BTHB at different scan rates

On drawing the relation between peak currents i_p and the square root of scan rate $v^{1/2}$, straight lines were obtained as shown in

Figures (5, 6). The slopes of the two lines indicate the diffusion-reaction mechanism in the presence and absence of H_2BTHB .

Thermodynamic parameters for interaction of Cd^{+2} with H_2BTHB : We used the Langmuir equation as explained in previous work [39] to calculate the stability constant and Gibbs free energies of complexation for the interaction of $CdSO_4$ with H_2BTHB . The evaluated data were given in Table (5) with the effect of scan rate data shown also in Table (6). Very large thermodynamic stability constant β and Gibbs free energy ΔG of complexation were obtained indicating very strong complexation interaction is happened for the interaction of Cd^{+2} with H_2BTHB forming very strong covalent bonds

Table 4 Effect of different scan rates on Cd- H_2BTHB complex at 291.15K

v (V/sec)	(-) $E_{p,a}$ (volt)	(-) $E_{p,c}$ (volt)	ΔE_p (volt)	(-) $I_{p,a} \times 10^{-5}$ (Amp)	$I_{p,c} \times 10^{-5}$ (Amp)	$I_{p,a}/I_{p,c}$ (Amp)	(-) E°
0.1	0.665	1.286	0.621	2.90	2.23	1.301	0.975
0.05	0.678	1.257	0.579	2.36	1.83	1.288	0.967
0.02	0.681	1.193	0.512	2.13	1.27	1.677	0.937
0.01	0.689	1.2	0.511	1.34	0.82	1.628	0.944
$D_a \times 10^{-6} (cm^2/s)$	$D_c \times 10^{-6} (cm^2/s)$	α_{na}	$k_s \times 10^4 (cm/sec)$	$\Gamma_c \times 10^{-9} (mol/cm^2)$	(+) $Q_c \times 10^{-5}$	$\Gamma_a \times 10^{-9} (mol/cm^2)$	(-) $Q_a \times 10^{-5}$
2.597	1.53	0.645	75.9	1.889	1.14	2.458	1.49
3.44	2.072	0.604	26.6	3.105	1.88	4.001	2.42
7.015	2.493	0.555	4.81	5.386	3.26	9.033	5.47
5.52	2.081	0.5547	3.05	6.958	4.22	11.33	6.87

Table 5 : Stability constant for $CdSO_4$ in presence of H_2BTHB by the molar ratio (1:1) at 291.15K

$M \times 10^{-6} (mol/cm^3)$	$L \times 10^{-6} (mol/cm^3)$	$E^\circ M$	$E^\circ C$	ΔE (mv)	$\log \beta_{MX}$	ΔG (KJ/mol)
2.94	2.94	-0.77	-0.828	0.058	4.556	-25.401
2.78	5.56	-0.77	-0.932	0.162	10.135	-56.502
2.63	7.89	-0.77	-0.96	0.19	12.902	-71.926
2.50	10	-0.77	-0.962	0.192	14.663	-81.744
2.38	11.9	-0.77	-0.973	0.203	16.665	-92.906
2.13	16	-0.77	-0.981	0.211	20.799	-115.947
1.92	19.2	-0.77	-0.994	0.224	24.914	-138.887
1.61	24.2	-0.77	-1.005	0.235	32.379	-180.503

Table 6: Effect of scan rate on stability constant of Cd- H_2BTHB by the molar ratio (1:1)

v (V/se)	$E^\circ M$	$E^\circ C$	ΔE (mv)	$\log \beta_{MX}$	ΔG (KJ/mol)
0.1	-0.77	-0.975	0.205	9.645	-53.767
0.05	-0.77	-0.967	0.197	9.368	-52.224
0.02	-0.757	-0.937	0.18	8.762	-48.846
0.01	-0.76	-0.944	0.184	8.901	-49.618

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