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Full Paper

Cyclic Voltammetry of Nano Cadmium Chloride (NCCl) with Glycine using Glassy Carbon Electrode

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Abstract

The nano cadmium chloride (NCCl) was prepared by ball milling of normal $CdCl_2$. The redox behavior for nano cadmium chloride (NCCl**)** was explained by Cyclic Voltammetry in the presence and absence of ligand Glycine using glassy carbon electrodes in 0.1M HCl supporting electrode. Scan rates were done for explaining the redox behaviors for cadmium chloride in absence and in the presence of amino acid, glycine. Stability constants for the interaction of cadmium chloride with glycine were evaluated.The stability constants and Gibss free energies of interaction evaluated for interaction between nano cadmium chloride (NCCl) and glycine in 0.1M HCl are decreased by increasing nano cadmium chloride concentrations favoring more complex interactions. All mechanisms were discussed.

Keywords: Cyclic Voltammetry, Nano cadmium chloride (NCCl**)** , glassy carbon electrode, Glycine.

1. Introduction

Cadmium chloride was used in the synthesis of ketones from alkyl chlorides. These reagents have largely been supported by organo- copper compounds, which are much less toxic [1]. Glycine was first isolated from gelatin [2] and also it is biosynthesized in the body from the amino acid serine, which is in turn derived from 3-phosphoglycerate, but the metabolic capacity for glycine biosynthesis does not satisfy the need for collagen synthesis[3,4]. Its structure is shown in HOMO and LUMO orbital distribution calculated by Gaussian09 is shown in Fig. 1 and the calculated results are also shown in Table 1 with dipole moment of 14 D indicating the high activity of glycine in water. Also the calculated Gaussian data for glycine in water proves that the energy level of last HOMO orbital is -0.1713 ev and 0.05805 ev for first LUMO orbital.

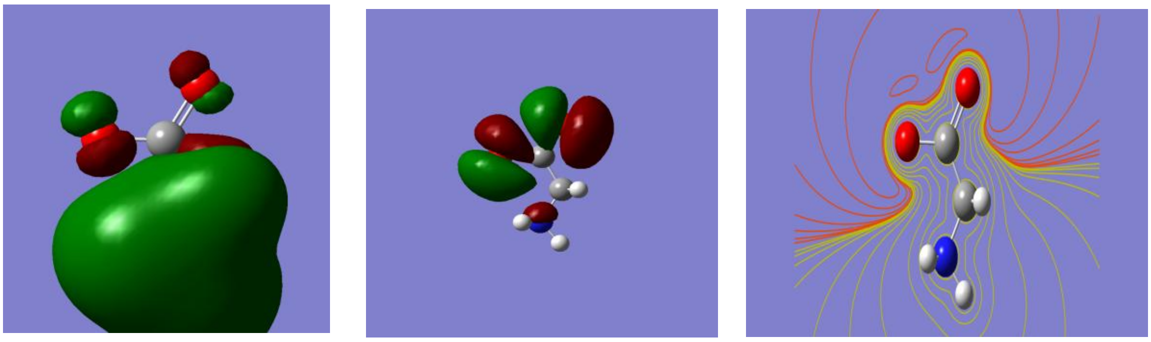

Fig. 1: HOMO and LUMO orbital's and counters structure for glycine in water.

Table 1 : Properties of Glycine calculated by Gaussian09

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Title Card Required **File Name = GLYCINE NONAME 01 WATER** **File Type = .log** **Calculation Type = SP** **Calculation Method = RB3LYP** **Basis Set = 3-21G** **Charge = 0** **Spin = Singlet** **E(RB3LYP) = -282.76432786 a.u.** **RMS Gradient Norm = a.u.** **Imaginary Freq =** **Dipole Moment = 14.0130 Debye** **Point Group = CS** **Job cpu time: 0 days 0 hours 0 minutes 43.0 seconds.**

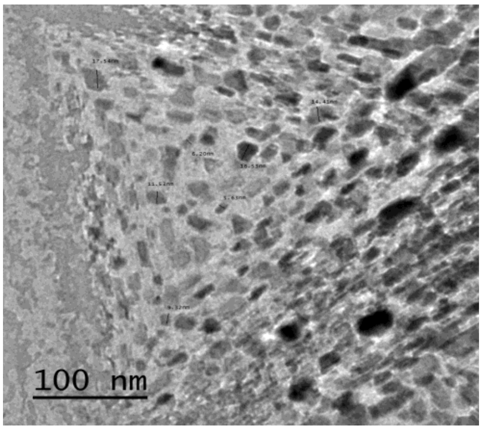

Fig. 2: TEM Image of nano cadmium chloride (NCCl).

2. Experimental

2.1 Preparation of Nano Cadmium Chloride (NCCl) Salt

The nano cadmium chloride material studied in the study was prepared using a ball milling technique by the use of Retsch MM 2000 swing mill with 10 cm^3 stainless steel double walled tube. The cadmium chloride solutions used is prepared by the use Al Nasr Chemicals Company materials. In ball milling two balls, stainless steel, diameter of 12 mm were used, the ball milling process was performed at 20225 Hz and balling process was done usually at room temperature for one hour. The temperature was kept at room temperature during the material preparation.

2.2 Experimental Measurements

DY2000 Multichannel Potentiostat was used for voltammetry measurement. Voltammetry analyzer were done using conventional three - electrode electrochemical cell to perform cyclic voltammetry (CV). Measurements were done by using glassy carbon made in our laboratory from pure carbon piece, polished with alpha aluminum oxide using wool piece, as working electrode with an area of 0.64 cm2, platinum wire electrode as a counter electrode and Ag/AgCl standard electrode.

2.3 Cyclic Voltammetry Measurements (CV)

Cyclic voltammetry is the most common technique used to study the electrochemical systems obtained in undivided glass cell of 30 ml solution by utilizing the three electrodes mentioned above. Cyclic voltammetry experiments were carried out using different concentrations of nano cadmium chloride in water at 19.3°C. HCl (0.1M) as supporting electrolyte was used at different scan rates. After each run, the working electrode was cleaned and polished with aluminum oxide (α alumina), rinsed with distilled water to obtain reproducible results. Nitrogen gas was passed for (10) minutes before each experiment.

3. Results and Discussion

3.1 TEM Image for Nano $CdCl_2$

The picture from the TEM transmission electron microscope is presented for nano cadmium chloride (NCCl). The image in Fig. 2, which shows the crystalline forms of nano cadmium chloride, indicates that nano cadmium chloride is either in the form of irregular spheres or in the form of distorted spheres. In this image, boundaries ranging from 9 to 27.2 nm were shown .

3.2 Cyclic Voltammetry Analysis

The interaction of nano cadmium chloride with glycine has been studied using cyclic voltammetry technique in the potential range (+1.5 to - 1.5) V at different scan rates in water at 292.25K using HCl (0.1M) as supporting medium and glassy carbon as a working electrode. The study is valuable for evaluating various thermodynamic properties [5-7].

3.3 Mechanism of the redox reactions

The cadmium (II) ions used show one oxidation peak (at-0.5 V vs.Ag/AgCl) and one (at 0.0 V vs.Ag/AgCl) reduction peak.All voltamograms in Figs.3-6 explained the electro chemical behaviour of the used $CdCl_2$ metal ion,concentration,scan rate and after addition of glycine on the ratio 1:1 ,1:2 &1:3 M to glycine.The voltammograms given indicate quasireverible and diffusion control systems. These two peaks consuming two electrons in both steps as follows in reduction and vice versa in oxidation [5] :

$$Cd^{+2}{}_{(aq.)} + 2e^{-} = Cd^{o}{}_{(aq.)} \qquad (1)$$

The stability constant is a measure of the strength of the interaction between the reagents that come together to form the complex. The stability constant (β_{MX}) for nano- $CdCl_2$ (NCCl) complexes in 0.1 M HCl and scan rate 100 mV/S in water were calculated [5-8] by applying Eq. (2).

The Gibbs free energy of interaction for Nano- $CdCl_2$ (NCCl) with glycine were calculated [9-17] from stability constant (β_{MX}) using Eq (3).

The calculated stability constants and Gibbs free energies of complex formation from the interaction of nano cadmium chloride with glycine are given in Table (2) showing high values indicating good complexation interaction.

The chemical properties for glycine in water were calculated using Gaussian 09 quantum program. The resulted data are the zero point vibrational energy, vibration temperatures, sum of electronic energy with zero point energy, thermal energy, thermal enthalpy and thermal free energy in Hartree / particle .The thermal energy E, activation energy CV' and entropy for translation , rotation and vibration were also done and explained in Table (3).The partition functions(Q) for the vibrating , electronic , translational and rotational atoms in glycine molecule were also clear in Table (3) . All the quantum thermodynamic results indicate the big activity of glycine molecule.

$$(E_p)_M + (E_P)_C = 2.303\frac{RT}{nF}Log\beta_{MX} + 2.303\frac{RT}{nF}LogC_X \qquad (2)$$

Where $(E_p)_M$ is the peak potential of metal at final adding in absence of ligand, $(E_p)_C$ is the peak potential of metal complex, R is a gas constant (8.314 J.mol^{-1}.degree^{-1}), T is the absolute temperature and C_x is the concentration of metal in the presence of ligand (glycine).

$$\Delta G = -2.303RTLog\beta_{MX} \qquad (3)$$

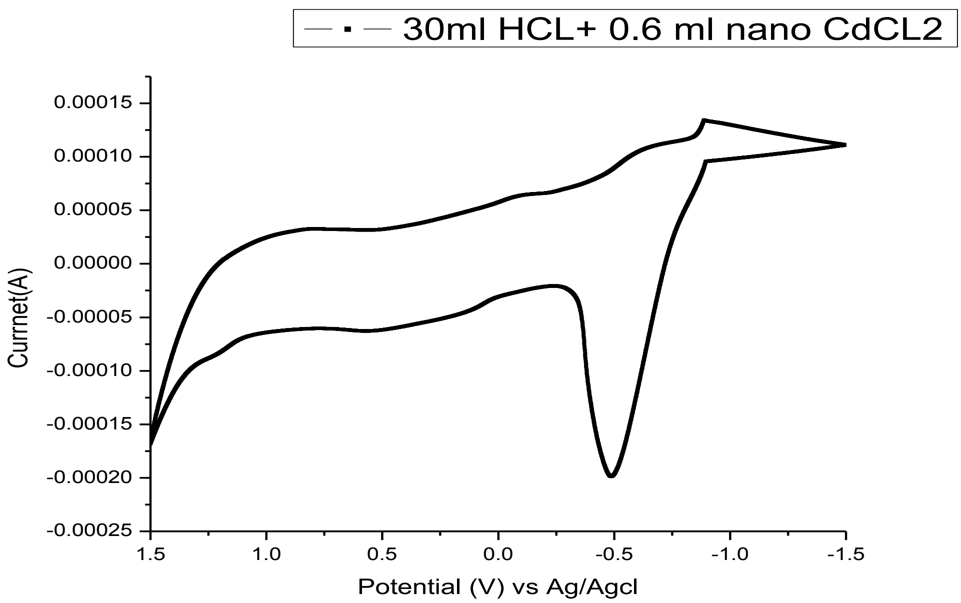

Fig. 3: Cyclic Voltammetry for Nano $CdCl_2$ (NCCl) (concentration =2x10^{-3}) in 30 ml HCl (0.1M) with glassy carbon electrode at scan rate 0.1 (V/Sec), Sens (A/V) = 1x10^{-3}, initial E (V) = 1.5, high E (V) = 1.5 and low E(V) = -1.5

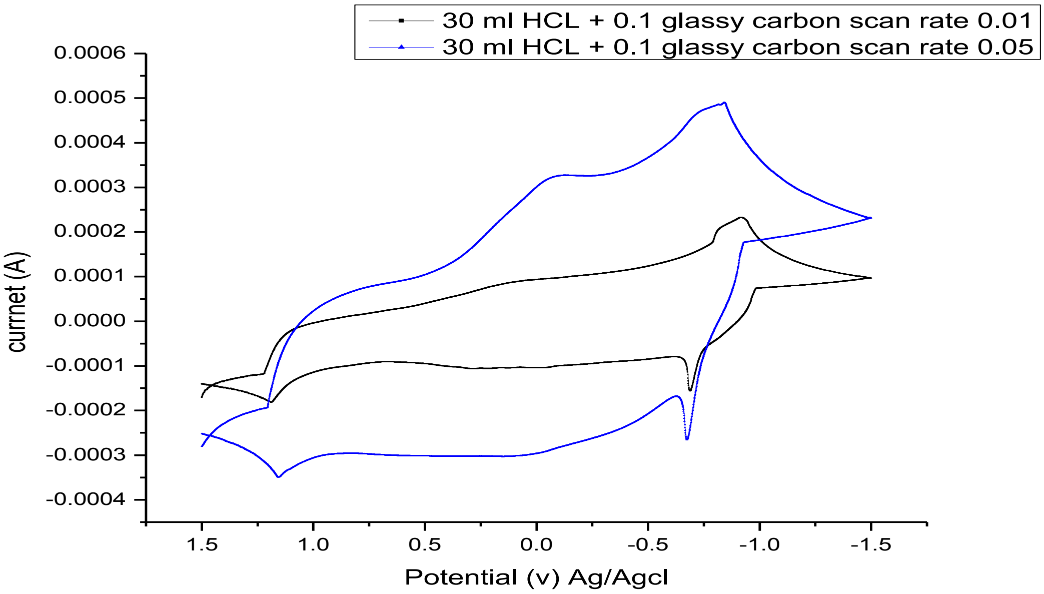

Fig. 4: Effect of different scan rate for nano $CdCl_2$ (NCCl) at Concentration 1 mM. The scan rates were maintained at 0.01, 0.05 (V/Sec), Sens (A/V) = $1x10^{-3}$, initial E (V) = 1.5, high E (V) = 1.5 and low E(V) = -1.5.

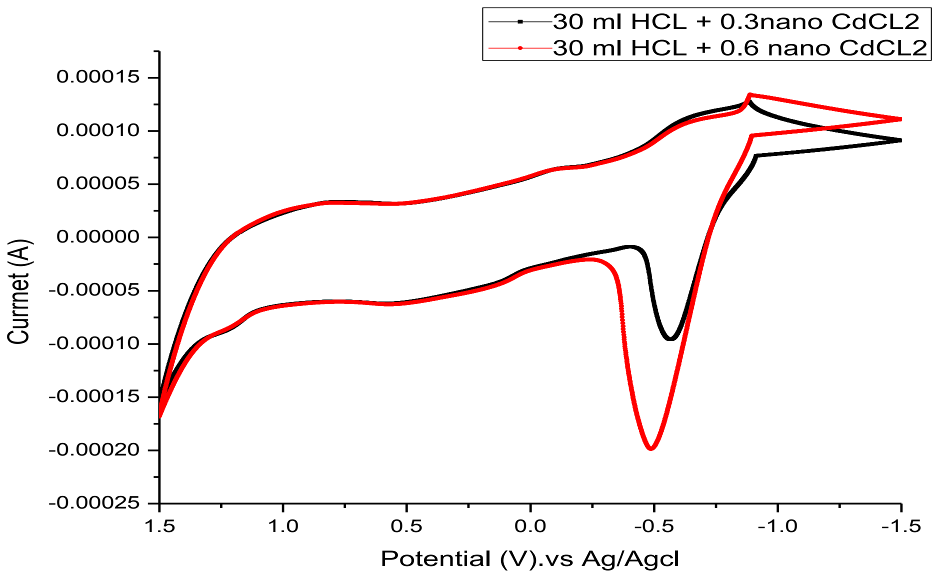

Fig. 5: Comparsion between adding 1mM (concentration =$1x10^{-3}$) and 2 mM (concentration =$2x10^{-3}$) of nano $CdCl_2$ (NCCl) in 0.1M HCl solutions.

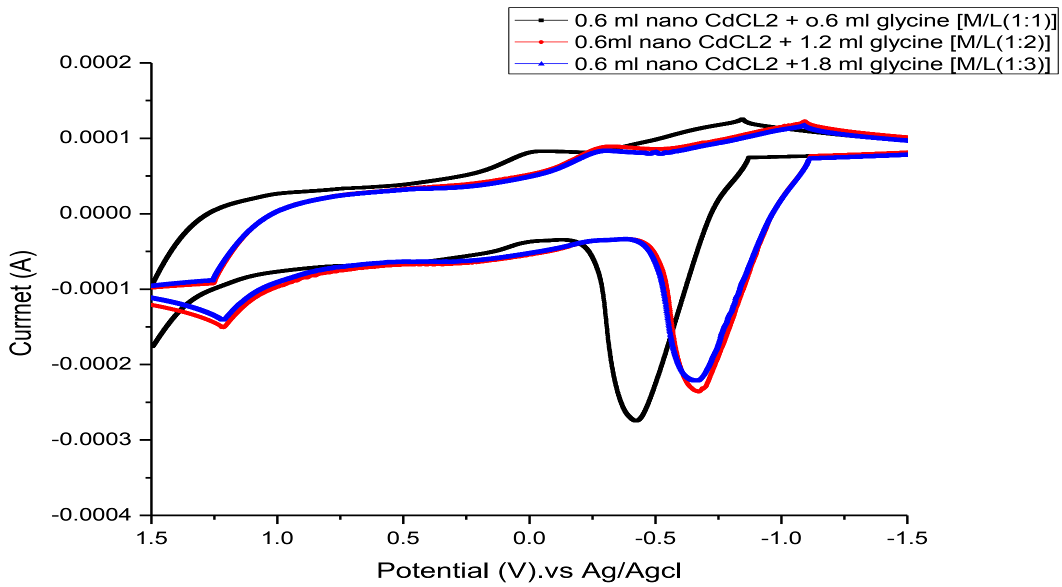

Fig. 6: Cyclic voltammetry for Nano $CdCl_2$ (NCCl) $2x10^{-3}$ and Glycine with concentration ($1.9x10^{-3}$, $3.9x10^{-3}$ and $5.8x10^{-3}$) at scan rate 0.1 (V/Sec), Sens (A/V) = $1x10^{-3}$, initial E (V) = 1.5, high E(V) = 1.5 and low E(V) = -1.5

Table 2: Analysis of voltogramms for adding Glycine (L) to nano $CdCl_2$ (NCCl) in 0.1 M HCl

$[M]*10^{-3}$	$[L]*10^{-3}$	LogƔ±	Ɣ±	(Ep,a)M	(Ep,a)C	$Ip,a*10^4$	ΔE1/2	βMX	ΔG(KJ/mol)
2	0.327	-0.0309	0.931	0.488	0.497	-2.86	0.985	1.89E+20	-112.935
2	0.654	-0.0217	0.951	0.488	0.492	-2.83	0.98	1.45E+20	-111.483
2	0.098	-0.0251	0.943	0.488	0.490	-3.01	0.978	6.99E+19	-110.852
2	1.307	-0.0282	0.937	0.488	0.489	-2.93	0.977	4.65E+19	-109.105
2	1.634	-0.0306	0.931	0.488	0.485	-3.46	0.973	3.81E+19	-108.134
2	1.931	-0.0331	0.926	0.488	0.484	-3.45	0.972	2.14E+19	-107.655
2	2.288	-0.0354	0.922	0.488	0.474	-3.15	0.962	1.49E+19	-106.284
2	2.614	-0.0415	0.908	0.488	0.468	-3.41	0.956	9.31E+18	-105.424
2	3.595	-0.0451	0.901	0.488	0.462	-3.07	0.95	5.59E+18	-104.312
2	4.248	-0.0485	0.894	0.488	0.453	-3.03	0.941	4.27E+18	-103.076
2	4.902	-0.0531	0.884	0.488	0.447	-2.98	0.935	2.19E+18	-102.430
2	5.882	-0.0546	0.881	0.488	0.432	-2.93	0.92	1.37E+18	-100.833
2	6.209	-0.0561	0.878	0.488	0.422	-.291	0.91	5.63E+17	-99.718
2	8.000	-0.0583	0.871	0.488	0.401	-3.15	0.889	4.22E+17	-97.595

Table 3: Quantum mechanical thermodynamic calculation of glycine in water using DFT calculation.

Zero-point vibrational energy 223486.3 (Joules/Mol)
53.41451 (Kcal/Mol)
Vibrational temperatures: 667.75 808.05 918.79 1300.63
(Kelvin) 1568.05 1719.38 1833.14 2019.57 2097.33
2142.54 2149.08 2269.46 2330.29 2385.49
2701.19 4679.03 4827.42 5265.51 5377.25
5394.53

Zero-point correction=	0.085121 (Hartree/Particle)
Thermal correction to Energy=	0.088723
Thermal correction to Enthalpy=	0.089667
Thermal correction to Gibbs Free Energy=	0.058191
Sum of electronic and zero-point Energies=	-282.621283
Sum of electronic and thermal Energies=	-282.617681
Sum of electronic and thermal Enthalpies=	-282.616737
Sum of electronic and thermal Free Energies=	-282.648213

	E (Thermal) Cal/mol	CV KCal/Mol	S Cal/Mol-Kelvin
Total	55.675	11.515	66.247
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	38.862
Rotational	0.889	2.981	25.231
Vibrational	53.897	5.553	2.154
Vibration 1	0.822	1.330	0.754
Vibration 2	0.917	1.114	0.521

	Q	Log10(Q)	Ln(Q)
Total Bot	0.171358D-26	-26.766096	-61.631213
Total V=0	0.243760D+13	12.386963	28.522036
Vib (Bot)	0.920226D-39	-39.036106	-89.883955
Vib (Bot) 1	0.365234D+00	-0.437429	-1.007218
Vib (Bot) 2	0.276300D+00	-0.558619	-1.286268
Vib (V=0)	0.130904D+01	0.116953	0.269294
Vib (V=0) 1	0.111919D+01	0.048904	0.112605
Vib (V=0) 2	0.107126D+01	0.029896	0.068839
Electronic	0.100000D+01	0.000000	0.000000
Translational	0.255461D+08	7.407325	17.055997
Rotational	0.728928D+05	4.862685	11.196745

Conclusion:

The stability constants and Gibbs free energies of interaction between glycine and nano cadmium chloride (NCCl) are big and decrease with increase of glycine concentration favoring direct complex formed .All Gibbs free energies are negative values indicating the possibility for complex interaction is spontaneous. The translational, rotational and vibrational energies and their entropy values for glycine in water are big indicating those statistical mechanics calculation theoretically good activity of glycine in water as seen from statistical mechanics calculations.

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