Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.7 No.5, 2015

Polarographic Study of Nickel (II) Electrolytes with Malonic acid

Juhaina Alghdir* M.A Al-Cheikh
Department of Chemistry, Faculty of Science , Al-Baath University, Homs, Syria
* E-mail of the corresponding author: juhaina.ghdayer@yahoo.com

Abstract

In this research we studied the mechanism of the reaction in the [Nickel(II)–Malonic acid–water] medium by using Electrochemical Methods (Polarography) proved that the particle which is reduced on The Mercury Drops Electrode is Nickel Malonics , and that reduction is a semi–reversible process, takes place by participation of two electrons (n=2) in a one stage mechanism at relatively high cathodal polarizability. The half-wave potential reduction process of nickel ions with malonic acid is shifted compared with the hydrated ion reduction potential in all studied solutions, the amount of this shift is equilateral (≈30-35mv). Thus, this study could introduce a new electrolyte for painting with nickel which has good properties, free from defects.

Keywords: Nickel, Malonic acid, Potential, Reduction, polarizability.

1. Introduction

Recently it has been found that the painting of minerals starting with their complexes differs from other well-known a set of features:

It allows to control the thickness of the paint, its structure ,and its features. Also allows regularity distribution glphanic painting on mineral commodities that have different shapes [1].

Numerous studies have shown that the physico-mechanical properties of the nickel coating depend on the deposition parameters and the bath composition [2-9].

New buffering components have been studied because they offer higher buffer capacity than the boric acid does [10,11,12].

So, when selecting the Ligand it is preferred to choose the one which constitutes fixed complexes with metal ions, because the stability of the complex shapes of the metal in the electrolyte leads to maintain the high cathodal potential.

Thus, the crystallization of mineral leads to the emergence of a large number of crystal centers, then we get a soft, smooth and cohesive coating layer, which prolongs its age and increases their brightness.

Based on all of that, malonic acid has drawn our attention as binary Ligand that can form annular compounds with nickel ions to perform the aim, as malonic acid shows a set of convenient properties that meet these requirements, and the requirements of the galphanic industry too [13].

2. Experimental Procedure:

The materials used: malonic acid ($C_3H_4O_4$), Nickel sulfate ($NiSO_4.6H_2O$), Sodium hydroxide (NaOH), Nitric acid (HNO_3), potassium chloride (KCl), ammonium chloride (NH_4Cl), and ammonium hydroxide (NH_4OH), all of these were of high purity. The type of water used, is the binary distillation water. The experiments were carried out the lab temperature using solvents newly prepared.

We also used to study the electrical reduction of nickel, sophisticated voltage ampere-metric station model (Metrohm Comutrace 797 VA) Swiss Mitrom company production, with a three-cell electrodes operate on all mercury electrode patterns, and the dissolved oxygen has been expelled by bubbling it with nitrogen gas for 10-15 minutes.

3. Results and Discussion:

In order to ensure accuracy in the interpretation of the experimental data, it was necessary to know the behavior of malonic acid, So it has been clear that malonic acid reduction does not give any polarographic tops on any matrix, figure 1.

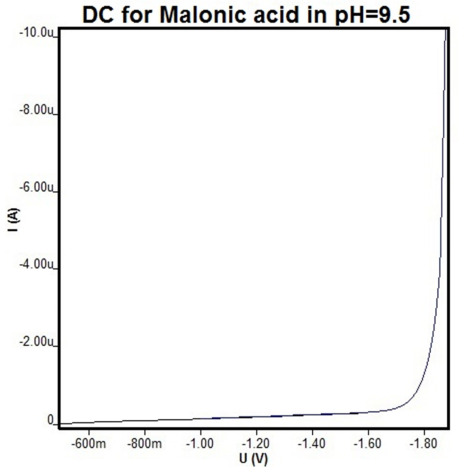
DC for Malonic acid in pH=9.5

Figure-1:The DC polarogram for malonic acid; (NH_4Cl+NH_4OH); 1M, pH=9.5

But when drawing the polarographic curves of nickel sulfate solution we get polarographic waves, in presence of malonic acid in studied solution, and also in its absence.

We draw the classic polarogram (DC) and the differential pulse polarogram (DPP) on three matrix as shown in the following figures 2, 3, 4, 5,6.

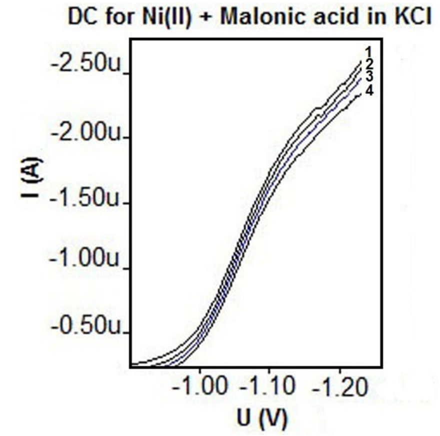
DC for Ni(II) + Malonic acid in KCl

Figure-2:The DC polarogram for nickel(II) with malonic acid in KCl; 1-nickel sulfate, 2-[1:1], 3-[1:2], 4-[1:3]
$[Ni^{2+}]=1X10^{-3}$, [KCl]=0.5M

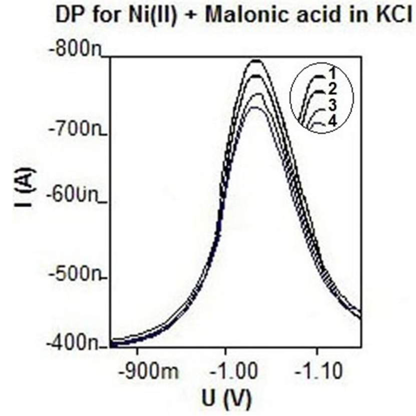
DP for Ni(II) + Malonic acid in KCl

Figure-3:The DPP polarogram for nickel(II) with malonic acid; 1-nickel sulfate, 2-[1:1], 3-[1:2], 4-[1:3]
$[Ni^{2+}]=1X10^{-3}$, [KCl]=0.5M

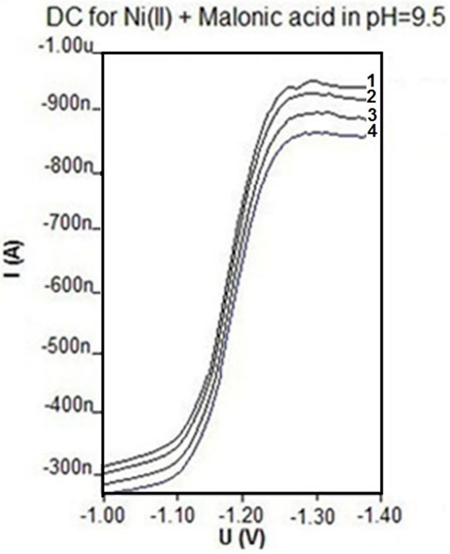

Figure-4:The DC polarogram for nickel(II) with malonic acid; 1-nickel sulfate, 2-[1:1], 3-[1:2], 4-[1:3] [Ni^{2+}]=1X10^{-4} , (NH_4Cl+NH_4OH): pH=9.5

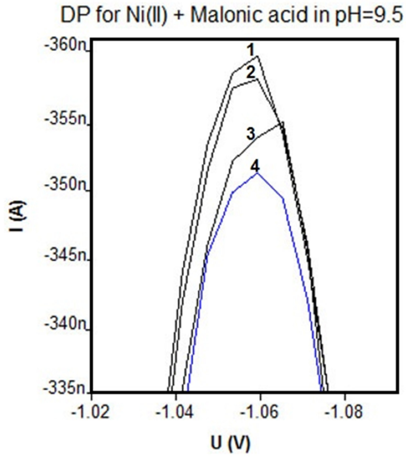

Figure-5:The DPP polarogram for nickel(II) with malonic acid; 1-nickel sulfate, 2-[1:1], 3-[1:2], 4-[1:3] [Ni^{2+}]=1X10^{-4} , (NH_4Cl+NH_4OH); 1M, pH=9.5

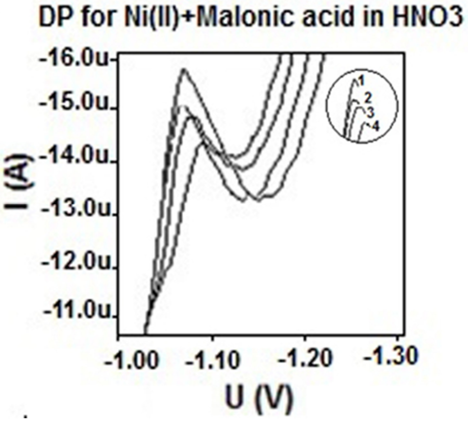

Figure-6:The DPP polarogram for nickel(II) with malonic acid; 1-nickel sulfate, 2-[1:1], 3-[1:2], 4-[1:3] [Ni^{2+}]=0.6X10^{-2} ,[HNO_3]=0.5M

In order to determine the reversibility of the electrodic process, we used the Tamamushi argument described in the work [14], where the relationship was drawn: Log $^{i}/_{id-i}$ = f(E) , as in figures (7) and (8).

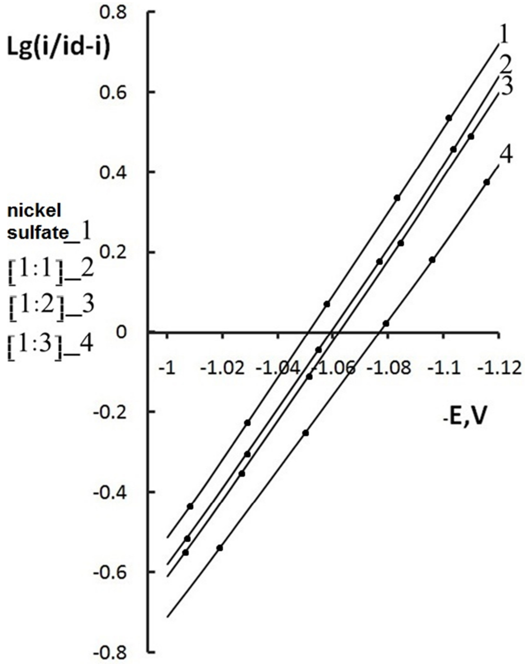

Figure-7:The dependence of the lg(i/id-i) on E; [Ni^{2+}]=1X10^{-3}, [KCl]=0.5M

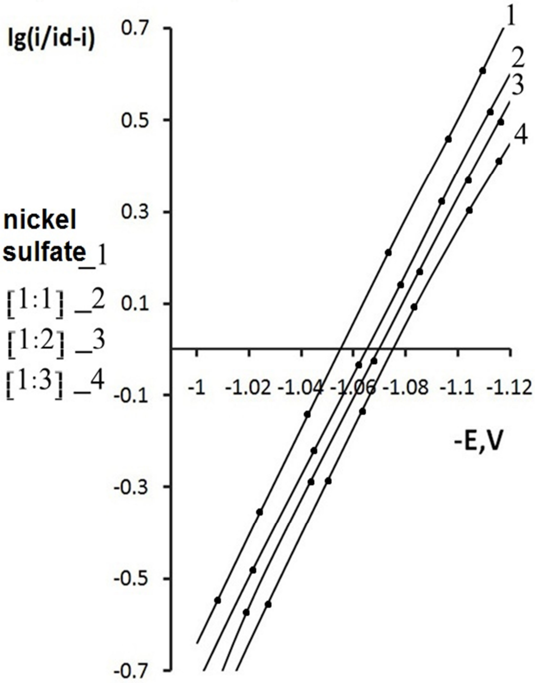

Figure-8: The dependence of the lg(i/id-i) on E; Ni^{2+}]=1X10^{-4}, (NH_4Cl+NH_4OH);1M, pH=9.5

Each figure (7) and figure (8) shows that the nickel ions reduction process in the absence of malonic acid is reversible. The Semi-logarithmic relationship: Log $^{i}/_{id-i}$ = f(E) is a straight line and the point of intersection with the X-axis is determined by the half-wave potential reduction interaction, and this line achieves Tamamushi argument. The Mile of this line (≈30 mv) and this indicates reversibility of nickel ions reduction process from its simple salts solutions, which corresponds well with the reference data [15].

When we add malonic acid to the studied solution whereas its percentage to nickel ions is [1: 1], is noted a slight decline in the peak current values to the nickel ions reduction, and shift the half -wave potential reduction by (30-35 mv) in the direction of negative potential values. And when the percentage of nickel ions and malonic acid becomes [1:2], the value of the Peak Current decline more. This is because of the dilution of the solution, while half-wave potential reduction stays practically constant, and the peak current value decline more when nickel ions percentage becomes [1: 3] to malonic acid.

The conjugated polarizability attaches with the discharge of nickel ions process from nickel malonics electrolyte [1: 1] (according to the new perceptions) with the slowness of the special discharge action [16].

Where the presence of nickel ions in a fixed annular compound leads to the decrease in their effectiveness and to shift their deposition potential to negative potential.

We also note in Figures (7), (8) that the electric reduction of nickel ions with malonic acid is half-reversible (quasi-reversible), and the Mile of this line doesn't achieve the Tamamushi argument.

The cause of the disorder in the reversibility is either malonic acid adsorption on the surface of the electrode or forming the [1: 1] compound in the solution.

Determining the number of shared electrons in the nickel ions reduction process:

There are two ways to determine the number of electrons:

a)- By differential polarographic curve with the relationship used for reversible and quasi-reversible operation [17]: $n = 98 . \frac{mv}{s}$ (**S**- half of the peak width)

b)- Or by the Mile of lines resulting in figures (12), (13) and from the polarographic wave equation data (reversible and quasi-reversible): $E = E_{1/2} - \left(\frac{0.059}{\theta . n}\right) \log \frac{i}{id-i}$

θ- conversion factor and its value ranging between (0-1), depending on the reversible degree, and we consider : (θ=1) for reversible polarographic waves, (θ=1/2) for half-reversible polarographic waves, So it has been clear that: n = 2 means that the reduction process takes place in one stage mechanism by two electrons: $Ni^{2+} + 2e^{-} \rightarrow Ni^{0}$

4. Conclusion

1_The half-wave potential reduction process of nickel ions with malonic acid is shifted compared with the hydrated ion reduction potential in all studied solutions,the amount of this shift is equilateral (≈30-35mv). This means that the contribution of forming the compound with electrodic polarizability process is similar, related to the reduction of the same particle, and these particle is Nickel Maolnics [1:1].

2_ The malonic acid that increases twice by amount leads to shift the half-logarithmic relationship:

$\text{Log}\ ^{i}/_{id\ -\ i}\ f(E)$ just little, but the graph line form remains constant as in Figure (7), (8) This shows the stability of the nature and mechanism of the reduction process.

The small displacement for polarographic wave in anodic direction resulting from the increase of malonic acid percentage to become in nickel [1: 1] can be explained as follows:

Dissolving malonic acid in water is accompanied by its hydration, the more the solution is more alkaline the more a larger number of malonic acid molecules dissociate and decrease the pH- solution. By adding another similar amount of malonic acid to the studied solution, pH of the solution reduces by the same amount and the practical polarizability declines regularly.

3_ The pH is an important factor in determining the kinetics of nickel malonics reduction, increasing the acidity leads to increase the interaction reduction speed. The effects of the hydroxyle ions is likely to appear in the alkaline solution at the same time of discharging the ion. Where the later is involved in a reaction with hydroxyle ions and forms nickel hydroxyle on the surface of the electrode, which is expected to decrease the repelled of the painting process according to the current [18].

4_ The process of nickel reduction take place by the participation of two electrons in a one stage, and it is a quasi-reversible process at relatively high polarizability.

Finally, we can say that this study could introduce a new electrolyte for painting with nickel which has good propertier, free from defects**.**

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