

*Journal of Medicinal and Chemical Sciences 2019 (2) 41-45**J. Med. Chem. Sci.***Solvation Parameters for The Interaction of HgCl<sub>2</sub> with Valporic Acid (VaA) in KNO<sub>3</sub> Using Silver Working Electrode (Cyclic Voltammetry)**Esam A. Gomaa<sup>a</sup>, Moustafa A. Diab<sup>b</sup>, Adel Z. El Sounbati<sup>b\*</sup>, Hamed M. Abou El-Nader<sup>a</sup>, Gannat S. Abd Elraoof<sup>b</sup><sup>a</sup>Chemistry Department, Faculty of Science, Mansoura University, 35516-Mansoura, Egypt<sup>b</sup>Chemistry Department, Faculty of Science, Damitta University, Damitta, Egypt.**ARTICLE INFO***Article history:*

Received 30 May 2018

Revised 27 July 2018

Accepted 20 August 2018

Available online 29 November 2018

*Keywords:*

Cyclic voltammetry

Thermodynamic parameters

Copper bromide,

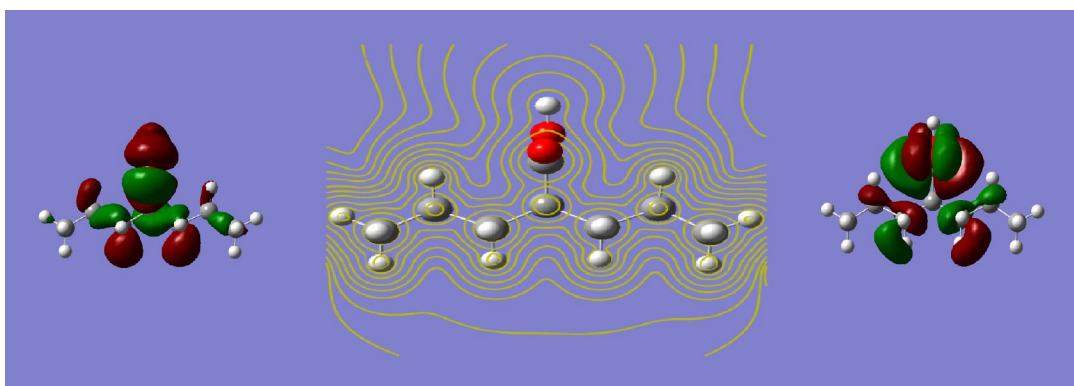
Solvation parameters

Stability Constants

**ABSTRACT**

Redox reaction mechanism in absence and presence of Valporic Acid (VaA) was studied in cyclic voltammetry, we used a new silver electrode made from pure Silver piece jointed to copper wire and isolated by heat shrink polymer to insure Complete isolation, during measurements. The Silver electrode was polished with Al<sub>2</sub>O<sub>3</sub> in woolen piece, washed and used for the cyclic voltammetric Study. The stability constants and Gibbs free energies of complex reactions between HgCl<sub>2</sub> and Valproic acid (VaA) in 0.01 M KNO<sub>3</sub> at 22 C were evaluated and their results were discussed.

DOI: 10.26655/JMCHMSCI.2019.3.1

**GRAPHICAL ABSTRACT****1. Introduction**

On the use at cyclic Voltammetry, the interaction of ionic salts with organic ligands can be followed and explained active salts.<sup>1-6</sup> In this sense, divalent or trivalent salts can interact with organic ligands or drugs to form complexes. The interaction can take place by the interaction of metal ion with active chelating group in the organic compounds like azo, hydrozo, amino, amide, carboxylic and hydroxyl groups.<sup>7</sup> Complexation can be followed and explained by the change in peak heights and shift in both anodic and cathodic potentials and half wave potentials of measured peaks.<sup>6-7</sup> We can use other techniques like, emission spectroscopy, absorption spectra, potentiometry, polarography and other electrochemical methods to follow and explain the complex interactions in solutions for the interaction of different salts with active organic compounds.<sup>8</sup> Here in our laboratory, we prepared new silver electrode from pure silver piece jointed

with high conducting copper wire isolated from medium heat shrink polymer. Valproic acid can cause liver failure that may be fatal, especially in children under age 2 and in people with liver problems caused by a genetic mitochondrial disorder. It is worth mentioning that liver problems is caused by genetic mitochondrial ,a history of depression, mental illness, a family history of a urea cycle disorder or infant deaths with unknown cause.<sup>8</sup>

**2. Results and Discussion**

The cyclic voltammetry of different HgCl<sub>2</sub> concentrations was studied in 0.01M KNO<sub>3</sub> and at 22 °C. The potential range used is from 1.5 V to -1.5 V and the cyclic voltammograms are shown in Fig 1.

Voltammograms of different concentration of HgCl<sub>2</sub> in 0.01M KNO<sub>3</sub> solutions at 22°C together with the blank solution of

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0.01M KNO<sub>3</sub> is visible. We noticed two cathodic peaks and two anodic peaks; the reduction of mercuric ions from divalent to monovalent and then to zero valent is responsible for the reduction at ~ 0 V and ~ -0.2 Vand consuming one electron in each step as suggested in the mechanism. One

electron in each step as suggested in the following mechanism:

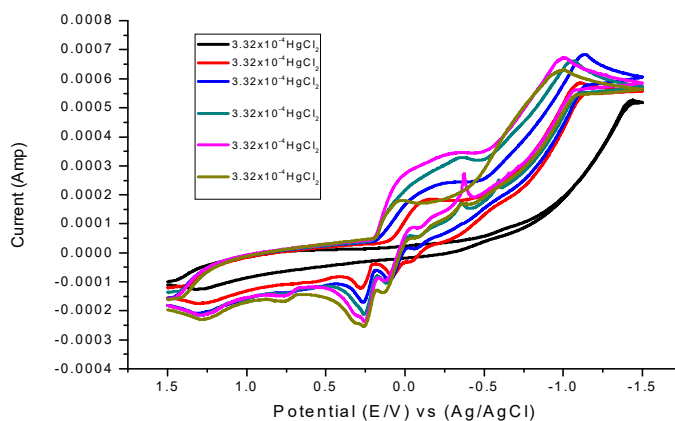
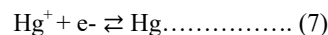
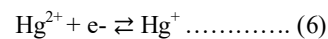


Fig 1. Voltammograms of different concentration of HgCl<sub>2</sub> in 0.01M KNO<sub>3</sub> solutions at 22 °C.

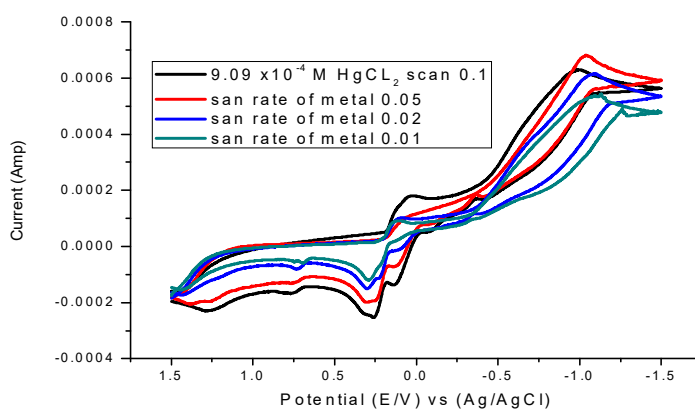


Fig 2. Different scan rate of HgCl<sub>2</sub> in 0.01M KNO<sub>3</sub> solutions at 22 °C.

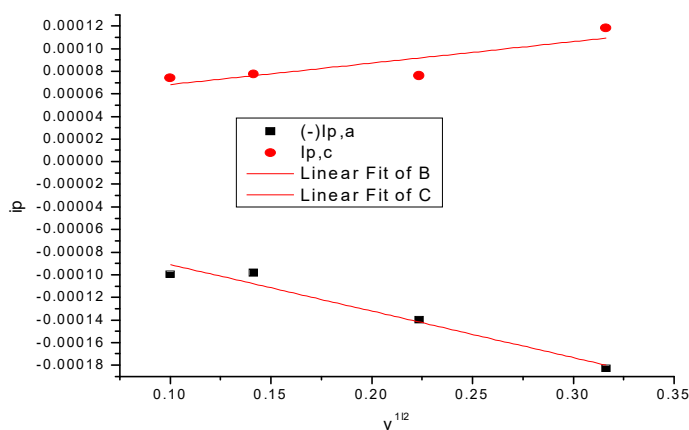
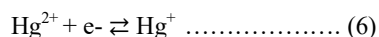


Fig 3. The relation between  $i_p$  and  $v^{1/2}$  for the wave in absence of ligand.

The oxidation peaks appear at  $\sim 0.1V$  and  $\sim 0.25V$  at  $22^\circ C$ , explaining the opposite trend or the reverse direction of equation (6), (7). The oxidation peaks appear. At  $\sim 0.1V$  and  $\sim 0.25 V$ ; involving one electron. For every step explaining the oxidation of zero valence mercury to monovalent mercurous and further oxidation to mercuric ions Fig 1.

The effect of scan rate and the kinetic parameters like, solution electron transfer rate constant  $k_s$ , cathodic surface coverage ( $T_c$ ), anodic surface coverage ( $T_a$ ), cathodic electricity quantity, anodic electricity quantity and  $Ana$  are clearly represented in Table 1, indicating the increase in all kinetic parameters summarized before by the decrease in scan rates (Fig 2). Fig. 3 explains the relation between  $IP$  and  $v^{1/2}$  indicating a reversible mechanism of the salvation. together with the blank solution of  $0.01M KNO_3$  in absence of ligand. We noticed two cathodic peaks and two anodic peaks the reduction of mercuric ions from divalent to monovalent and then to zero valence The reactions where cyclic voltammetry shifted apart with increasing scan rate are quasi-reversible reactions.

For the reduction at  $\sim 0 V$ ,  $\sim -0.2 V$  and consuming one electron in each step as suggested mechanism. Consuming one electron in each step as suggested mechanism:



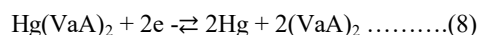
The reactions where cyclic Voltammetry shifted apart with increasing scan rate (Fig. 4) are quasi-reversible reaction. When we use different scans, the reduced species at silver

working electrode (SWE) is oxidation back to return to the starting conditions. The electron transfer rate is constant for the reverse reaction (oxidation).

### 2.1. Voltammograms of $HgCl_2$ in presence of ligand to form a complex.

Electrochemical behaviour of  $HgCl_2$  in the presence of valproic acid (VaA) in  $0.01M KNO_3$  at Silver working electrode (SWE): The effect of valproic acid (VaA) using different Concentration on  $HgCl_2$  were studied and represented in Fig 3. The Complex studies were followed by the decrease in any one of mercury waves. May this happen by following any reduction or oxidation peaks?

The new reduction wave was obtained at  $\sim -0.3 V$  (Figure 5-6) indicating the reduction of the formed complex resulted from the interaction between  $HgCl_2$  and Valproic acid as being visible in the digested mechanism.



From peak potentials for cyclic Voltammetry for the formed complex, the stability constants and Gibbs free energies of Complex formation were obtained<sup>20-42</sup> and their date are represented in Table 6. Scanning voltammograms of the complex showed that it was formed in  $HgCl_2$  in the presence of Valproic acid (VaA) in order to form a complex. The range 1 to  $-1V$  shows two cathodic peaks. In the reverse direction anodic two peaks are formed.

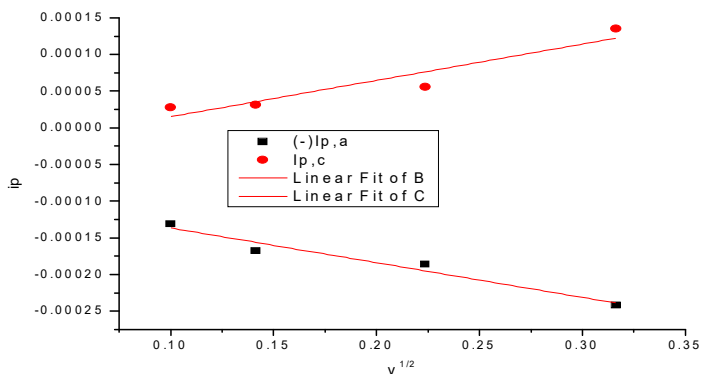


Fig.4. The relation between  $ip$  and  $v^{1/2}$  for the wave in the presence of ligand.

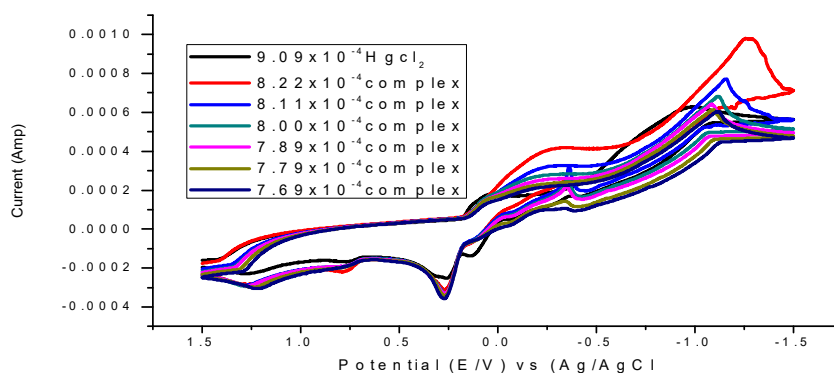


Fig 6. Voltammograms of the interaction of different ligand concentrations in  $0.01M KNO_3$  supporting electrode.

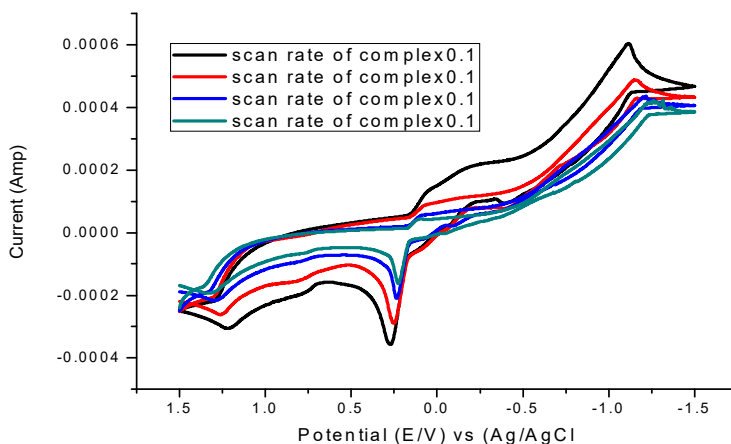


Fig 7. Effect of different scan rates on 1:1 (Metal/Valproic acid) stoichiometric complexes.

It is clear from Table 6 that the thermodynamic parameters, stability constants and Gibbs free energies of complexation are in ceased by in cease in valproic acid (VaA) Contraptions indicating more Complexation.

## 2.2. Analysis of voltammograms obtained.

$$i_p = (2.69 \times 10^{-5}) n^{3/2} A D^{1/2} v^{1/2} C \dots \dots \dots (1)$$

The redox processes for  $HgCl_2$  at silver working electrode were Studied at steady state equilibrium Conditions. The obtained cyclicwaves were analyzed by Eq (1) where  $i_p$  is measure-ement current in amper, A is the electrode surface area ,D diffusion Coefficient in  $cm^2/s$ ,  $v$  the scan rate in  $v/s$  and C is salt Concentration C mercuric chloride. The voltammo-grams were recorded using Silver working electrode (SWE) from start potential 1.5 V to final potential -1.5 V. The measured Cyclic Voltammetry depend on ion movement for  $Hg^{2+}$  and electron transfer reaction

$$k_f = k^0 \exp \frac{-\alpha n F}{RT} (E - E^0) \dots \dots \dots (2)$$

$k_f$  is the electron transfer rate constant in the forward direction,  $k^0$  is the standard electron transfer rate Constant for interaction. E is the potential for reduction and  $\alpha$  is the transfer Coefficient we take  $\alpha \cong 0.5$  for better results.<sup>30-43</sup> When we using scan the reduced species at silver working electrode (SWE) is oxidation back to return to the starting. The electron transfer rate constant for reverse reaction  $k_r$  (oxidation), is controlled by equation (3).

$$k_r = k^0 * \exp[(1-\alpha)nF/RT] (E - E^0) \dots \dots \dots (3)$$

If reaction proceeds reversibly, the peak potential Separation  $\Delta E_p$  will be near  $.58/n$  (at  $25^\circ C$ ). This relation, can be used for electron evaluation for reversible reactions, the reduction process is fast for obtaining the oxidized and reduced ions or Species in equilibrium. The equilibrium between the two forms of ions has determined the use of Nernst equation (4).

$$E = E^0 - [RT/nF] \ln [R]/[O] \dots \dots \dots (4)$$

The [R] and [O] are the reduced and oxidized forms concentration. When the reaction is fast, reversible reaction can proceed.  $\Delta E$  shows decrease in trend. The reaction is reversible if  $h^0$  is greater than  $0.3 v^{1/2} [q]$ , where is selected scan rate when the electron transfer reaction is greater than 10  $cm/s$ . The reaction will be reversible. The reactions where cyclic Voltammetry shifted apart with increasing scan rate are quasi-reversible reactions. Some examples for irreversible reactions involve bond breaking. For quasireversible systems, the peaks are widely separated from some other works<sup>15-20</sup> used as the half wave potential values, for explaining the reversibility mechanisms as

$$E_{p/2} = E_{1/2} \pm 28/2 (mv) \dots \dots \dots (5)$$

The sign is positive for reduction processes when rate is increased, slow electron transfer makes a shift in peak potential, explaining no symmetry about  $E_{1/2}$ . The ratio of the anodic to cathodic peak currents explains the behavior of  $HgCl_2$  in absence of Valproic acid (VaA).

## 3. Conclusion

The different theoretical calculations (Gaussian 09 calculations) for Valproic acid in water gave good values for different dipole, multipole moments, statistical vibration, rotation, and electroic modes of movements, IR.active groups and Raman Spectra indicate the activity of the used reagent in water. From the peak potentials and current height, the stability constants and the Gibbs free energies were evaluated as presented in Table 1. It is clear also that the increase in ligand concentration on  $HgCl_2$  as shown on using 1:3, metal to ligand molar ratio indicating less positive free energies supporting stronger complexation results Table 5.

## 4. Experimental

Sodium perchlorate was prepared in our laboratory by adding NaOH to freshly prepared perchloric 0.1M and from Al Gomheria pharmaceutical company and titrating till first appearance of neutral medium.<sup>6-7</sup> Valproic acid (VaA) from Oxford Co. with structure of its electronic clouds as shown in Fig. 7, we used DY2000 potentiostat applied for measuring

cyclic voltammograms at different scan rates. We passed  $N_2$  gas in each solution for about 10 minutes and insured the scapping of dissolved oxygen. the electrode systems were applied, here, by the use of Ag/AgCl as reference electrode.

Platinum wire electrode as auxiliary electrode and the prepared silver electrode (SWE) as working electrode were also applied. Besides, deionized water with conductivity of  $2.7 \mu$  was used.

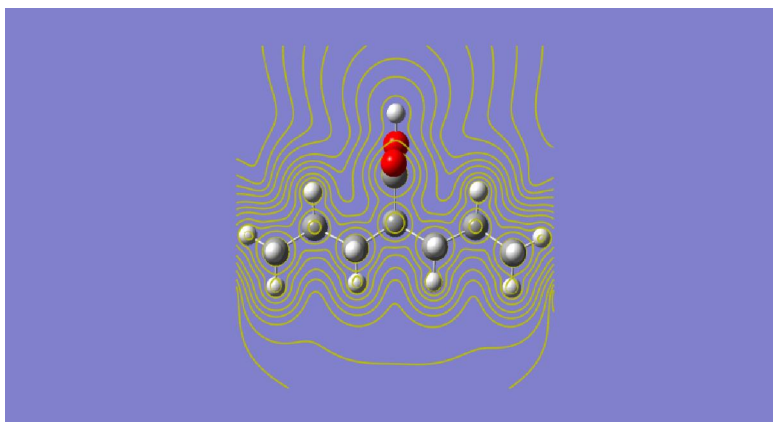


Fig 1. Contour lines for the ligand used.

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