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# Cyclic Voltammetry for the Interaction between Bismuth Nitrate and Methyl Red in Potassium Nitrate Solutions

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**ABSTRACT**

Cyclic Voltammetry of bismuth nitrate (BN) using different concentrations was practically measured by the use of DY2000 potenstiostat. We used 0.1 M $KNO_3$ as a transporting medium for the diffusion of the ions used as the glassy carbon electrode (GCE). Moreover, it was prepared in our laboratory, well polished and washed before use. Besides, Ag/AgCl reference electrode and auxiliary platinum electrode were also used. Scan rates of the redox reactions of bismuth nitrate were studied in the presence and absence of methyl red. The complexation interaction between bismuth nitrate (BN) and methyl red (MR) was studied. The redox reactions' stability constant for forming complex and Gibbs free energy of complex interactions was evaluated. The data are discussed.

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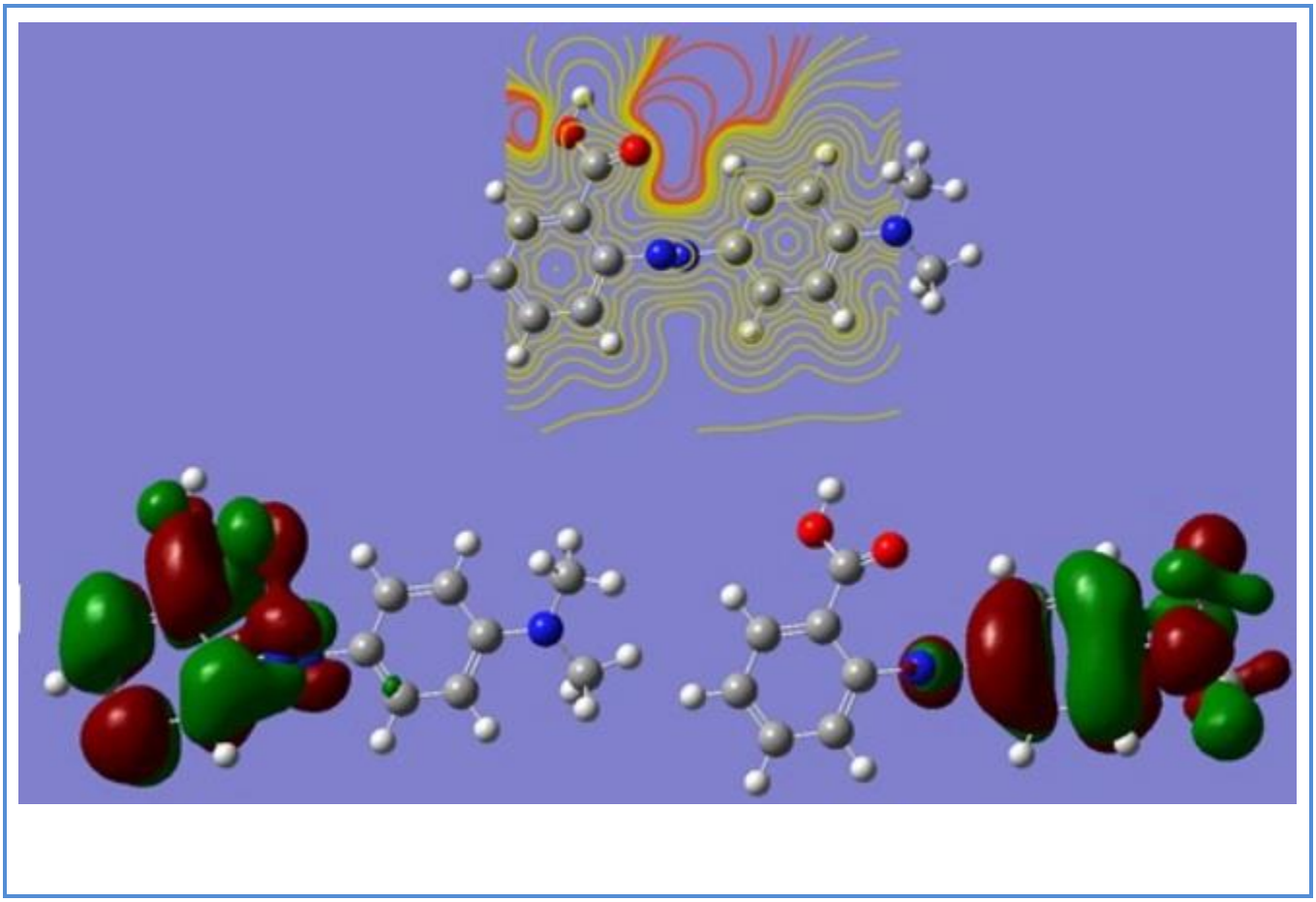
## Graphical Abstract



## Introduction

Cyclic Voltammetry can be used for studying the complex reactions of metal salts with organic ligands [1]. Bismuth was found to build complexes by the interaction with nitrogen, hydroxyl group or any active group in the ligands [2]. The complexation study for interaction of metal ions with organic ligands in solutions studied cyclic voltammetrically can be observed by measuring the shift in both anodic and cathodic peaks characteristics [3]. Bismuth nitrate dissolves in nitric acid, but is readily hydrolysed to form a range of oxynitrates when the pH increases. It is also soluble in acetone, acetic acid and glycerol. Some uses in organic synthesis have been reported, for example the nitration of aromatic compounds and selective oxidation of sulfides to sulfoxides [3, 4].

In our laboratory, here, we prepared glassy carbon electrode (GCE) from a pure piece of carbon metal jointed by high conductance copper wire isolated by heat shrink polymer to prevent damage of the electrode, polished, well with aluminum oxide powder put on wool peace of cloth till mirror

luster appears and used for studying the redox reaction between bismuth nitrate (BN) and methyl red (MR) at steady state limiting currents, where interaction is complete and stable.

## Experimental

The Bismuth nitrate (BN) is from Merck and methyl red (MR) from Sigma Aldrich Co. Its structure, contour lines, HOMO orbital and LUMO orbital structure are seen in Figure (1) calculated from Gaussian 09 quantum mechanics calculations. Also, $KNO_3$ is provided from Sigma Aldrich Co. The used chemicals are applied without any purification to avoid any bad effect on them. Potentiostat DY 2000 was used for measuring cyclic Voltammetry at different scan rates. Deionized water was used in the experimental part and dearation with nitrogen for 10 minutes for every sample before being measured in the apparatus. The measuring system consists of three electrodes for clearing the cyclic voltammograms. They are Ag/AgCl electrode filled with saturated KCl reference electrode. Platinum wire was used as an auxiliary electrode to protect the used cell. Glassy carbon electrode (GCE) was well polished with $Al_2O_3$ powder and put in the wet wool piece. Experiments were repeated three times to ensure the cyclic obtained voltammograms.

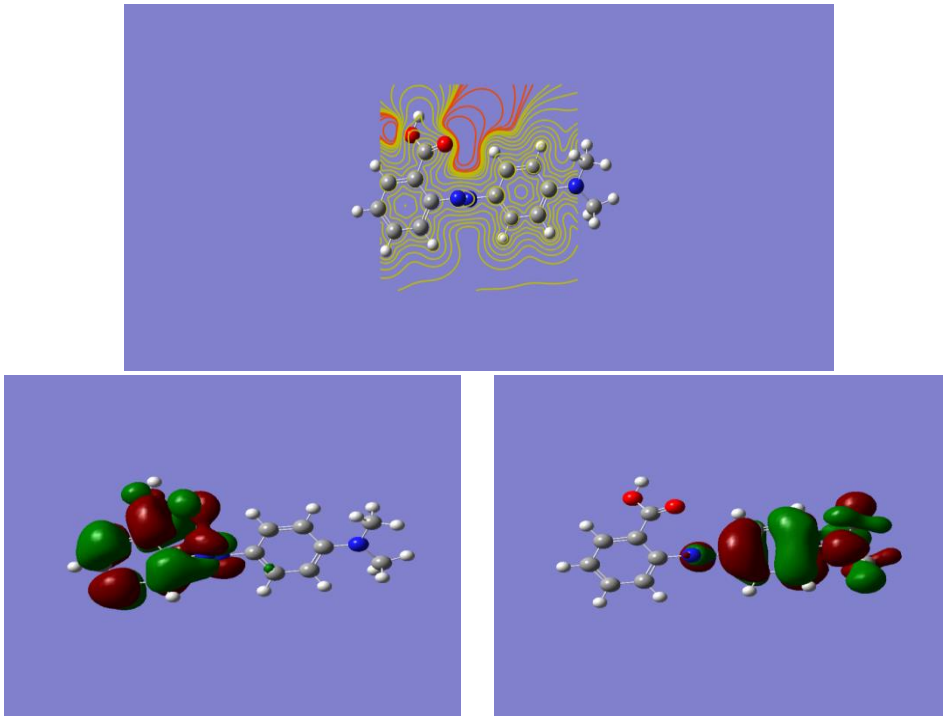


**Figure 1.** Contour lines of methyl red orbital type, ESP, density Matrix SCF, LUMO orbital of level 72 (energy =0.0759 ev) and HOMO orbital structure of orbital 71 (energy=-0.28759 ev)

## Results and discussion

### Redox reactions of bismuth nitrate (BN) in the absence of methyl red (MR):

The electrochemical behavior for metal ion bismuth at the Glassy carbon electrode (GCE) was studied by measuring the obtained currents on bringing the potentials at the steady state. The voltametric data were obtained and analyzed with the use of equation (1) after Randles and Sevick [5-9].

$$i_p=(2.69*10\text{^}5)\ n^{3/2}\ A\ D^{1/2}\ v^{1/2}\ C \qquad (1)$$

Where $i_p$, is current in Ampere, A is the electrode area in $cm^2$, D is the diffusion coefficient in $cm^2$/sec, V is the selected scan rate in V/s (second) and C is the metal ion concentration. The recorded voltammograms use the glassy carbon electrode from starting potential 1.5 V till-1.5 V. The measured current depends on the diffusion of the electroactive bismuth salt to the surface of the working electrode. For reversible reactions, the separation in peak potentials, $\Delta E_p$ will close to values of 58/nm V (at 25˚C). This last one can be used for electron determination consumed in redox reactions. In reversible reactions the reduction is fast in order to obtain the concentration of the oxidized and reduced forms in equilibrium. Some irreversible reactions involve bond breaking and the reaction is known as irreversible reactions. For quasi reversible system, the peak current is not proportional to the square root of scan rate $v^{1/2}$.

**Electrochemical study of bismuth nitrate (BN) in absence of methyl red (MR) :**

Bi $(NO_3)_3$ concentrations was voltammetrically studied using 0.1 M $KNO_3$ supporting electrolyte in the range from 1.5 V to -1.5 V. The obtained data are illustrated in Figure (2).

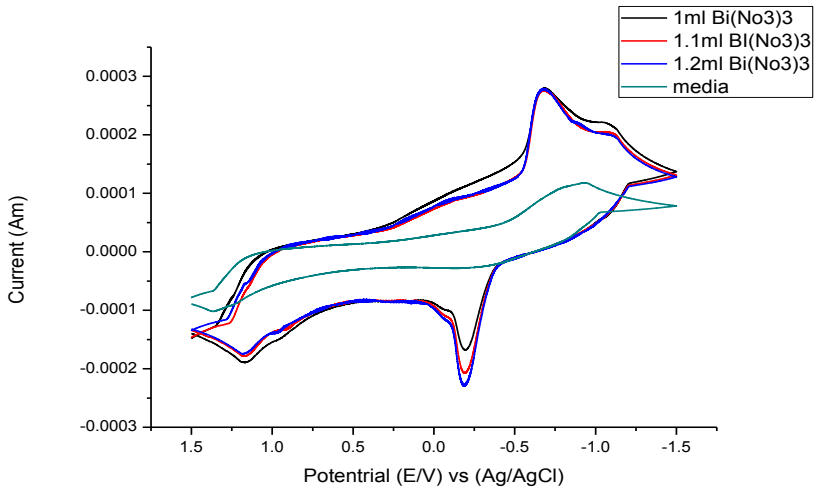



**Figure 2.** Cyclic voltammograms of different concentrations of bismuth nitrate in 0.1 M $KNO_3$

We saw two cathodic peaks appear at ~0 V and ~0.6 V due to three electron transfer reaction. These steps are continued till the formation of the zero valence Bi deposited on the glassy carbon electrode (GCE).

The reduction mechanism proceeds via the following steps:

$$Bi^{+3} + 2e^- \rightarrow Bi^+ \qquad (2)$$

$$Bi^+ + e^- \rightarrow Bi \qquad (3)$$

The oxidation peaks appear at ~ -0.2 V for the first sharp peak and at ~ -0.05 V for the second peak. The oxidation mechanism is opposite to that of the reduction to complete the cycle and the redox system under consideration as follows:

$$Bi \rightarrow Bi^+ + e^- \qquad (4)$$

$$Bi^+ \rightarrow Bi^{+3} + 2e^- \qquad (5)$$

The oxidation mechanisms by two and one electron processes, respectively, were also supported from the height (peak current) of the first oxidation peak is double than that of the first indicating the ratio is 2 to 1. Effect of scan rates is presented in Figure (3).

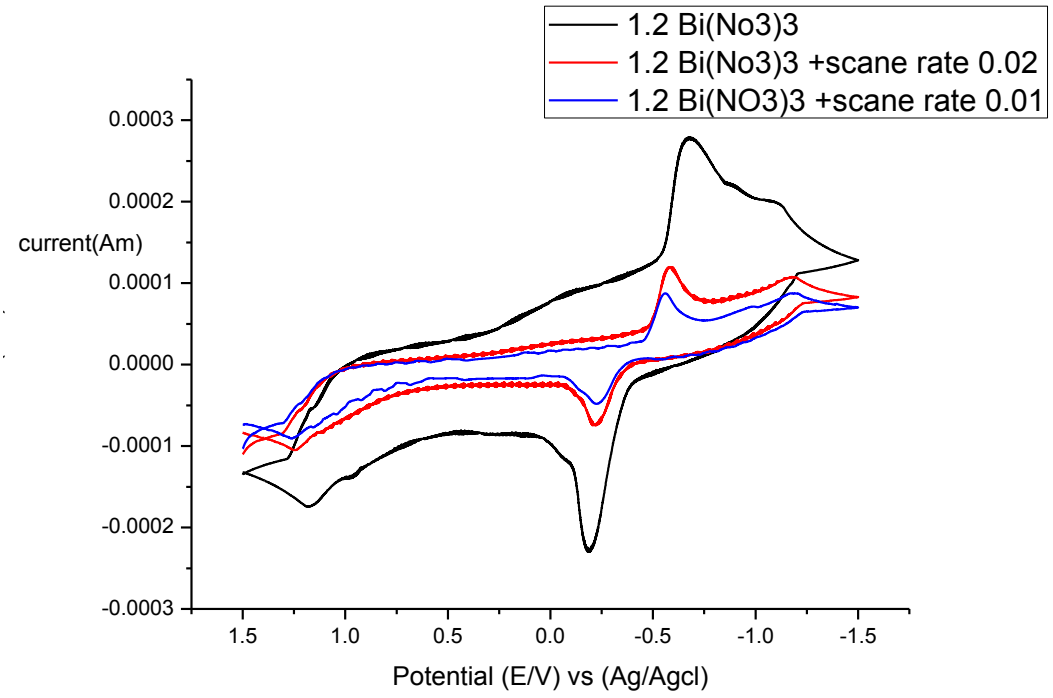



**Figure 3.** Effect of scan rates on bismuth nitrate

**Table 1.** Solvation parameters for $3.85*10^{-4}$ M $Bi(NO_3)_3$ in 0.1M $KNO_3$

| [M] *10^-4 | (-) $E_{p,a}$ (V) | (-) $E_{P,C(V)}$ | ΔEp (V) | -$Ip_{,a}$ *10^-5 (A) | -Ip,c *10^-5 (A) | Ip,a/Ip,c | (-) $E^{\circ}$ (V) |
|---|---|---|---|---|---|---|---|
| 3.85 | 0.189 | 0.677 | 0.488 | -0.301 | 0.226 | -1.3326 | 0.433 |
| 3.85 | 0.217 | 0.583 | 0.366 | -0.128 | 9.46 | -1.3559 | 0.4 |
| 3.85 | 0.2247 | 0.5611 | 0.3364 | 9.71 | 7.02 | 1.3828 | 0.3929 |

| $D_a$ *10^-8 | $D_c$*10^-9 $cm^2.cm^{-1}$ | ks | $\Gamma_c$*10^-9 ($mol.cm^{-2}$) | +$Q_c$ *10^-4 (C) | $\Gamma_a$ *10^-9 ($mol.cm^{-2}$) | $Q_a$ *10^-4 (C) |
|---|---|---|---|---|---|---|
| 1.59 | 8.9499 | 4.50E+00 | 4.76353 | 1.16 | -6.3477 | -1.54 |
| 1.44 | 7.8255 | 2.17E-01 | 9.9600 | 2.42 | -0.1350 | -3.27 |
| 1.65 | 8.6329 | 8.91E-02 | 0.1479 | 3.59 | 0.2046 | 4.96 |

We can observe from Figure (3) that the currents decreased by the decrease of the scan rates indicating the diffusion control reactions. Analysis of the voltammograms was done and resulted data are shown in Table (2).

**Table 2.** Analysis wave parameters for different bismuth nitrate concentrations

| [M] *10^-4 ($mol.L^{-1}$) | (-) $Ep_{,a}$ (V) | (-)$Ep_{,c}$ (V) | ΔEp(V) | -Ip,a *10^-4 (A=Ampere) | -$Ip_{,c}$ *10^-4(A) | Ip,a/Ip,c |
|---|---|---|---|---|---|---|
| 3.23 | 0.194 | 0.686 | 0.492 | 2.30 | 2.01 | 1.1438 |
| 3.54 | 0.191 | 0.683 | 0.492 | 2.77 | 1.99 | 1.3884 |
| 3.85 | 0.189 | 0.677 | 0.488 | 3.01 | 2.26 | 1.3326 |

| (-) $E^{\circ}$(V) | $D_a$ *10^-10 ($cm^2.s^{-1}$) | $D_c$ *10^-10 ($cm^2.s^{-1}$) | ks *10^-3 | $\Gamma_c$ *10^-9($mol.cm^{-2}$) | +$Q_c$ *10^-4 (C) | $\Gamma_a$ *10^-9($mol.cm^{-2}$). | - $Q_a$ *10^-4 (C) |
|---|---|---|---|---|---|---|---|
| 0.44 | 5.5563 | 4.25 | 2.90 | 4.2347 | 1.03 | 4.8436 | 1.17 |
| 0.437 | 6.6948 | 3.47 | 1.63 | 4.1989 | 1.02 | 5.8296 | 1.41 |
| 0.433 | 6.7132 | 3.78 | 2.41 | 4.7635 | 1.16 | 6.3479 | 1.54 |

V,volt, A,ampere, C coulomb

Increasing bismuth ion depolizer concentration is followed by increase cathodic surface coverage $\Gamma_c$, anodic surface coverage $\Gamma_a$, cathodic quantity of electricity $Q_c$ and anodic quantity of electricity $Q_a$. Also $I_{p,a}/I_{p,c}$, $\Delta E_p$ and electron transfer rate constant $K_s$ show increasing tendency generally by increasing $Bi(No_3)_3$ concentration in the used solutions.

**Electrochemical study of bismuth nitrate (BN) in presence of methyl red (MR):**

The interaction of bismuth nitrate (BN) with methyl red (MR) has been studied via cyclic Voltammetry technique at also potential range from +1.5 V to -1.5 V at different scan rates in 0.1M $KNO_3$ at 296.45 K. The study is interesting for evaluating various thermodynamic parameters. The

bismuth ions under consideration show two oxidation and two reduction peaks as clarified in Figure (4).

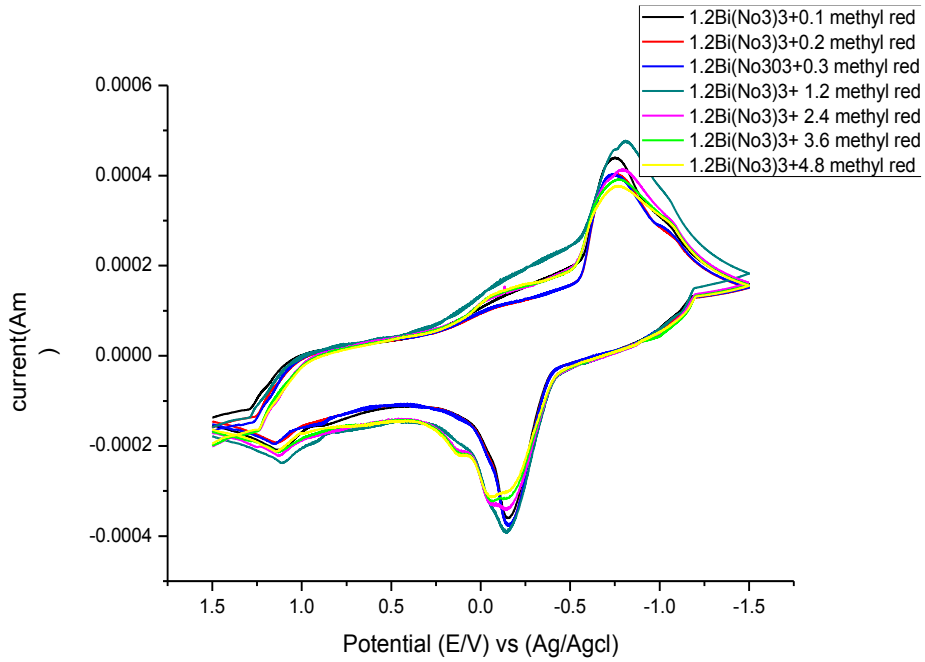



**Figure 4.** Effect of different methyl red concentrations on the voltamogram of bismuth nitrate in 0.1M $KNO_3$.

The resulted voltammograms indicate quasireversible and diffusion control systems. These reduction and oxidation peaks consumed and liberated 1 electron and 2 electrons in the reduction and 2 electrons followed by one electron for the oxidation processes. The stability constant is a good measure for the strength of interaction between the metal ions, bismuth ions and methyl red (MR) forming complex. The stability constant (BMX) for bismuth nitrate (BN) + methyl red (MR) in 0.1 M $KNO_3$ was calculated by applying Eq(6) [5-8]:

$$\Delta E_p = (E°)_M - (E°)_C = 2.303\frac{RT}{nF}\log\beta_{MX} + 2.303\frac{RT}{nF}\log_{CX} \qquad (6)$$

Where (E°) M is the peak potential of metal at final adding in the absence of ligand, (E°) C is the peak potential of metal complex, R gas constant, T absolute temperature and C is the concentration of metal in the presence of ligand methyl red (MR).

The complexation Gibbs free energy of interaction for bismuth nitrate (BN) with methyl red (MR) were calculated [9-26] from stability constants evaluated and by the use of equation (7).

$$\Delta G = -2.303\ RT\ \log\beta_{MX} \qquad (7)$$

The calculated stability constants and complexation Gibbs free energies for the formed complex from the interaction of bismuth nitrate (BN) with methyl red (MR) are given in Table (3) Showing higher values with an increase in methyl red (MR) concentration indicating more complexation.

The transfer rate conctant Ks can be calculated by the use of the following equation (eq.8):

$$K_s = ko\ \exp(-\propto nf) / \frac{-\propto nf}{RT}(E-E^{\circ}) \qquad (8)$$

Where: ks is forward rate constant, ko is the electron transfer rate constant. E is the potential for reduction and α is the transfer coefficient [23] we take α≅0.5 because it depend on the shape and surface free energies for reactants and products.

**Table 3.** Solvation parameters for bismuth nitrate in presence of methyl red

| [M] *10^-4 (mol.L$^{-1)}$ | (-)Ep$_{,a}$ (V) | (-)Ep$_{,c}$ (V) | ΔEp(V) | -Ip$_{,a}$ *10^-4 (A) | -Ip$_{,c}$ *10^-4(A) | Ip,a/Ip,c |
|---|---|---|---|---|---|---|
| 3.83 | 0.154 | 0.751 | 0.1 | 4.30 | 3.75 | 1.1460 |
| 3.82 | 0.155 | 0.755 | 0.6 | 4.46 | 3.13 | 1.4262 |
| 3.81 | 0.156 | 0.742 | 0.586 | 4.58 | 3.05 | 1.5018 |
| 3.70 | 0.144 | 0.809 | 0.665 | 3.37 | 3.65 | 0.9246 |
| 3.57 | 0.143 | 0.802 | 0.659 | 4.17 | 3.00 | 1.3899 |
| 3.45 | 0.139 | 0.77 | 0.631 | 3.94 | 5.81 | 0.6783 |
| 3.33 | 0.131 | 0.758 | 0.627 | 3.79 | 2.48 | 1.5314 |

| (-) E°(V) | Da*10^-10 (cm$^2$.s$^{-1}$) | D$_c$*10^-10 (cm$^2$.s$^{-1}$) | ks C *10^-4 | Γ$_c$ *10^-9(mol.cm$^{-2)}$ | +Q$_c$ *10^-4(C) | Γ$_a$ *10^-9(mol.cm-2) | - Q$_a$ *10^-4(C) |
|---|---|---|---|---|---|---|---|
| -0.4525 | 0.1377 | 0.105 | 8.06 | 7.9069 | 1.92E | 9.0615 | 2.20 |
| -0.455 | 0.1493 | 7.34 | 3.32 | 6.5944 | 1.60 | 9.4049 | 2.28 |
| -0.449 | 0.1581 | 7.01 | 4.15 | 6.4249 | 1.56 | 9.6493 | 2.34 |
| -0.4765 | 9.0621 | 0.106 | 3.30 | 7.6815 | 1.86 | 7.1021 | 1.72 |
| -0.4725 | 0.1489 | 7.71 | 1.97 | 6.3163 | 1.53 | 8.7791 | 2.13 |
| -0.4545 | 0.1427 | 0.310 | 4.19 | 0.1223 | 2.97 | 8.2988 | 2.01 |
| -0.4445 | 0.1414 | 6.03 | 2.41 | 5.2154 | 1.26 | 7.9869 | 1.94 |

| Log βj | βj | (-) ΔG (KJ/mol) |
|---|---|---|
| 0.9489 | 8.8903 | 5.3862 |
| 1.3199 | 20.8877 | 7.4919 |
| 0.3140 | 2.0606 | 1.7823 |
| 1.9529 | 89.73148774 | 11.0852 |
| 5.5207 | 331687.9274 | 31.3366 |
| 9.5645 | 3668320574 | 54.2895 |
| 13.3362 | 2.16886E+13 | 75.6987 |

Scan rate was also studied for the formed complexes. Besides, the diffusion mechanism was strongly supported. All the kinetic and thermodynamic parameters $D_a$, $D_c$, $\Gamma_a$, $Q_a^-$, $\Gamma_c$, $Q_c^+$, $K_s$ are increased with increase of methyl red (MR) concentration indicating more complexation. The apparatus used for developing cyclic voltammograms are shown in Figure (5) explaining the electrodes, potiostata recording Lab, deairation and printing system.

The properties of methyl red (MR) were discussed by the theoretical calualtions using quantum mechanics calculation, given in Table (4), and all obtained data which prove the activity of methyl red in water from the energy gap, Gibbs free energy, enthalpy, thermal energies E (thermal), heat capacities at constant volume (CV), entropies (S) for the electronic, translational, rotational and vibrational motions for the electronic, vibrational and rotational movment support also MR activity.

**Table 4.** Gaussian 09 statistical thermodynamic quantities for methyl red in water

| **Zero-point correction=** | **0.296418 (Hartree/Particle** |
|---|---|
| Thermal correction to Energy= | 0.311001 |
| Thermal correction to Enthalpy= | 0.311945 |
| Thermal correction to Gibbs Free Energy= | 0.253889 |
| Sum of electronic and zero-point Energies= | -884.494366 |
| Sum of electronic and thermal Energies= | -884.479784 |
| Sum of electronic and thermal Enthalpies= | -884.478840 |
| Sum of electronic and thermal Free Energies= | -884.536896 |

| | **E(Thermal) KCal/Mol** | **CV Cal/Mol-Kelvin** | **S Cal/Mol-Kelvin** |
|---|---|---|---|
| Total | 195.156 | 57.706 | 122.189 |
| Electronic | 0.000 | 0.000 | 0.000 |
| Translational | 0.889 | 2.981 | 42.669 |
| Rotational | 0.889 | 2.981 | 34.223 |
| Vibrational | 193.379 | 51.744 | 45.298 |

| | **Q** |
|---|---|
| Electronic | 0.100000D+01 |
| Translational | 0.173526D+09 |
| Rotational | 0.672604D+07 |

**Figure 5.** The apparatus used for cyclic Voltammetry

## Conclusion

The stability constants and complexation Gibbs free energies of interaction between bismuth nitrate (BN) and methyl red (MR) are big and will increase by increasing methyl red concentrations. All the complexation Gibbs free energies have negative values indicating the plausibility for the formed complexes.

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