The Study of Electrochemical Reduction of Cd(II)- Pyrimidines Complexes at Dropping Mercury Electrode

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ABSTRACT: The effect of the adsorption of tetraethylammonium (TEA) cations, which present both ionic and organic characteristics, on the reduction of Cd(II) ions have been studied from dc and ac measurements at the dropping mercury electrode. The resistance to the charge transfer (Rct) and Warburg coefficient (σ) parameters have been determined through impedance measurements. Thus, the global velocity constant has been obtained. The reduction process of Cd(II) in perchloric media is reversible and is affected by the adsorption of TEA cations, especially at high TEA concentrations. Values of $E_{1/2}$, half wave potential, and D_O, diffusion coefficient, obtained from both dc and ac measurements agree. The velocity constants show a decrease as TEA concentration increases, with values ranging from 0.6 to 0.01 cm·s^{-1}. The inhibitory effect of TEA adsorption on the electrode process and the relationship between electrode coverage, θ, and velocity constants, K, using several isotherm equations, have been discussed. The best fit was obtained with the equation K = $_0$K$(1 - \theta)^a$ with an a value close to three, indicating a blocking effect and electrostatic repulsion due to TEA.

KEYWORDS: dropping mercury electrode (DME); tetraethylammonium cation (TEA); electrochemical impedance; electrochemical reduction of Cd(II); Randles circuit; adsorption of TEA; adsorption isotherm

I. INTRODUCTION

Electrochemistry is the branch of physical chemistry concerned with the relationship between electrical potential difference, as a measurable and quantitative phenomenon, and identifiable chemical change, with the potential difference as an outcome of a particular chemical change, or vice versa. These reactions involve electrons moving via an electronically-conducting phase (typically an external electrical circuit, but not necessarily, as in electroless plating) between electrodes separated by an ionically conducting and electronically insulating electrolyte (or ionic species in a solution).[1,2,3]

When a chemical reaction is driven by an electrical potential difference, as in electrolysis, or if a potential difference results from a chemical reaction as in an electric battery or fuel cell, it is called an electrochemical reaction. Unlike in other chemical reactions, in electrochemical reactions electrons are not transferred directly between atoms, ions, or molecules, but via the aforementioned electronically-conducting circuit. This phenomenon is what distinguishes an electrochemical reaction from a conventional chemical reaction.[1]

The term "redox" stands for reduction-oxidation. It refers to electrochemical processes involving electron transfer to or from a molecule or ion, changing its oxidation state. This reaction can occur through the application of an external voltage or through the release of chemical energy. Oxidation and reduction describe the change of oxidation state that takes place in the atoms, ions or molecules involved in an electrochemical reaction. Formally, oxidation state is the hypothetical charge that an atom would have if all bonds to atoms of different elements were 100% ionic. An atom or ion that gives up an electron to another atom or ion has its oxidation state increase, and the recipient of the negatively charged electron has its oxidation state decrease.

For example, when atomic sodium reacts with atomic chlorine, sodium donates one electron and attains an oxidation state of +1. Chlorine accepts the electron and its oxidation state is reduced to −1. The sign of the oxidation state (positive/negative) actually corresponds to the value of each ion's electronic charge. The attraction of the differently charged sodium and chlorine ions is the reason they then form an ionic bond.

The loss of electrons from an atom or molecule is called oxidation, and the gain of electrons is reduction. This can be easily remembered through the use of mnemonic devices. Two of the most popular are "OIL RIG" (Oxidation Is Loss, Reduction Is Gain) and "LEO" the lion says "GER" (Lose Electrons: Oxidation, Gain Electrons: Reduction). Oxidation and reduction always occur in a paired fashion such that one species is oxidized when another is reduced. For cases where electrons are shared (covalent bonds) between atoms with large differences in electronegativity, the electron is assigned to the atom with the largest electronegativity in determining the oxidation state.[4,5,6]

The atom or molecule which loses electrons is known as the reducing agent, or reductant, and the substance which accepts the electrons is called the oxidizing agent, or oxidant. Thus, the oxidizing agent is always being reduced in a reaction; the reducing agent is always being oxidized. Oxygen is a common oxidizing agent, but not the only one. Despite the name, an oxidation reaction does not necessarily need to involve oxygen. In fact, a fire can be fed by an oxidant other than oxygen; fluorine fires are often unquenchable, as fluorine is an even stronger oxidant (it has a weaker bond and higher electronegativity, and thus accepts electrons even better) than oxygen.

For reactions involving oxygen, the gain of oxygen implies the oxidation of the atom or molecule to which the oxygen is added (and the oxygen is reduced). In organic compounds, such as butane or ethanol, the loss of hydrogen implies oxidation of the molecule from which it is lost (and the hydrogen is reduced). This follows because the hydrogen donates its electron in covalent bonds with non-metals but it takes the electron along when it is lost. Conversely, loss of oxygen or gain of hydrogen implies reduction.

The reduction of Cd(II) ions at the dropping mercury electrode (DME) has been widely used to test models for electrode reactions. Nowadays, some characteristics of the process seem well established, as the CEE mechanism (C: chemical reaction, E: electron transfer) [1,2,3,4], but other questions remain unsolved when adsorption or complexation is present [5,6,7,8,9]. The catalytic effect or inhibition by organic substances could introduce changes in the mechanism or only influence values of the parameters and velocity constants. Particularly, the catalytic effect of thiourea has been studied [5,6], and it was concluded that thiourea adsorption changes the mechanism of Cd(II) reduction; however, the inhibition effect of sucrose [8] only influence the values of the velocity constants but the CEE mechanism remains. It seems interesting to study the effect of other adsorbing substances. Tetraethylammonium (TEA) ions have been selected because of their double character of ionic and organic, and because their adsorption has been studied previously [10,11]. TEA was selected formerly due to it be an organic cation but with an organic character in between that of TMA and TBA. TMA exhibits a behavior somewhat similar to an inorganic cation with a weak specific adsorption [12,13,14,15]. On the other hand, TBA presents a high organic character with a high specific adsorption, which induces a high adsorption of the salt anion [16]. In a previous polarographic study of the Eu(III)/Eu(II) reduction in the presence of TEA [11,17], both surface blocking and electrostatic interaction effects between the adsorbate and the electroactive ions were observed.

In this paper, the reduction of Cd(II) in the presence of TEA in a perchloric acid medium is presented, using dc and ac measurements. The activity of the perchloric acid was maintained constant [10,18,19] in order to apply a correct thermodynamic treatment. The adsorption results, obtained previously, are related to the electrode kinetic values obtained in the present study.

Measurements were performed in a three-electrode cell. The working electrode (WE) was a DME (see ref. [20] for general details); the counter electrode (CE) was a pool of mercury; and the reference electrode (RE) was a sodium-saturated calomel electrode (SSCE or NaSCE) connected to the cell via a salt bridge filled with the supporting electrolyte. The temperature was 25 ± 0.1 °C. Solutions were prepared from twice-distilled water and analytical-grade chemicals. The supporting electrolyte was perchloric acid maintained at constant activity $a_{\pm} = 0.418$ (c ≈ 0.55 m), according to previous thermodynamic studies on the activity coefficients of perchloric acid and TEA perchlorate mixtures [10,18,19]. The concentrations of TEA perchlorate were 0, 0.75, 2, 5, 10 and 20 mM, but the results for the 20 mM concentration are only taken as a qualitative indication due to their significant dispersion.

Before measurements, oxygen was removed by bubbling argon through the cell. The dc and ac measurements were performed at 1.5 mM Cd(II) concentration (as $CdSO_4$) and at 4 s after the mercury drop birth. A new drop was used for each measurement. For these measurements, the network analyzer system described earlier [23,24] was used. The cell impedance was analyzed in the frequency range of 80–10,000 Hz at 5 mV intervals of the dc potential within the Faradaic region. The dc polarograms were also obtained at 5 mV intervals.[7,8,9]

Although cadmium usually has an oxidation state of +2, it also exists in the +1 state. Cadmium and its congeners are not always considered transition metals, in that they do not have partly filled d or f electron shells in the elemental or common oxidation states.[9] Cadmium burns in air to form brown amorphous cadmium oxide (CdO); the crystalline form of this compound is a dark red which changes color when heated, similar to zinc oxide. Hydrochloric acid, sulfuric acid, and nitric acid dissolve cadmium by forming cadmium chloride ($CdCl_2$), cadmium sulfate ($CdSO_4$), or cadmium nitrate ($Cd(NO_3)_2$). The oxidation state +1 can be produced by dissolving cadmium in a mixture of cadmium chloride and aluminium chloride, forming the Cd_2^{2+} cation, which is similar to the Hg_2^{2+} cation in mercury(I) chloride.[6]

$$Cd + CdCl_2 + 2\ AlCl_3 \rightarrow Cd_2(AlCl_4)_2$$

The structures of many cadmium complexes with nucleobases, amino acids, and vitamins have been determined.[10]

The dropping mercury electrode (DME) is a working electrode made of mercury and used in polarography. Experiments run with mercury electrodes are referred to as forms of polarography even if the experiments are identical or very similar to a corresponding voltammetry experiment which uses solid working electrodes. Like other working electrodes these electrodes are used in electrochemical studies using three electrode systems when investigating reaction mechanisms related to redox chemistry among other chemical phenomena. A flow of mercury passes through an insulating capillary producing a droplet which grows from the end of the capillary in a reproducible way. Each droplet grows until it reaches a diameter of about a millimeter and releases. The released droplet is no longer in contact with the working electrode whose contact is above the capillary. As the electrode is used mercury collects in the bottom of the cell. In some cell designs this mercury pool is connected to a lead and used as the cell's auxiliary electrode. Each released drop is immediately followed by the formation of another drop. The drops are generally produced at a rate of about 0.2 Hz. A major advantage of the DME is that each drop has a smooth and uncontaminated surface free from any adsorbed analyte or impurity. The self-renewing electrode does not need to be cleaned or polished like a solid electrode. This advantage comes at the cost of a working electrode with a constantly changing surface area. Since the drops are produced predictably the changing surface area can be accounted for or even used advantageously. In addition, the drops' growth causes more and more addition of capacitive current to the faradaic current. These changing current effects combined with experiments where the potential is continuously changed can result in noisy traces. In some experiments the traces are continually sampled, showing all the current deviation resulting from the drop growth. Other sampling methods smooth the data by sampling the current at the electrode only once per drop at a specific size. The DME's periodic expansion into the solution and hemispherical shape also affects the way the analyte diffuses to the electrode surface. The DME consists of a fine capillary with a bore size of 20–50 μm. The hanging mercury drop electrode (HMDE) is a working electrode variation on the dropping mercury electrode (DME). Experiments run with dropping mercury electrodes are referred to as forms of polarography. If the experiments are performed at an electrode with a constant surface (like the HMDE) it is referred as voltammetry.[10,11,12]

Like other working electrodes these electrodes are used in electrochemical studies using three electrode systems when investigating reaction mechanisms related to redox chemistry among other chemical phenomenon

The hanging mercury drop electrode produces a partial mercury drop of controlled geometry and surface area at the end of a capillary in contrast to the dropping mercury electrode which steadily releases drops of mercury during an experiment. The disadvantages a DME experiences due to a constantly changing surface are not experienced by the HMDE since it has static surface area during an experiment. The static surface of the HMDE means it is more likely to suffer from the surface adsorption phenomenon than a DME. Unlike solid electrodes which need to be cleaned and polished between most experiments, the self-renewing HMDE can simply release the contaminated drop and grow a clean drop between each experiment.

II. DISCUSSION

In electrochemistry, the working electrode is the electrode in an electrochemical system on which the reaction of interest is occurring.[1][2][3] The working electrode is often used in conjunction with an auxiliary electrode, and a reference electrode in a three-electrode system. Depending on whether the reaction on the electrode is a reduction or an oxidation, the working electrode is called cathodic or anodic, respectively. Common working electrodes can consist of materials ranging from inert metals such as gold or platinum, to inert carbon such as glassy carbon, boron-doped diamond[4] or pyrolytic carbon, and mercury drop and film electrodes.[5] Chemically modified electrodes are employed for the analysis of both organic and inorganic samples. Pyrimidines are a group of six-membered aromatic heterocycles [1] that are important chemical compounds due to their wide application in the pharmaceutical field [2], [3], [4], [5]. The ability of the pyrimidine ring nitrogen atoms to act as a chelating ligand enables such compounds to be used to form supramolecular assemblies and as sensors [6]. For example, they have applications in light sensors for color-sensitive solar cells [7] and polarity sensors [8]. They are used for a diverse range of applications [9], [10].

To extend the chemistry of this class of compounds, in this work, the preparation, characterization (elemental analysis, FT-IR, ^{1}H NMR spectroscopy), and crystal structure of a new cadmium(II) complex, [Cd(μ-APPH)Br]$_2$ (1), with N′-(amino(pyrimidin-2-yl)methylene)pyrimidine-2-carbohydrazonamide (APPH) as a ligand is presented. The structure of the isolated molecules of APPH^{opt} and 1^{opt} have been determined by density functional theory (DFT) studies to compare the results with the solid-state data. The variation of the charge values of atoms/ions during the complexation process was investigated by natural bond orbital (NBO) analysis.[13,14,15]
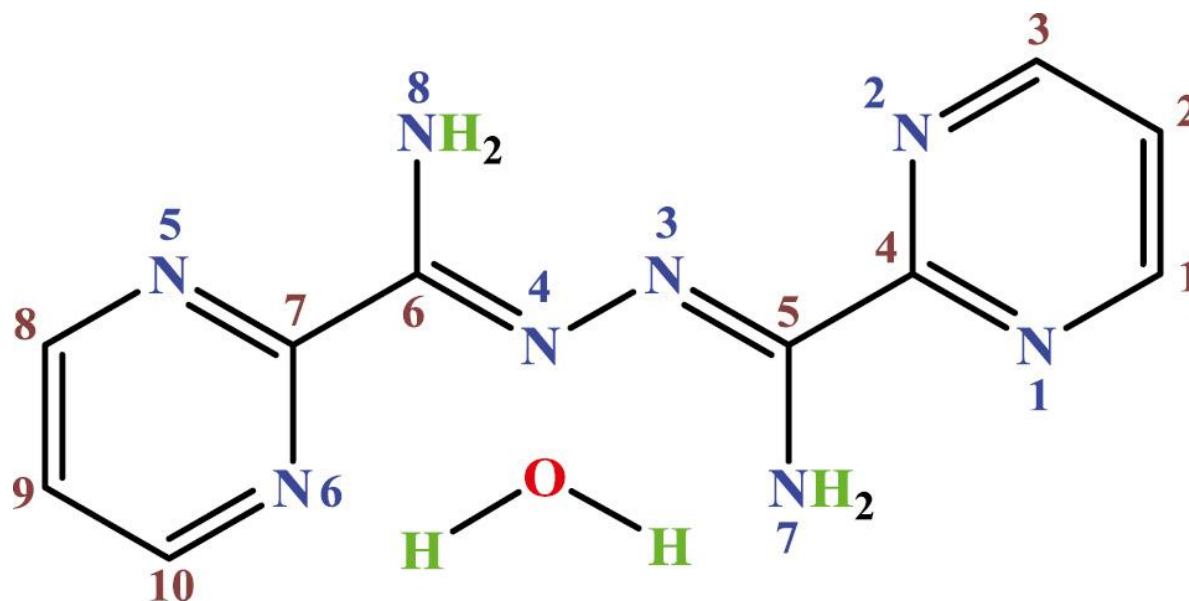
A new binuclear complex of cadmium(II), [Cd(μ-APPH)Br]$_2$ (1); APPH: N′-(amino(pyrimidin-2-yl)methylene)pyrimidine-2-carbohydrazonamide, and the hydrate of this pyrimidine-based ligand, APPH·H$_2$O, were synthesized and their spectral properties were investigated. The crystal structure of the complex has been determined, in which the cadmium atom has a CdN$_4$Br$_2$ environment with a distorted octahedral geometry formed by two cis-N$_2$-donor APPH ligands (each ligand acts as N$_4$-donor toward two cadmium atoms) and two cis-bromo ligands. Two APPH ligands bridge two cadmium atoms to form a six-membered 2L:2M^{1,4} ring. In the crystals of 1, the N–H···Br interactions form different types of hydrogen bonding motifs including, R22(12,14),R66(24,26,…,46),R22(12, 14), R66(24, 26, …, 46), and there are π-π stacking interactions between pyrimidine rings on adjacent ligands. DFT calculations reveal that the octahedral geometry of the cadmium atom observed in the solid phase is closer to ideal than in the isolated molecule. An NBO analysis of both the nitrogen and carbon atoms was carried out to follow the effect of the donor/acceptor interaction.[16,17,18]

The polarographic curve for the solution without TEA shows a reversible reduction of the Cd(II) ions. The half-wave potential is $E_{1/2}^r = -575$ mV (vs. SSCE), with a value only slightly more negative than that of $E_{1/2}^r$ reported for other perchlorate media: the value of $E_{1/2}^r = -570$ mV (vs. SSCE) in 0.8 M NaClO4 was reported by [8,9], and the value of $E_{1/2}^r = -567$ mV or -569 mV (vs. SSCE) in 0.5 M NaClO$_4$ + 0.5 M HClO$_4$ medium is reported in the bibliography. plots $\log(i/(i_d - i))$ vs. E. The slope of $\log(i/(i_d - i))$ vs. E is 0.033 mV^{-1} =33 V^{-1}, practically the value of the reversible case (nF/(2.3RT).The diffusion coefficients for Cd(II) obtained from the Ilkovic equation and considering the correction of sphericity are 12.6 and 9.1×10^{-6} cm^2·s^{-1}, respectively.These coefficients were also obtained from ac measurements.[19,20]
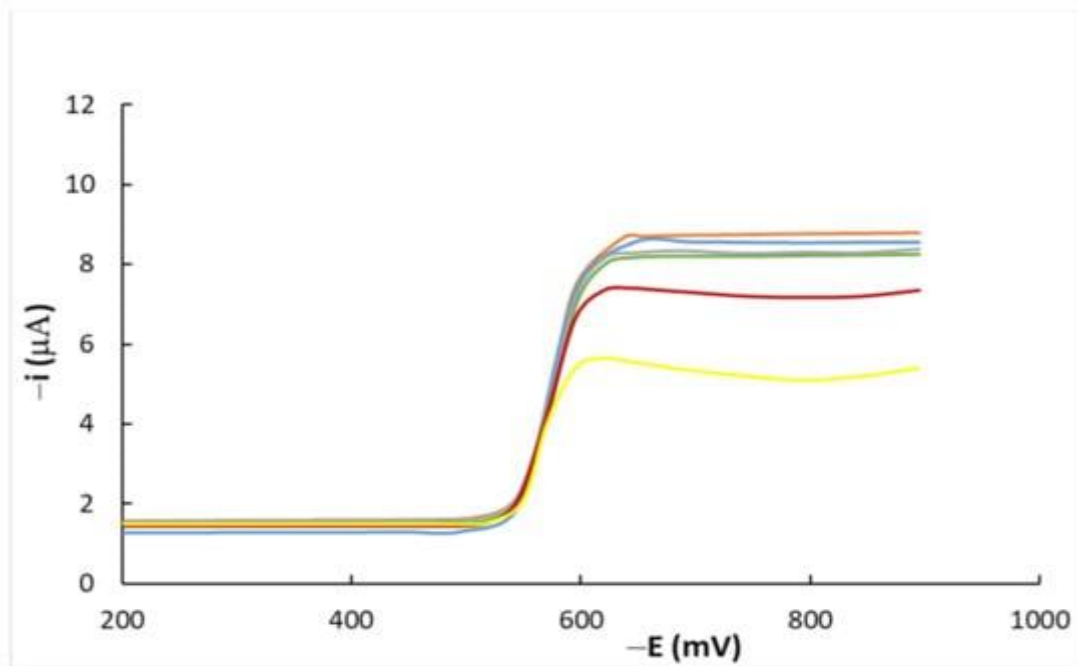
Figure 1. Polarograms for Cd(II) in the presence of TEA in 0.55 M perchloric acid solutions. TEA concentrations (mM): 0 (orange), 0.75 (blue), 2 (green), 5 (grey), 10 (red), 20 (yellow).

III. RESULTS

The values of D_O obtained with the Ilkovic equation are higher than those reported in the bibliography (even the experimental conditions of the concentration and electrolyte are different), but the latter are more similar to the value of D_O obtained with the equation that considers the sphericity correction. As we will see later, the value of D_O obtained with the equation that considers the sphericity correction also agrees better with the value obtained from impedance analysis. The values of D_O reported in the bibliography are 8.0×10^{-6} cm$^2 \cdot$s^{-1} in 0.8–1 M NaClO$_4$ medium [8,9], and 7.0 (or 8.0) $\times 10^{-6}$ cm$^2 \cdot$s^{-1} in 0.5 M NaClO$_4$ + 0.5 M HClO$_4$ medium.[21,22]
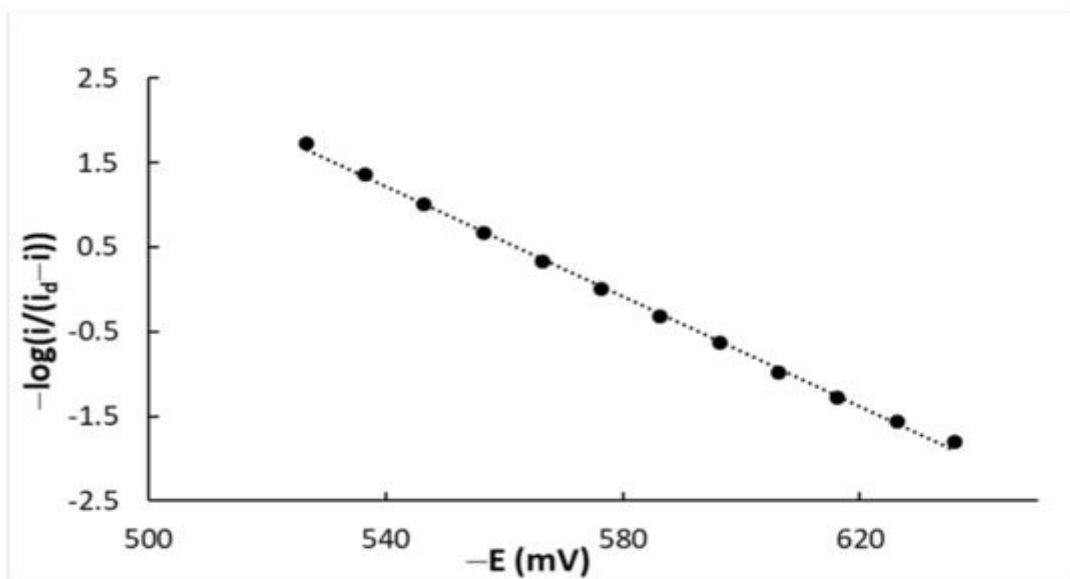
Plot of the irreversibility quotient p′ vs. E at different TEA concentrations. TEA concentrations (mM): 0 (orange), 0.75 (grey), 2 (yellow), 5 (blue), 10 (green).
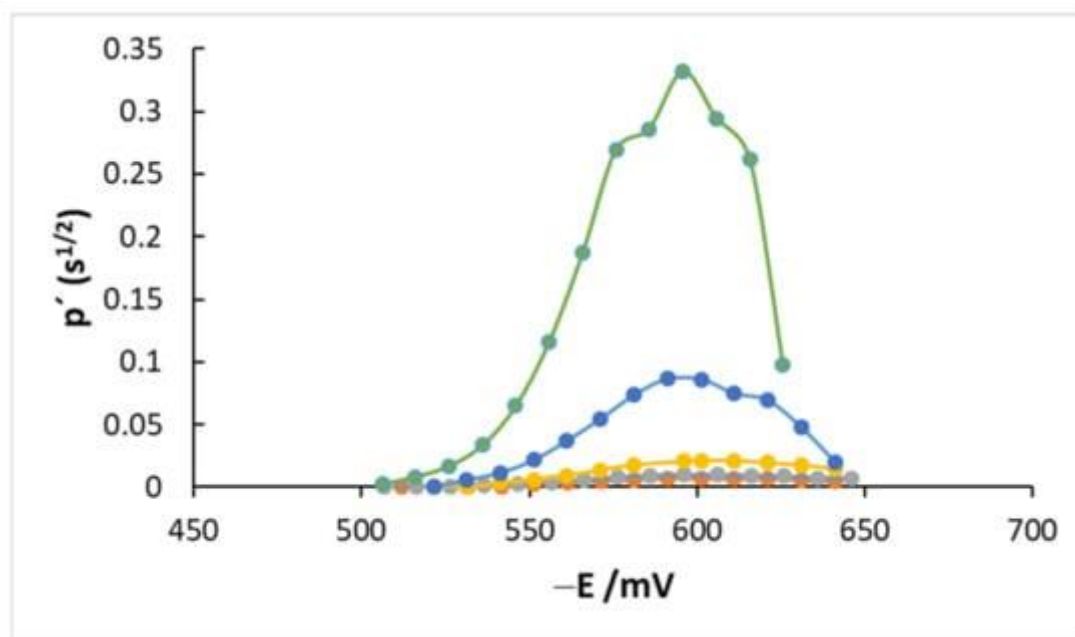
The existence of two waves in polarograms when the TEA concentration is high, with the second wave shifted to more negative potentials, indicates that a strong TEA adsorption inhibits the second electron transfer. A big change on the surface coverage, θ, at low TEA concentrations provokes little change in the current intensity. A slight change in the adsorption at high TEA concentrations provokes a strong change in the current intensity. Thus, it seems that adsorption especially effects the second electron transfer.[23,24]

Values of $E_{1/2}$ and D_O obtained from both dc and ac measurements agree. The velocity constants showed a decrease as TEA concentration increased, with values ranging from 0.6 to 0.01 cm·s^{-1}. The change in the value of α (α_{ap} is potential-dependent) could indicate that the adsorption of TEA changes the mechanism or perhaps influences the electron transfer energy.

Testing the relationship between electrode coverage and velocity constant using several isotherm equations shows that the best fit is obtained with the equation $K = {}_0K(1 - \theta)^a$, with an a value close to three, indicating a blocking effect and electrostatic repulsion due to the TEA cation.[25]

IV. CONCLUSIONS

Advantages and disadvantages of dropping mercury electrode.

Some of the advantages of dropping mercury electrode(DME) are as follows:

- Mercury form amalgam with most metals.
- Mercury has a high hydrogen overvoltage.
- It provides a smooth, fresh surface for the reaction.
- Each drop remains unaffected and does not become contaminated by the deposited metal.
- Diffusion equilibrium is readily established at mercury-solution interface.

Some of the disadvantages of dropping mercury electrode(DME) are as follows:
- It is poisonous so care should be taken in its handling.
- Surface area of a drop of mercury is never constant.
- Applied voltage produces changes in surface tension and hence change in drop size.
- Mercury has limited applications in analysis of more positive potential range.

Following care must be taken while using dropping mercury electrode:
- Pure and triple distilled mercury should be used in DME

- Tip of DME should be always immersed in water when not in use.
- Tip of DME should be cleaned by dipping in nitric acid.
- The DME assembly should be mounted vertical on a heavy stand to be free from vibrations.
- It is essential to use clean and dust free tubing while setting the DME.
- There should be sufficient mercury in reservoir so that the pressure changes are negligible.[23,24,25]

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