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Original Research Article

Thermodynamic data (voltammetrically) estimated for the interaction of nano cadmium chloride (Ncc) with isatin using glassy carbon electrode

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ABSTRACT

The redox behavior for nano cadmium chloride (Ncc) was studied using cyclic Voltammetry in the absence and presence of isatin (Isa) on the use of carbon glassy electrode (CGE)prepared in our laboratory in 0.1M KCl electrolytic solution at two different temperatures. All cyclic voltamograms were carried out at the two selected temperatures in the absence and presence of isatin (Isa) as ligand. The redox reactions and reaction mechanism were suggested. All available cyclic Voltammetry and thermodynamic data were calculated from cyclic Voltammetry measurements and their values were explained for the interaction of nano $CdCl_2$ with isatin (Isa).

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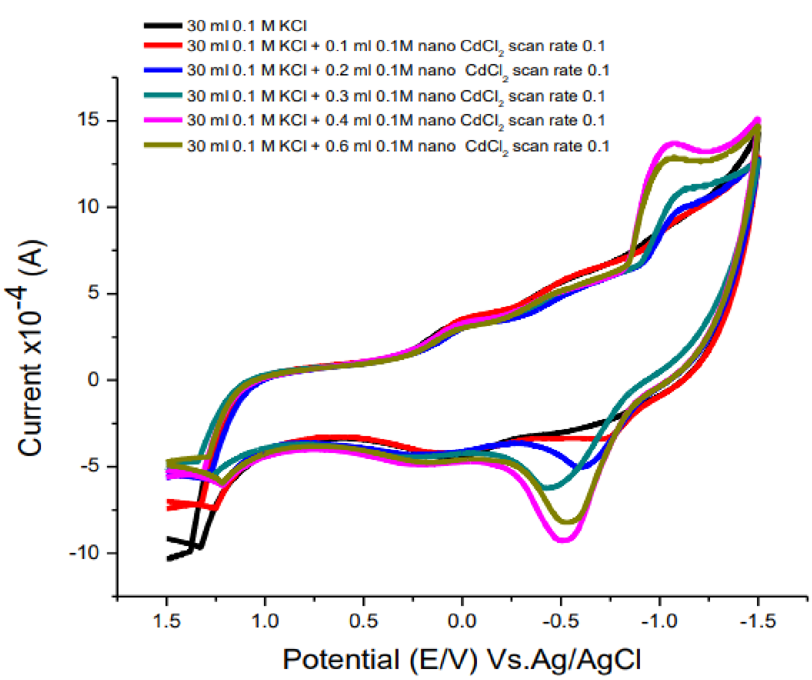
Graphical Abstract



Introduction

Heavy metal ions like cadmium ions are dangerous pollutants in environment [1-3]. Some experimental methods for the removal of heavy elements are used with a combination for different techniques such as membrane and electrolysis [3-5]. The extraction of heavy metal ions as pollutants from water pollution, using electrochemical methods, is important [6-9]. Several metal ions in solutions can be recovered by reduction at the cathode. The recovery and extraction of metals from Ni-Cd batteries have been studied [10, 11]. Cadmium ion is highly toxic and responsible for poisoning the food. Binding Cd with organic compounds is a treatment for remediation of Cd in vivo and vitro [12, 13]. In this work electrochemical cyclic Voltammetry behavior of nano cadmium ions in chloride form was studied.

Experimental

The used chemicals $CdCl_2$, KCl, Isatin are of high purity 98% of the Sigma Aldrish Company. Pure water was used after distillation. The cell has three electrodes connected to potentiostat DY2000, Ag/AgCl, KCl_{sat} was used as reference electrode, carbon glassy electrode (CGE) was used as working electrode, and platinum wire as auxiliary electrode. The electrochemical studies were done in a potentiostat of the type DY2000.Flow of purified N_2 was done to ensure diffusion experiment. The carbon glassy electrode (CGE) is locally prepared in our laboratory from pure carbon piece and polished with fine aluminium oxide on wool piece. Area of electrode is 0.502 cm^2. All cyclic Voltammetry parameters are measured at the selected two temperatures 26.5 and 40 °C using ultra thermostat of the type Assistant 3193.

The nano cadmium chloride (Ncc) was prepared by the ball milling method, it is technically used for reducing material particle size. This nano cadmium chloride (Ncc) was prepared by being shaken in a ball-mill apparatus of type Retsch MM2000 swing mill for a period of two days. The mill contains 10 cm^3 stainless steel tubes and Three stainless steel balls of 12 mm diameter were used. After the ball milling process which was performed at 20225 Hz at room temperature, the particles have a nano size. The nanoparticles were investigated using JEM-2100 TEM, Transmission electron microscope in Mansoura University.

Results and Discussion

TEM Image for nano cadmium chloride (Ncc)

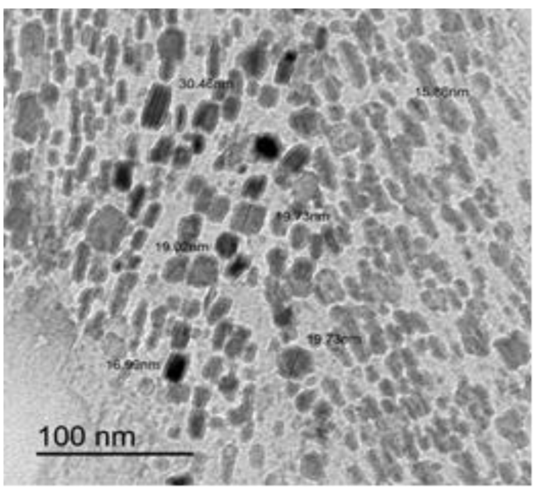


Figure 1. The TEM image of nano cadmium chloride (Ncc) from JEM-2100 TEM, transmission electron microscope

From this image with 72,000 X, we conclude that the nano cadmium chloride is in the form of a nano scale and dimensions of particles lie between 15.86 and 30.46 nm.

Electrochemical behavior of nano cadmium chloride (Ncc) in absence of (Isatin)

The electrochemical behavior of nano cadmium ions in carbon glassy electrode (CGE) was examined and hemi cycle waves were obtained. Cyclic Voltammetry of cadmium ions show charge transfer at the carbon glassy electrode (CGE) in 0.1 M KCl. Ag/AgCl was used as a reference electrode to follow the redox of Cd(II) ions in aqueous solution. One cathodic peak and one anodic peak were observed according to the suggested mechanism:

Cathodic reaction $Cd^{2+} + 2e^{-} \rightarrow Cd$

Anodic reaction $Cd \rightarrow Cd^{2+} + 2e^{-}$

Effect of metal ion concentrations

Effect of cadmium ion concentrations for nano cadmium chloride (Ncc) was examined at two selected temperatures, 26.5 and 40 °C.Cyclic voltammograms for different concentrations from 3.3×10^{-4} till 1.96×10^{-3} $mol.L^{-1}$ in 0.1 M KCl were done.

It was found that peak current gradually and linearly increases with increase in metal ion (salt) concentration due to the presence of ions active species at the carbon glassy electrode (CGE) as shown in Figures 2-4, at the two different temperatures.

Figure 4 illustrates the effect of raising the temperature on the redox behavior of nano $CdCl_2$. It was observed that increasing temperature increases the peak current for the two redox waves.

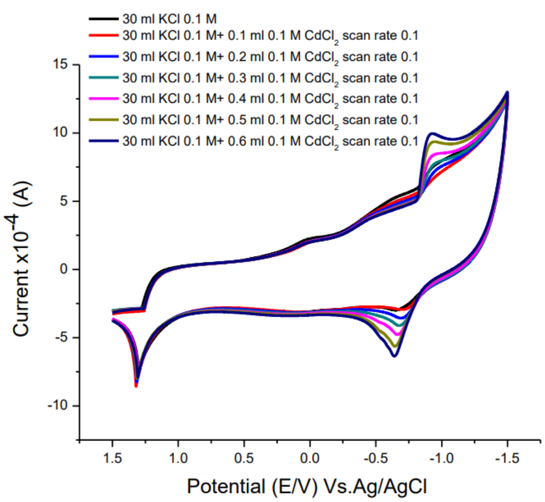


Figure 2. Different cyclic voltammograms for different nano $CdCl_2$ concentrations in 0.1M KCl at 26.5 °C

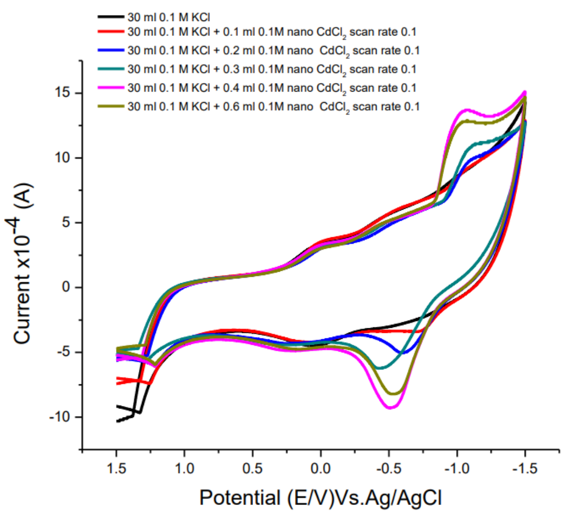


Figure 3. Different cyclic voltammograms for different nano $CdCl_2$ concentrations in 0.1 M KCl at 40 °C

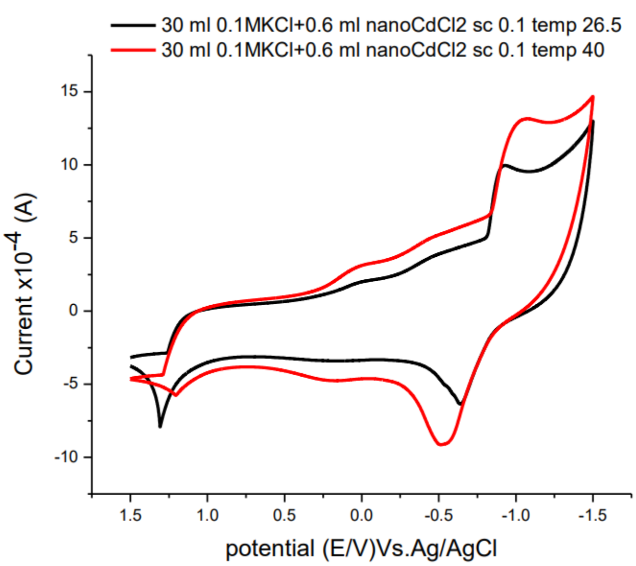


Figure 4. The effect of temp on redox behavior of nano $CdCl_2$

Effect of different scan rates

Effect of scan rate of the redox behavior of and nano $CdCl_2$ (Ncc) in 0.1 M KCl was studied in the range 0.01, 0.02, 0.05 and 0.1 ($V.s^{-1}$) as given in Figures 5 , 6. The different cyclic Voltammetry analysis data were calculated and the obtained data are Ip_a (anodic current), Ip_c (cathodic current), ΔE_P (difference in potentials), D_a (anodic Diffusion coefficient), D_c (cathodic diffusion coefficient), $E_{1/2}$ (half wave potential), K_s (electron transfer rate constant) , Γa (anodic surface coverage), Γc (cathodic surface coverage), q_a (anodic quantity of electricity) and q_c (cathodic quantity of electricity) and **α** na (transfer coefficient). Quasireversible mechanism was observed in the redox behavior of bulk and nano $CdCl_2$ (Ncc) in 0.1 M KCl from all cyclic Voltammetry CV analysis data and specially Ip_a/Ip_c. Increase of scan rate is followed by increasing in the diffusion parameters, especially, K_s,Γ_a,Γ_c ,q_a and q_c indicating the increased in the diffusion process by an increase in scan rate as the data given in Tables 1, 2.

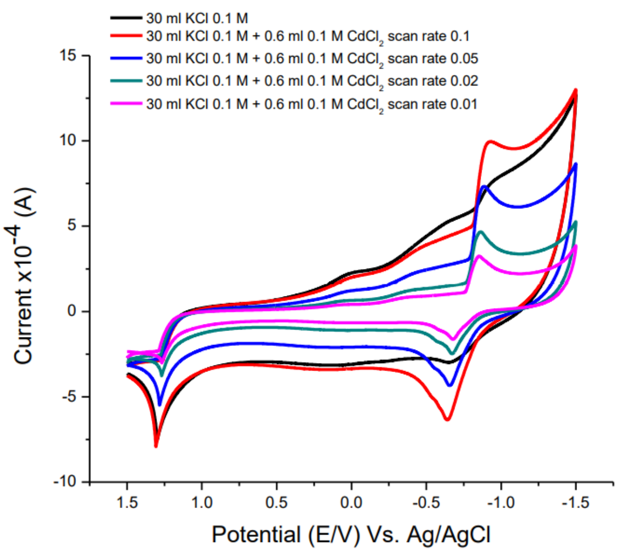


Figure 5. Different scan rates of 1.96×10^{-3} M nano $CdCl_2$ at 26.5 °C

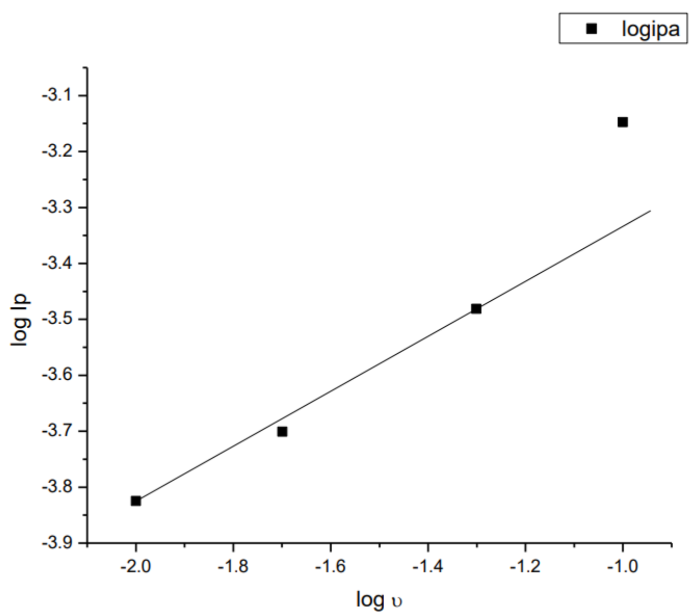


Figure 6. The relation between log Ip_a and logν of 1.96×10^{-3} M nano $CdCl_2$ at 26.5 °C

The relationship between log Ip and log giving straight lines indicate that the redox mechanisms are diffusion controlled for nano $CdCl_2$ in 0.1 M KCl. Randles Sevick equation was used for the relation between peak current (anodic and cathodic) and square root of scan rate which gives straight lines. In this sense, it indicates that the redox reaction is the diffusion process.

The electrochemical behavior of bulk and nano $CdCl_2$ (Ncc) in presence of isatin in aqueous solution

Effect of different isatin concentrations

Figures 7 and 8 represent the electrochemical behavior of complex interaction between nano $CdCl_2$ (Ncc) and ketone (isatin) in 0.1 M KCl at the two selected temperatures 26.5 and 40 °C. As shown from the previous figures by increasing the isatin concentration, the peak currentdecreases due to decreasingof concentration of dissolved cadmium ions at the carbon glassy electrode (CGE). Also, peak potentionl shifts to more negative values in case of oxidation and more positive value shift in case of reduction indicate complex formation.

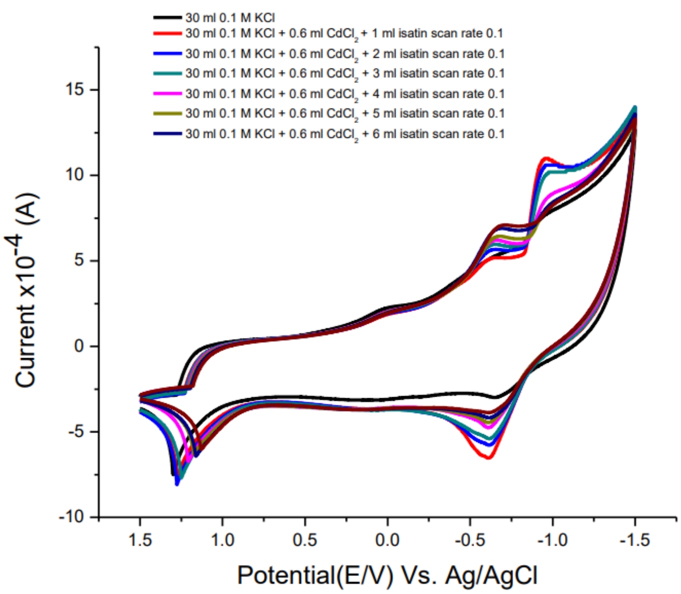


Figure 7. Cyclic voltammograms for interaction of 1.96×10^{-3} M nano $CdCl_2$ and different concenterations of isatin at 26.5 °C.

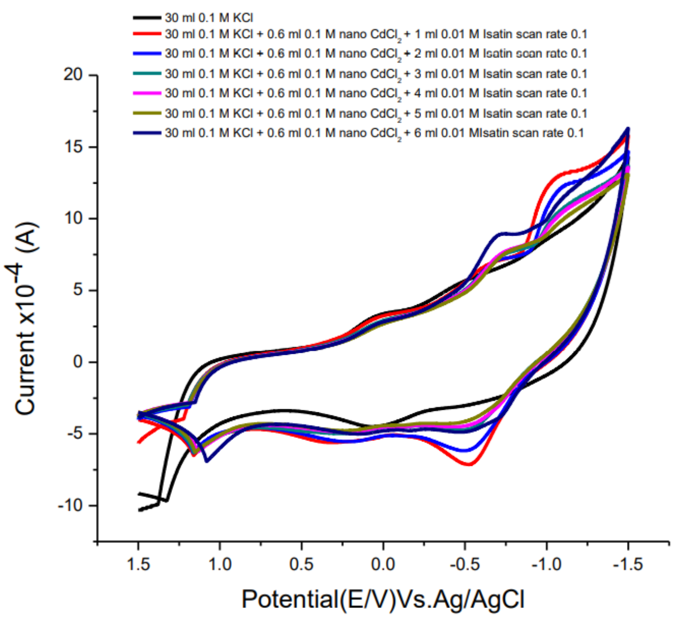


Figure 8. Cyclic voltammograms for interaction of 1.96×10^{-3} M nano $CdCl_2$ and different concenterations of isatin at 40 °C

Figures 7 and 8 illustrates that temperature causes more decrease in peak current (anodic and cathodic) which means that the complex formation reaction became more accelerated by increasing temperature. It is also worth mentioning that the reaction was an endothermic one.

Effect of different scan rates

Effect of scan rate on the interaction between bulk,nano $CdCl_2$ and Ketone Isatin was studied in 0.1, 0.05, 0.02 and 0.01 V.s^{-1} Figure 9.

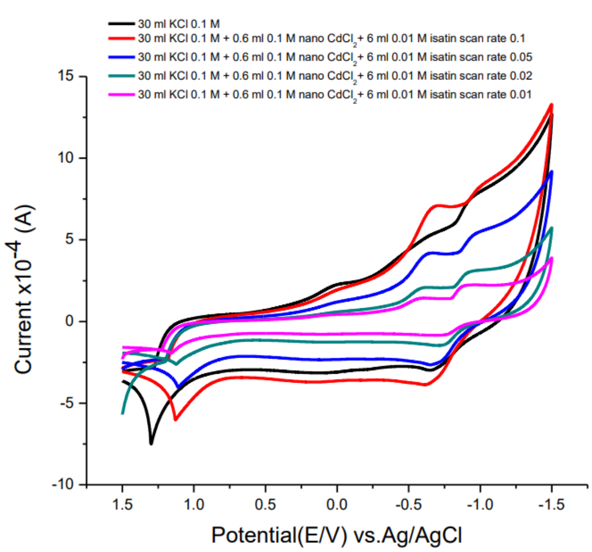


Figure 9. Different scan rates of 1.96×10^{-3} M nano $CdCl_2$ interacted with 1.63 x 10^{-3} M isatin at 26.5 °C.

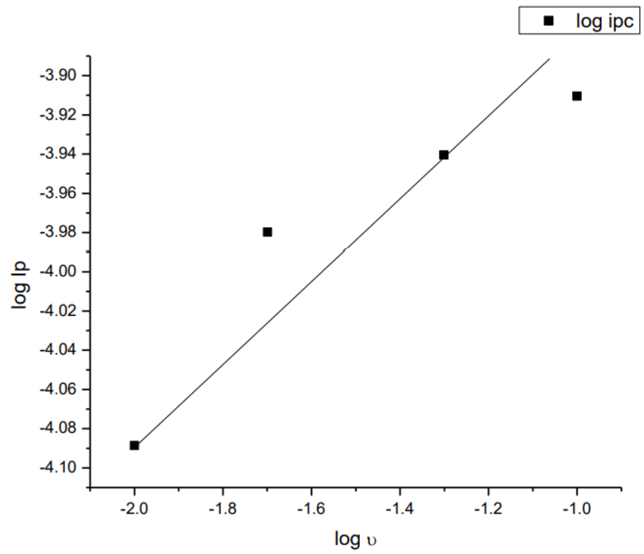


Figure 10. The relation between log Ip_c and log ν of 1.96×10^{-3} M $CdCl_2$ interacted with 1.63×10^{-3} M isatin at 26.5 °C

Figure 11 illustrates the relation between log Ip and log ν for interaction between nano $CdCl_2$(Ncc) in 0.1 M KCl giving straight lines. Besides, it indicates the reversibility of the mechanisms and the redox mechanisms which are diffusion controlled. Randless Sevicek equation was used to apply the relation between peak current (anodic and cathodic) and square root of scan rate which gives straight lines.

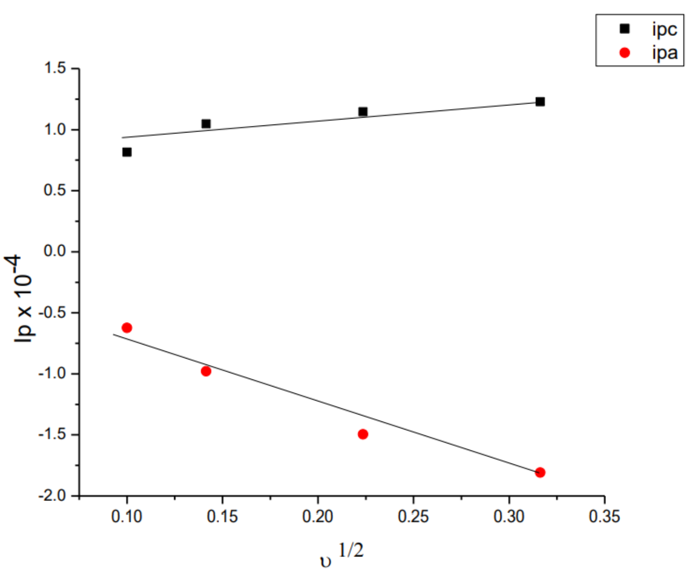


Figure 11. The relation between Ip_c ,IP_a and $\nu^{1/2}$ of 1.96×10^{-3} M nano $CdCl_2$ interacted with 1.63×10^{-3} M isatin at 26.5 °C.

Table 1. Effect of different scan rates for interaction between 1.96×10^{-3} M nano $CdCl_2$ (Ncc) and 1.63×10^{-3}M isatin(ketone) at 26.5 °C on the diffusion parameters

Scan rate ($V.S^{-1}$)	mL added (mL)	[L] (mol.L-1)	Ipa x10^{-5} (A)	Ipc x10^{-5} (A)	Ipa/Ipc	Epa (V)	Epc (V)	ΔEp (V)	E ½ (V)
0.1	6	0.00163	18.10	12.30	1.4722	-0.6722	-0.9965	0.3242	0.8343
0.05	6	0.00163	14.90	11.50	1.3036	-0.7017	-0.9521	0.2503	0.8269
0.02	6	0.00163	9.79	10.50	0.9343	-0.7383	-0.9304	0.1920	0.8343
0.01	6	0.00163	6.23	8.15	0.7638	-0.7461	-0.8930	0.1469	0.8195

Table 2. Cont. effect of different scan rate for interation between 1.96×10^{-3} M nano $CdCl_2$ (Ncc) and $1.63x10^{-3}$ M isatin(ketone) at 26.5 °C on the diffusion parameters

Scan rate ($V.S^{-1}$)	mL added (mL)	[L] (mol.L^{-1})	Da x10 -14 ($cm^2.s^{-1}$)	Dc x10^{-14} ($cm^2.s^{-1}$)	Ks x10^{-6} ($cm.s^{-1}$)	Γa x10^{-10}($mol.cm^{-2}$)	Γc x 10-10 ($mol.cm^{-2}$)	qa x10^{-5} (C)	qc x10^{-5} (C)	**α**na
0.1	6	0.00163	59.27	27.34	3.13	9.68	6.57	9.34	6.34	0.3241
0.05	6	0.00163	40.46	23.81	2.74	7.99	6.13	7.71	5.92	0.4322
0.02	6	0.00163	17.34	19.87	2.12	5.23	5.60	5.05	5.40	0.5864
0.01	6	0.00163	7.02	12.03	1.49	3.33	4.36	3.21	4.20	0.8098

The equations used for the electrochemical cyclic Voltammetry calculations [14-17]

$$Ip = \frac{0.4463\, n^{3/2} F^{3/2} D^{1/2} AC}{(RT)^{1/2}}\, \nu^{1/2} \quad \text{Randless Sevick equation} \qquad (1)$$

$$D^{1/2} = (\text{slope, } I_p \text{ Vs. } \nu^{1/2}) \times \frac{(RT)^{1/2}}{0.4463\, n^{3/2} F^{3/2} AC} \qquad (2)$$

$$\Delta E_p = Ep_a - Ep_c = 2.303 \frac{RT}{nF} \qquad (3)$$

$$\varphi = \frac{\gamma^{\alpha} Ks}{\sqrt{\pi \frac{nf}{RT} \nu Da}} \qquad (4)$$

$$\gamma = \sqrt{\frac{Da}{Dc}} \qquad (5)$$

Where φ, charge transfer parameter taken as one for better approximation[13], **α** charge transfer coefficient, K_s standard rate constant for electron transfer coefficient, ν scan rate, D_a diffusion coefficient for the reduced species, D_c diffusion coefficient of the oxidized species, n electrons, F faraday constant, R gas constant and T is the absolute temperature for the experiment , **α** = 0.5 which can be used for a good approximation for calculations, A is the area of the electrode used [18-20].

The complex stability constant measuring the strength and power of the interaction between $CdCl_2$ and isatin (Isa) is important. The complexation stability constant (β) nano $CdCl_2$ (Ncc) complexes in 0.1 M KCl are calculated by applying Equation 7. [13, 16-18]

$$(E_P)_C - (E_P)_M = 2.303 \frac{RT}{nf} \log \beta_c + 2.303 \frac{RT}{nf} \log C_L \qquad (7)$$

Where $(E_P)_M$ is peak potential for metal in absence of ligand, $(E_P)_C$ is peak potential of the complex, R gas constant, C_L analytical concenteration of ligand (ketone) isatin (Isa). Gibbs free energies of interaction, solvation of nano $CdCl_2$ (Ncc) with ketone isatin (Isa) was calculated [21, 22] using Equation 8.

$$\Delta G = - 2.303\, RT \log \beta c \qquad (8)$$

Enthalpy (ΔH) of complex formation reaction between nano $CdCl_2$ (Ncc) with isatin (Isa) was calculated using Equation 9 [17-20].

$$\text{Log} \frac{\beta 2 \text{ at } T2}{\beta 1 \text{ at } T1} = \frac{\Delta H}{2.303\, R} \left(\frac{T2 - T1}{T1T2}\right) \qquad (9)$$

Where β_1 is a complex stability constant at lower temperature T_1 (26.5 °C), β_2 is the complex stability constant at higher temperature T_2 (40 °C).

The entropy (ΔS) for bulk CdCl2 and nano $CdCl_2$ (Ncc) at the two used temperatures iscalculated by using Equation (10)

$$\Delta G = \Delta H - T\Delta S \qquad (10)$$

Table 3. Solvation parameters for the interaction between nano $CdCl_2$ (Ncc) and isatin (ketone) at 26.5 °C

T °C	T °K	mL added	[L] (mol.L^{-1})	E ½ C (V)	E ½ M (V)	ΔE ½ (V)	βj	ΔG(KJ)
26.5	299.5	1	0.00031	0.7900	0.7826	0.0073	5600.08	-21.49
26.5	299.5	2	0.00061	0.7900	0.7826	0.0073	2888.65	-19.84
26.5	299.5	3	0.00089	0.7935	0.7826	0.0108	2603.16	-19.58
26.5	299.5	4	0.00115	0.7974	0.7826	0.0147	2717.68	-19.69
26.5	299.5	5	0.00140	0.8195	0.7826	0.0369	12455.29	-23.48
26.5	299.5	6	0.00163	0.8343	0.7826	0.0517	33526.41	-25.95

Table 4. Solvation parameter for the interaction between nano $CdCl_2$ (Ncc) and isatin (ketone) at 40 °C

T °C	T °K	mL added	[L]	E ½ c (V)	E ½ m (V)	ΔE ½ (V)	*βj*
40	313	1	0.00031	0.7939	0.7826	0.0112	7287.88
40	313	2	0.00061	0.8087	0.7826	0.0260	11241.93
40	313	3	0.00089	0.8118	0.7826	0.0291	9727.69
40	313	4	0.00115	0.8304	0.7826	0.0478	29966.79
40	313	5	0.00140	0.8343	0.7826	0.0517	32912.29
40	313	6	0.00163	0.8674	0.7826	0.0847	326875.77

Table 5. Solvation parameter for the interaction between nano CdCl2 (Ncc) and isatin (ketone) at 40 °C

T °K	T °C	mL added	[L]	ΔG(KJ)	ΔH(KJ)	ΔS(KJ)
40	313	1	0.00031	-23.1488	15.21	0.1225
40	313	2	0.00061	-24.2769	78.46	0.3282
40	313	3	0.00089	-23.9004	76.11	0.3195
40	313	4	0.00115	-26.8288	138.59	0.5285
40	313	5	0.00140	-27.0728	56.10	0.2657
40	313	6	0.00163	-33.048	131.49	0.5256

From data in Tables 3, 4, 5 we deduce that interaction between nano $CdCl_2$ and isatin (Isa) leads complex is formed with high stability , cleared from the values of βj Increasing temperature accelerate complex formation in case of nano salt because values of βj at higher temperature are higher than at lower temperature.Enthalpy change are positive which indicate endothermic reaction.All the thermodynamic data support the formation of a complex between nano $CdCl_2$ (Ncc) and isatin (Isa).

Conclusion

As shown from all cyclic voltamograms for nano $CdCl_2$ (Ncc), one cathodic peak and one anodic peak were observed at the carbon glassy electrode (CGE) with a suggested reaction mechanism including two electrons $Cd^{2+} + 2e^{-} \leftrightharpoons Cd$

- The relationship between log Ip and log*v* which gives straight line indicates the reversibility and the diffusion controlled mechanism.
- The redox reaction of nano salt was affected by temperature.
- The complex formation reaction was accelerated by increasing the temperature.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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