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Synthesis and Theoretical Calculating Properties of 2-(2-Cyanoacetamido)-4,5-Dimethylthiophene-3-Carboxamide (2-CDTC) and its Cyclic Voltammetry Interaction with $CuCO_3$

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- ✓ Spectral analysis,
- ✓ Cyclic Voltammetry,
- ✓ Stability constant,
- ✓ Gibbs free energy,
- ✓ thermal energies.

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Abstract

The synthesis of 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) via cyanoacetylation of 2-amino-4,5-dimethylthiophene-3-carboxamide with 3-(3,5-dimethyl-1H-pyrazol-1-yl)-3-oxopropanenitrile in dioxane, the structure confirmed by the spectral data analysis, The cyclic voltammetry of copper carbonate was done in 0.1M KCl in absence and presence of (2-CDTC) at 292.15 K, All the solvation and thermodynamic parameters for interaction of $CuCO_3$ with (2-CDTC) in 0.1 M KCl, like stability constant and Gibbs free energies of solvation were evaluated and their data were discussed, Theoretical calculations for (2-CDTC) were done quantum mechanically by using Gaussian 09 set of calculations in gas phase, ethanol, water and acetone for evaluating the different thermodynamic parameters, Different methods of calculation were proceeded like, Hartree-Fock 6-311G(d,p) and PM3 for estimating the different thermodynamic parameters in water were done and the results discussed, The different types of energies obtained by the two sets of calculations were discussed and supported the experimental part.

1. Introduction

The extraction of heavy metal ions as pollutants from any aqueous solutions applying electrochemical procedures is the aim and interesting study for environment [1-6]. Many ionic ions in solutions can be examined by the reduction of different cathode substances and materials [6, 7].

In our work here, the estimation and electrochemical voltammetric analysis of copper carbonate, $CuCO_3$ in 0.1M KCl was studied to illustrate the characteristics for evaluating it in the environmental samples. Also interaction with 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC), the treatment for remediation of Cu in vivo and vitro [7]. Long exposure of the human body to copper ions causes many problems, irritation in eyes, nose, mouth, causes headaches, dizziness, vomiting and diarrhea. High uptake copper influence kidney and liver [7]. Copper is vital dietary, small amount of it is needed [8]. Copper [9] is from the most abundant metal in the body [8-10].

In this work, estimation and electrochemical voltammetric copper ion analysis in the form of $CuCO_3$ and interaction with 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) in 0.1M KCl was studied to explaining the characteristics for the analytical investigation in the environmental samples.

2. Material and Methods

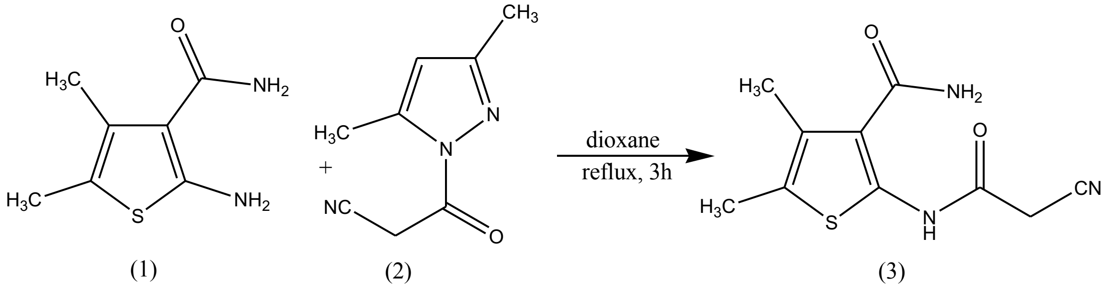
The TLC analysis was carried out on silica gel 60 F_{254} protected aluminum sheets. Infrared spectum was recorded on Mattson 5000 FTIR spectrometer (λ, cm^{-1}) using potassium bromide Wafer technique at the Microanalytical Unit, Faculty of Science Mansoura University. The ^{1}H-NMR spectra were determined on a Varian XL 200 MHz at the Microanalytical Center (Cairo University, Giza, Egypt) using $CDCl_3$ or DMSO as solvents and TMS as an internal standard. The mass spectra (EI) were recorded on 70 ev with Kratos MS equipment at the Microanalytical Center (Cairo University, Giza, Egypt).

The used chemicals, $CuCO_3$, KCl and dioxane are of high purity from Sigma Aldrich Co. The volume of the experimental solution is 30 ml. Three electrode cell was used to connect to potential DY 2000 , Ag /AgCl, KCl sat., reference electrode, carbon glassy electrode (CGlE) was used as working electrode, platinum wire was also used as counter electrode. N_2 flow was used to ensure oxygen removal. The carbon glassy electrode (CGlE) is prepared in our laboratory from pure carbon piece, polished with aluminum oxide on wool piece. Area of electrode is 0.502 cm^2.

3. Results and discussion

3.1. Synthesis of 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) :

The 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (3) was obtained via cyanoacetylation of 2-amino-4,5-dimethylthiophene-3-carboxamide (1) with 3-(3,5-dimethyl-1H-pyrazol-1-yl)-3-oxopropanenitrile (2), [11] in dioxane as in the following **Scheme 1**.



Scheme (1): Preparation of 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (3).

The structure 3 was confirmed by several spectroscopic techniques, including IR, ^{1}HNMR and mass spectroscopy. The IR spectra showed characteristic absorption bands at υ = 3423-3243 cm^{-1} owing to the stretching vibrations of NH and NH_2 groups. The bands at υ = 1702-1679 cm^{-1} are owing to the stretching vibrations of 2 carbonyl groups. Moreover, the band appeared at υ = 2210 cm^{-1} owing to cyano group. Beside the expected signals in the ^{1}HNMR spectrum, it displayed a characteristic broad signal at δ 11.098 ppm assigned to NH group. Also, showed singlet signal at δ 8.014 assigned to the NH_2 group protons and broad signal at δ 4.139 ppm assigned to CH_2 group. Moreover, showed broad signals at δ 2.500 and 2.252 ppm owing to 2 methyl groups protons. The mass spectrum showed the molecular ion peaks at m/z 239 (M^++2), 238 (M^++1), 237 (M^+) which is in agreement with the molecular formula of the compound $C_{10}H_{11}N_3O_2S$.

3.2. Electrochemical behavior of $CuCO_3$ alone:

Studying the electrochemical behavior for $CuCO_3$ dissolved firstly in 10 ml 0.1M HCl using supporting electrolyte 0.1 M KCl at 292.15K was done in the range from +1V to -1.5V. In the range -1V to +1.5V oxidation took place, but scanning in the range of +1V and -1.5V permits and allows the copper reduction procedure and ligand reduction. Cyclic voltammogram between 1 and -1.5 V(Volt) show redox parts, explaining C(II)/Cu(I) and Cu(I)/Cu(0) processes appearing in **Figure 1** [12]. The reduction first wave at ~ 0.1V, whereas the second reduction wave at ~ -0.4 V. The oxidation opposite reaction is at ~ 0.1 and ~ 0.2 V.

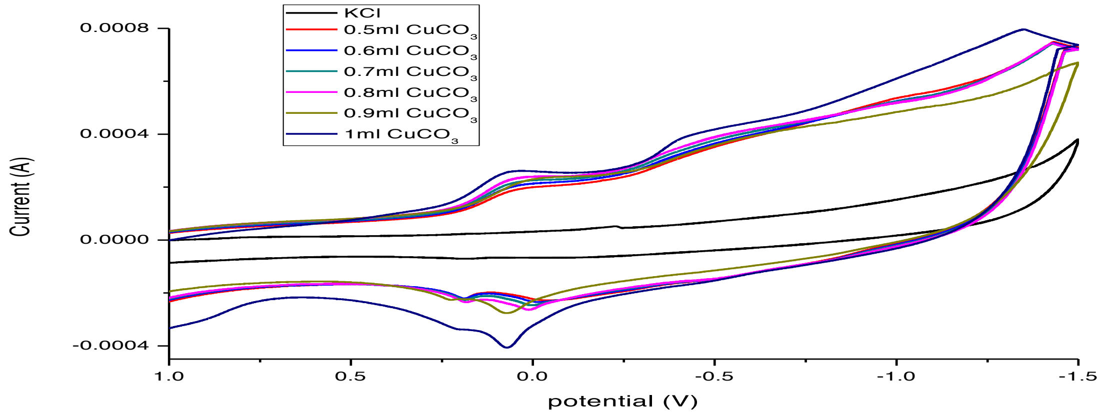


Figure 1 : Cyclic voltamogram of (30 ml KCl (0.1M)) by using glassy carbon electrode (CGlE) at different add (0.5ml, 0.6ml, 0.7ml, 0.8ml,0.9ml and 1ml) of $CuCO_3$(0.1M) in the potential range (+1 to -1.5 V) at 292.15K.

3.3. Cyclic Voltammetry of $CuCO_3$ in presence of presence for 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) at 292.15 K

The electrochemical behavior of the complex, formed from the interaction of $CuCO_3$ with 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) at 292.15K was studied cyclic voltammetrically in the range of 1 to -1.5V. The potential reduction of Cu(II)/Cu(I) processes are studied. The electrochemical activity in the range studied showed pattern at all $CuCO_3$ concentrations that may considered as the sum of individual processes [12-15] (Figure 2).

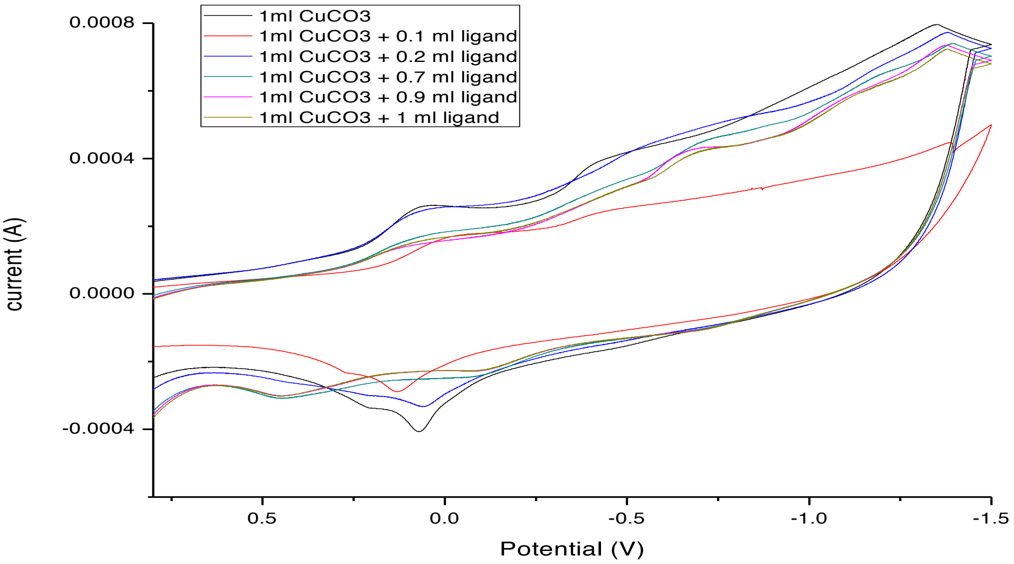


Figure 2 : Cyclic voltamogram of (30 ml KCl (0.1M)+1ml $CuCO_3$ (0.1m)) at different (0.1ml, 0.2ml, 0.7ml,0.9ml and 1ml) of by using glassy carbon electrode at different add (0.5ml, 0.6ml, 0.7ml, 0.8ml,0.9ml and 1ml) of 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) (0.01M) at 292.15K.

Table 1 : Cathodic peak potentials, cathodic peak current of [free ($CuCO_3$)] and [$CuCO_3$-2-(2-cyanoacetamido)- 4,5-dimethylthiophene-3-carboxamide complex] for the second reduction wave, values of log K_c and free energies at 292.15K.

Ml added of ligand	Ep(free) mV	Ep (complex) Mvolt	Ip (complex) (A)	ΔEp (Efree – Ecomplex)	Log K_c (c)	ΔG^o (c) KJ/mol
0.1	-411.5	-427.3	2.41E-04	15.8	2.182	-12.185
0.2	-411.5	-622.7	4.66E-04	211.2	0.163	-0.910
0.7	-411.5	-700.9	4.49E-04	289.5	0.119	-0.665
0.9	-411.5	-656.1	4.18E-04	244.6	0.141	-0.787
1	-411.5	-684.3	4.12E-04	272.8	0.126	-0.704

The complex stability constant which measure the strength and force power of interaction between $CuCO_3$ with 2-(2-cyanoacetamido)- 4,5-dimethylthiophene-3-carboxamide (2-CDTC) is very important. The complexation stability constant (K_c) for the interaction of $CuCO_3$ with (2-CDTC) forming complex in 0.1M KCl is calculated by applying **equation (1)** [16-18].

$\log K_c = 0.434\ ZF / RT\ \Delta E_p$ ……………………(1)

Where Z is the metal charge,F Faraday,s constant ,R is gas constant & ΔE_p is the the difference in potentials between complex and free metal.

The Gibbs free energy of interaction, salvation of $CuCO_3$ + (2-CDTC) were calculated [19-21] using equation (2).

$\Delta G = -2.303RT\ \log K_C$ …………………(2)

Thermochemical parameters for complex interactions between $CuCO_3$ with (2-CDTC) prove the stability of the complex formed **(Table 1)** following the second reduction wave of copper ions.

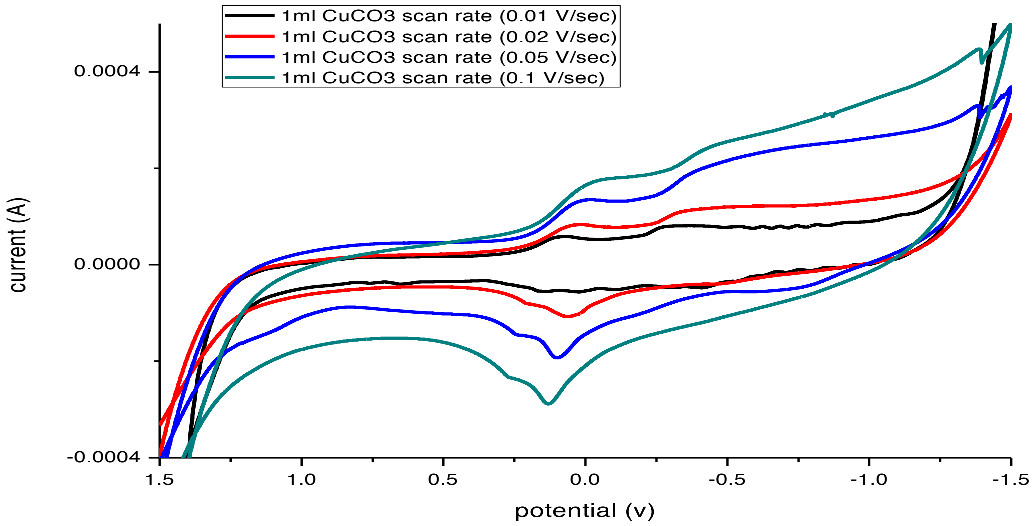


Figure 3 : Cyclic voltamogram of (30 ml KCl (0.1M)+1ml $CuCO_3$ (0.1M)) by using glassy carbon electrode at different scan rate (0.01, 0.02, 0.05 and 0.1 V/Sec) in the potential range (+1.5 to -1.5 V) at 292.15K.

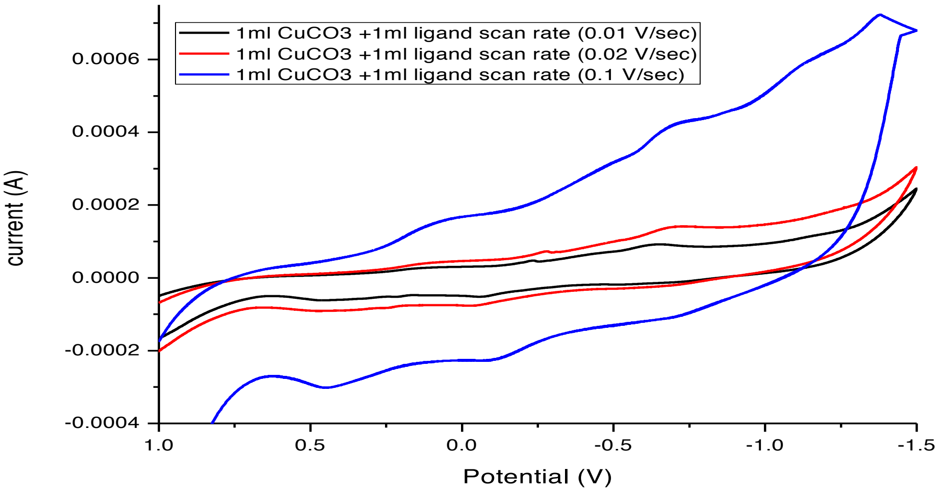


Figure 4: Cyclic voltamogram of [$CuCO_3$-2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide complex] by using glassy carbon electrode at different scan rate (0.01, 0.02 and 0.1 V/Sec) in the potential range (+1 to -1.5 V) at 292.15K.

Effect of scan rate

The redox reactions for $CuCO_3$ was examined cyclic voltammetrically, in absence and presence of presence for 2-(2-cyanoacetamido)- 4,5-dimethylthiophene-3-carboxamide (2-CDTC) at different scan rates (see **Figs.3&4**). The used scans are 0.1, 0.05, 0.02 and 0.01 V/Second. All the data given in Figures 3&4 show decrease of all current heights forth four redox waves, 2 reduction & 2 oxidation, are decreased by the decrease in scan rates, indicating the diffusion controlled reactions foe $CuCO_3$ in absence and presence of 2-(2-cyanoacetamido)- 4,5-dimethylthiophene-3-carboxamide (2-CDTC).

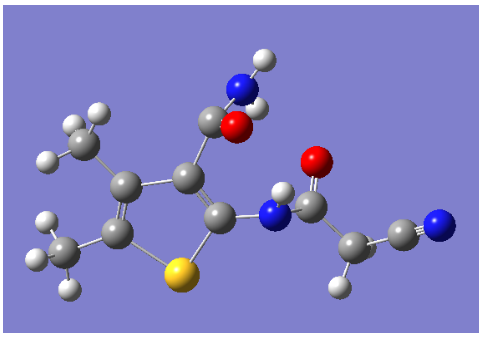
3.4. Theoretical Calculations of new 2-(2-cyanoacetamido)- 4,5-dimethylthiophene-3-carboxamide (2-CDTC)

The influence of different solvents includes water, ethanol, and acetone on 2-(2-cyanoacetamido)- 4,5-dimethylthiophene-3-carboxamide and its derivatives under investigation was approximated by the continuum solvation model based on Integral Equation Formalism polarized continnum model IEFPCM [Cancesetal, 1997] for asolute molecule interacting with a continnum description of the solvent .This to decide the best solvation for the solute will occur in. Different parameters include dipolemoment, quadrupole moment, total energy in KJ mol^{-1}, HOMO and LUMO energies are presented in **Table 2 & Fig.5.**

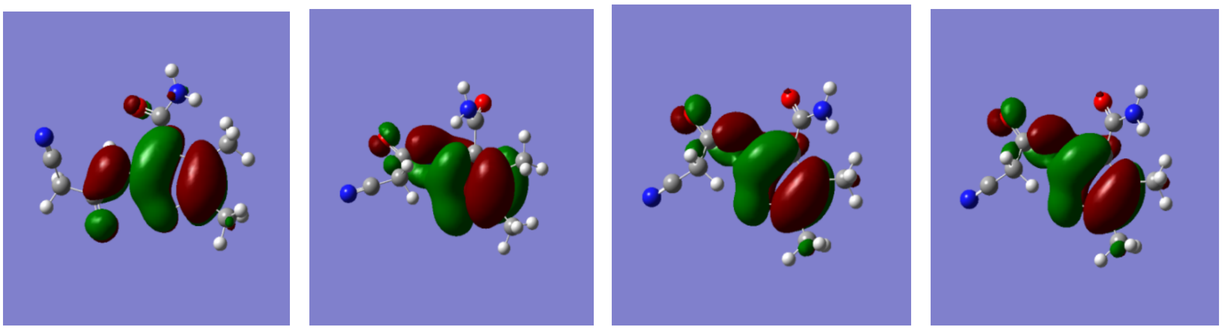
Table 2: Selected solvation parameters for 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) in different solvents as resulted from PCM/ RHF/6-311(d,p) calculations at 298.15K.

Solvent	Dipole moment (Debye)	Quadrupole moment (Debye)	Polarizability α	E (Thermal) (KJ mol^{-1})	HOMO Energy (ev)	LUMO Energy (ev)	Δ E	KE
Gas phase	6.2032	6.5815	160.546	614.1401	-0.32208	-0.01633	0.3057	1.0959D+03
Water (H_2O)	7.6539	8.3424	194.145	611.8389	-0.35035	-0.03515	0.3152	1.0934D+03
Ethanol(ETOH)	7.6032	8.2840	192.938	611.8514	-0.33439	-0.02620	0.3081	1.0934D+03
Acetone (Ac)	7.5875	8.2659	192.566	611.8556	-0.33443	-0.02624	0.3081	1.0934D+03

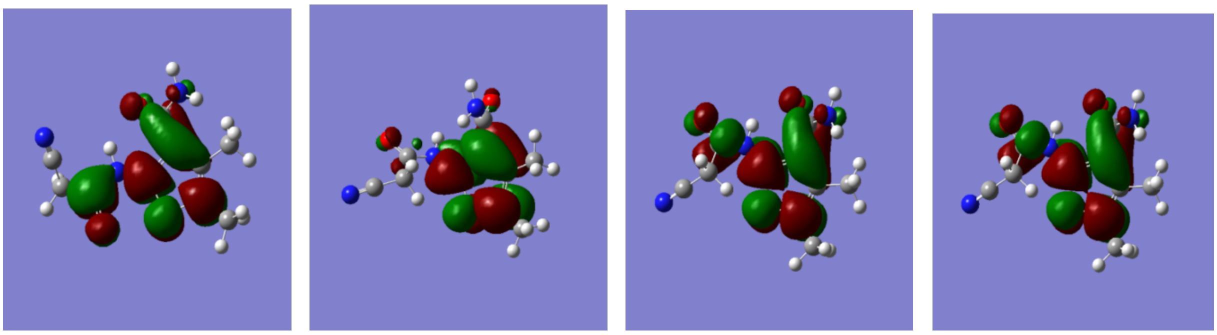
From **Table 2** ,the dipole moment and quadrupole values of continnum water are relatively higher than the other continnum solvents which give information about the molecular shape , the distribution of electronic charge in the molecule, it is therefore considered an important tool in characterizing and in elucidation of the molecular structure of several substances [21]. Polarizability values in continnum water recorded the higher value which depends upon the molecular size , shape , intra and intermolecular interactions and geometry of the molecule, the interactions in the solution effect on these quantities.



2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC)



HOMO in gas phase HOMO in H_2O HOMO in EtOH HOMO in acetone



LUMO in gas phase LUMO in H_2O LUMO in EtOH LUMO in acetone

Figure 5 : HOMO and LUMO for 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) in different solvents

From the frontier molecular orbital calculation for 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) in a various of solvents, HOMO (highest occupied molecular orbital) and LUMO (lowest un occupied molecular orbital) for the solvation process are evaluated in **Table 2** which illustrate the way that the solute interacts with other species.

$$\Delta E \text{ (The energy gap)} = \text{LUMO} - \text{HOMO}.$$

ΔE (The energy gap) = 0.3152 ev for 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2- CDTC) in water which is slightly higher (more negative) than the difference in other species as calculated. Alarge gap between HOMO and LUMO implies high stability for the salvation of 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) in water and their values are close in value to ones in other solvents.

Thermochemistry of new Schiff base compound (2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide) (2-CDTC)

The equation include entropy, heat capacity and energy at constant volume resulting from the calculated frequencies by using Gaussian 09 package are given below [20, 21]:

$$S = N K_B + N K_B \ln\left(\frac{Q\,(V,T)}{N}\right) + N K_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{\upsilon} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where $N = n N_A$, $K_B = R$, R is gas constant, N_A is Avogadro's number and Q is the partition function changing into logarithm we obtain:

$$S = R \ln (Q_t . Q_e . Q_r . Q_v . e) + T \left(\frac{\partial \ln Q}{\partial T}\right)_{\upsilon} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where Q is the total partition function, the Q_t, Q_e, Q_r, Q_v, are the translational, electronic, rotational and vibrational partition function.

The $E_{(\text{thermal})}$ is calculated from the partition function by using the equation below:

$$E = N K_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{\upsilon} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The heat capacity at constant volume is calculated by using the following equation:

$$CV = \left(\frac{\partial E}{\partial T}\right)_{N.\,\upsilon} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where CV is the heat capacity at constant volume, ∂E is the difference in internal energy and ∂T is the difference in temperatures used, N is the number of particles, υ is the quantum number of vibrational motion .

The above equations will be used for the estimation of the thermodynamic parameters for the organic compounds used from the evaluated partition functions.

The calculations evaluated from the contributions for the rotational motion, translational, and electronic contributions from vibrational mode of contribution.

The data obtained from frequency analysis by the need or partition function. For vibrational motion, choosing the first vibrational energy K, level to be zero level.

$$Qr.k = \frac{1}{1 - e^{-h\upsilon k / kBT}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where Qr is the rotational partition function, k_B is Boltzmann constant ($k_B = 1.38066 \times 10^{-23}$ J/K), h is planck's constant ($h = 6.626 \times 10^{-23}$ J.S), $h\upsilon k / k_B T = \theta \mathrm{v}$, k is defined as vibrational frequency.

The zero of energy is defined to be the fully dissociated limit (free electrons and bore nuclei), at absolute zero temperatures, there are small motions of molecules which is the zero-point vibrational energy (ZPVE or ZPE).

The ZPVE must be added to obtain energy at absolute zero temperature, T= 0 k. For all the 3N-6 (3N-5 for linear molecules) vibrational modes, the total ZPVE is:

$$ZPVE = \frac{1}{2}\sum_{k=1}^{3N-6} \frac{\square\upsilon k}{kBT} = \frac{1}{2}\sum_{K=1}^{3N-6} \theta\upsilon, E \qquad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

The ZPVE calculated for compounds used are obtained.

Different Motion contribution

The different types of motions were studied theoretically for 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) used as given in previous works [21].

Theoretical thermodynamic parameters for compound 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide used in water by using two different methods Hartree-Fock 6-311G (d,p) and PM3.

The different calculated theoretical parameters for 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) , electronic + zero-point (ZPVE) energies, electronic + thermal enthalpies, electronic + thermal energies. electronic + thermal free energies, dipole moment,translational,rotational vibrational, thermal energy E.,heat cacpacity at constant volume CV and entropies S are given in Tables 3 &4 indicating the activity of (2-CDTC).

Table 3: (Sum of electronic + zero point energies, sum of electronic+ thermal energies, sum of electronic + thermal enthalpies, sum of electronic + thermal free enegies and dipole moment for -(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide in water calculated by two calculation sets).

	Hartree-fock 6-311G	**PM3**
Sum of electronic and zero-point Energies	-1095.6854	0.1435
Sum of electronic and thermal Energies	-1095.6688	0.1608
Sum of electronic and thermal Enthalpies	-1095.6678	0.1618
Sum of electronic and thermal Free Energies	-1095.7321	0.0960
Dipole moment (Debye)	7.6539	5.8415

Table 4 : Thermal enthalpies (E), heat capacities at constant volumes (CV) and entropies (S) for 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide necessary for the translational, rotational, vibrational and total energies calculated by the two different sets used.

	Hartree-fock 6-311G (d,p)			**PM3**		
	E(Thermal) KJ/Mol	CV J/Mol-Kelvin	S J/Mol-Kelvin	E(Thermal) KJ/Mol	CV J/Mol-Kelvin	S J/Mol-Kelvin
Total	611.8389	243.2536	565.8567	572.7938	256.27	578.8313
Translational	3.719576	12.4725	176.9455	3.719576	12.4725	176.9455
Rotational	3.719576	12.4725	137.8754	3.719576	12.4725	138.2101
Vibrational	604.3997	218.3086	251.0358	565.3546	231.3292	263.6757

Conclusions

The Cyclic voltammetry studies were done for $CuCO_3$ alone in 0.1M KCl at 292.15K and found to give four redox peaks, two is responsible for the reduction and two for the oxiadation. Also the interaction between copper carbonate and 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) was studied and found complexes in solution formed with estimated Gibbs free energies and stability constants of complex reactions.

Different parameters theoretically was evaluated for 2-(2-cyanoacetamido)-4,5-dimethylthiophene-3-carboxamide (2-CDTC) from molecular orbital calculations by applying CPCM model of solvation with different approaches of quantum levels which includes:

- The total energies are found to decrease with the increase of basis set dimension. E(RHF)= - 611.8389 KJ/Mol by RHF (6.311G (d,p)) using CPCM solvation model in H_2O in room temperature which indicates that the most stable energy by hartree fock method than the other empirical method used (PM3).
- The dipole moment value resulted from RHF 6-311G (d,p) implies higher value than other method used which indicates that the most trend solubility in H_2O by hartree fock method

Finally, Hartree fock calculation is the most common type used of ab-initio calculation, with no dependents on experimental data, the good side of this method is that they converge to the solution , once all of the approximations and made sufficiently small in magnitude , while the bad side is that they often take enormous amounts of computer, disk space time and memory. While semi empirical methods are setup with the same structure as RHF calculation, but the strategy is parameterized by curve fitting in an exceedingly few parameters or numbers, so as to allow the most effective agree with experimental results.

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