Electrochemical Reduction of Nickel – Acrylic Acid Complexes : Quantum-chemical Analysis

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Abstract On the basis of quantum-chemical cluster calculations $[\text{Ni}^{z+}(\text{H}_2\text{O})_n\text{L}](\text{H}_2\text{O})_{5-n}$ in the interval $z = +2, +1, 0$ and $n = 0, 1-5$ the mechanism of electroreduction of complexes of Ni^{2+} and acrylic acid (HAK) has been proved. It has been demonstrated that the initial reactant is the $[\text{Ni}^{2+}(\text{H}_2\text{O})_5\text{Ak}^-]$, the intermediate is the $[\text{Ni}^+(\text{H}_2\text{O})_2\text{Ak}^-]$ and the end product exists in various forms among which the most stable is $[\text{Ni}^0(\text{H}_2\text{O})_2(\pi\text{-HAK})]$.

Keywords Complexes of Nickel, Acrylic Acid, The Mechanism of Electroreduction, Quantum-Chemical Modeling

1. Introduction

Nickel electrodeposition is a widespread process in electroplating industry due to a number of important properties of this metal [1]. The quality of nickel electrodeposited from aqueous solutions is impaired by the unwanted side processes of disproportionation of reaction intermediates

and their interaction with water

which leads to incorporation of nickel hydroxide compounds into the residuum [2 - 4].

A detailed study of the $\text{Ni}^{2+} + 2\bar{e} \rightarrow \text{Ni}^0$ reaction mechanism made it possible to establish that the mentioned specificity of this process is determined by the peculiarities of the electronic structure of nickel aqua complexes that are manifested in central atom insensibility to electron acceptance [5]. An electron incorporated into the aqua complex is located on water molecules of the internal coordination sphere and causes their reduction

The disproportionation of occurring hydroxo-aqua complexes leads to the emergence of nickel hydroxide $\text{Ni}(\text{OH})_2$ in the studied system.

Weak organic acids are traditionally used to suppress this

process [6, 7]. Under these acids, the amount of occurring nickel hydroxide actually decreases, but does not approach zero.

There are also known recommendations on the use in nickel plating electrolytes of substances that in containing the C = C-double bond (e.g., 1. 4-butindiol, natrium alylsulfonate), are often used as additives to nickel-plating solutions. Taking into account that the nickel electron structure contains a vacant d-orbital, organic molecules that have centers with excess electron density are able to form a sufficiently strong π -bond with nickel ions and even atoms [8] and, as a result, exert effective influence on electrocrystallization process. We considered it expedient to explore the pattern of organic acids exert influence on nickel ions electroreduction by means of computer modeling of this process.

In the present work, acrylic acid (HAK) was used. Earlier [9, 10], we explored the influence of this additive on the process of copper (II)-ions electroreduction from acidic sulfate solutions. By means of quantum-chemical modeling in [9] we gave a detailed description of the mechanism of Cu^{2+} -cations electroreduction process, and in [10] we examined the peculiarities of crystal copper grains formation over acrylic acid or its derivatives. It was shown that in all cases the cathode reaction mechanism involves Cu^+ -ions interaction with vinyl fragment of organic molecule forming π -complexes. It is expected that in the case of nickel ions, electroreduction undergoes over acrylic acid and the identified peculiarities of HAK influence will be embodied, particularly, it is possible to stabilize Ni^+ ions and prevent them from reducing water molecules.

2. Materials and Methods

Quantum-chemical modeling was carried out with the use of ab initio methods of WinGAMESS program [11, 12] Cluster systems were calculated using the spin-unlimited Hartree – Fock method. The central atom of metal was described via the 6-31G** basis set, while the atoms of ligands were described via 6-311G basis set. The B3LYP hybrid density functional method which includes five

functionals: the Becke, Slater and Hartree – Fock exchange and LYP + VWN5 correlation functionals was applied. In the process of modeling, the studied ions were optimized in the first solvation shell environment and the energies of the optimized complexes were calculated. Then, the energies were specified with regard to solvation using the Polarizable Continuum Model [13]. For Ni^{+} -cation, the energies in high-spin and low-spin states were calculated.

As comparison of electronic energies of various structures only makes sense if they contain equal number of atoms of each type, during calculation of energies of complexes with diverse geometry of the first hydration shell, we examined the cluster systems of the following composition: $[\text{Me}(\text{H}_2\text{O})_n\text{Ak}]^{z+}m\text{H}_2\text{O}$ assuming that $(n+m) = \text{const}$. In the given structure, n molecules of water are directly bonded to the central atom of the aqua complex, and the rest m molecules are somewhat distant, which eliminates their chemical interaction with metal ions.

The most energetically favorable was the cluster structure having the lowest (or minimal) sum of energies of the $[\text{Me}^{z+}(\text{H}_2\text{O})_n]$ metal hydrated aqua complex and those of m molecules of water transferred to the secondary shell.

As cations of 3-d metals are most likely to form aqua complexes with coordination number equal to 6, we selected the sum of $(n+m) = 5$ as a working draft. One coordination site was constantly occupied by the acrylate

ion. The calculation of energy of one water molecule deep in the $\text{E}(\text{H}_2\text{O}\cdot\text{aq})$ solution was performed in line with the following procedure: first of all, we calculated energies of $(\text{H}_2\text{O})_x$ clusters in a wide range of x (from 1 to 24). Then, we built relation of specific energy value, i.e., the energy of one water molecule in the $(\text{H}_2\text{O})_x$ cluster to $1/x$. The $\text{E}(\text{H}_2\text{O}_{\text{aq}})$ target value was identified via extrapolation of obtained relation to $1/x=0$.

Previously [14] it was demonstrated, that this particular calculation methodology provides high-level correspondence of the obtained model to real electrochemical process involving atoms of 3d-metals of various oxidation states.

3. Results and Discussion

The results of the optimized structures calculation are presented in Tables 1. 4. General structures of clusters and atoms numeration are provided on Figure.

The calculations showed that for the internuclear distance Ni-O more than 2.2 Å, the interaction energy of Ni atoms with oxygen was not higher than the energy of thermal motion of molecules, so they have not been assumed as the chemical bonds and were excluded from tables 1.4.

Table 1. Internuclear distances (Å) between Ni^{z+} and oxygen atoms of ligands in the $[\text{Ni}^{z+}(\text{H}_2\text{O})_5\text{Ak}]$ cluster

Atom №	Ligand	$z=2$	$z=+1$	$z=0$ σ - complex	$z=0$ π - complex
O1	H_2O	2.046	-	-	-
O2	H_2O	2.043	-	-	-
O3	H_2O	2.079	-	-	1.983
O4	H_2O	2.058	2.027	2.063	-
O5	H_2O	2.043	1.978	2.071	2.023
O6	$\text{CH}_2=\text{CH}-\text{COO}^-$	2.032	1.886	2.103	2.026
O7	$\text{CH}_2=\text{CH}-\text{COO}^-$	-	-	2.112	-
C3	$\text{CH}_2=\text{CH}-\text{COO}^-$	-	-	-	2.011

Table 2. Charge Distributions on nickel atoms and ligands in various complex structures. Index (*) denotes the transition state

Atom №	$[\text{Ni}^{2+}(\text{H}_2\text{O})_5\text{Ak}]$	$[\text{Ni}^+(\text{H}_2\text{O})_5\text{Ak}]^*$	$[\text{Ni}^0(\text{H}_2\text{O})_2\text{Ak}]$	$[\text{Ni}^0(\text{H}_2\text{O})_2\sigma\text{-Ak}]$	$[\text{Ni}^0(\text{H}_2\text{O})_2\pi\text{-Ak}]$
Ni	+1.650	+1.473	+0.645	+0.515	+1.159
H_2O_1	+0.029	-0.055	+0.053	-0.007	+0.083
H_2O_2	+0.022	-0.064	+0.056	-0.008	+0.084
H_2O_3	-0.016	+0.025	-	-	-
H_2O_4	-0.015	+0.015	-	-	-
H_2O_5	-0.014	+0.032	-	-	-
$\Sigma Z(\text{H}_2\text{O})$	+0.006	-0.047	+0.109	-0.015	+0.167
$\Sigma Z(\text{Ak}^-)$	-0.656	-1.426	-0.754	-1.500	-2.326

Table 3. Energetic properties of various cluster structures with Ni^+ - ions and Ni^0 - atoms

№	Cluster	Multiplicity	Coordination Number Ni	E, Hartree
1	$[\text{Ni}^+(\text{H}_2\text{O})_5\text{Ak}^-]$	2	6	-818.0719
2	$[\text{Ni}^+(\text{H}_2\text{O})_5\text{Ak}^-]$	4	6	-818.0766
3	$[\text{Ni}^+(\text{H}_2\text{O})_4\text{Ak}^-]\text{H}_2\text{O}$	2	5	-818.0888
4	$[\text{Ni}^+(\text{H}_2\text{O})_4\text{Ak}^-]\text{H}_2\text{O}$	4	5	-818.0754
5	$[\text{Ni}^+(\text{H}_2\text{O})_3\text{Ak}^-]2\text{H}_2\text{O}$	2	4	-818.0882
6	$[\text{Ni}^+(\text{H}_2\text{O})_3\text{Ak}^-]2\text{H}_2\text{O}$	4	4	-818.0836
7	$[\text{Ni}^+(\text{H}_2\text{O})_2\text{Ak}^-]3\text{H}_2\text{O}$	2	3	-818.1014
8	$[\text{Ni}^+(\text{H}_2\text{O})_2\text{Ak}^-]3\text{H}_2\text{O}$	4	3	-818.0719
9	$[\text{Ni}^+(\text{H}_2\text{O})_1\text{Ak}^-]4\text{H}_2\text{O}$	2	2	-818.0836
10	$[\text{Ni}^+(\text{H}_2\text{O})_1\text{Ak}^-]4\text{H}_2\text{O}$	4	2	-818.0745
11	$[\text{Ni}^+\text{Ak}^-]5\text{H}_2\text{O}$	2	1	-818.0088
12	$[\text{Ni}^0(\text{H}_2\text{O})_2\text{Ak}^-]3\text{H}_2\text{O}$	3	3	-818.1767
13	$[\text{Ni}^0(\text{H}_2\text{O})_1\text{Ak}^-]4\text{H}_2\text{O}$	3	2	-818.1376
14	$[\text{Ni}^0\text{Ak}^-]5\text{H}_2\text{O}$	3	1	-818.1121

Table 4. Internuclear distances (Å) between Ni^0 and some atoms of ligands in the $[\text{Ni}^0(\text{H}_2\text{O})_2\text{HAK}]$ cluster. (Distances of more than 4 Å are not given)

Atom №	Ligand	σ – complex	π – complex
O4	H_2O	2.001	2.009
O5	H_2O	2.049	1.984
O6	$\text{CH}_2=\text{CH}-\text{COOH}$	2.064	2.030
O7	$\text{CH}_2=\text{CH}-\text{COOH}$	2.228	-
C3	$\text{CH}_2=\text{CH}-\text{COOH}$	-	2.020

a

c

b

d

Figure 1. The Structure of Nickel Clusters: a - $[\text{Ni}^{2+}(\text{H}_2\text{O})_5\text{Ak}^-]$; b - $[\text{Ni}^+(\text{H}_2\text{O})_5\text{Ak}^-]^*$; c - $[\text{Ni}^+(\text{H}_2\text{O})_2\text{Ak}^-]3\text{H}_2\text{O}$; d - $[\text{Ni}^0(\text{H}_2\text{O})_2\sigma\text{-Ak}^-]3\text{H}_2\text{O}$; e - $[\text{Ni}^0(\text{H}_2\text{O})_2\pi\text{-Ak}^-]3\text{H}_2\text{O}$ (distances from atoms of Nickel less than 2,2 Å are stippled)

As you might expect, Ni^{2+} -ions demonstrated optimization of their octahedral structure with approximately equivalent Ni-O-bonds (Table 1).

In principle, nickel ions are also able to hold not only the acrylate ions but molecular form of acrylic acid in their primary coordination shell, however, considering $\text{pK}_a(\text{Hak})=4.25$ complexes with acrylate ions will prevail. The latter were treated as starting reagent.

The process of $[\text{Ni}^{2+}(\text{H}_2\text{O})_5\text{Ak}^-]$ complexes electroreduction was divided into two single electron reactions. The transfer of the primary electron to the vacant external orbital of the Ni^{2+} -acrylate complex causes the following transformations: three water molecules leave the primary coordination shell and move to the complex solvation shell (Table 1). The binding energy with one of the water molecules acting as a ligand somewhat increases. However, the charge of water molecules in the internal coordination sphere is close to zero, which makes the given system fundamentally different from nickel aqua complexes, in which the charge of water molecules in transient species reaches -0.329 [5].

Examination of the optimized clusters energies, where Ni^+ -ions embody various values of coordination number (Table 3) made it possible to elucidate a stable $[\text{Ni}^+(\text{H}_2\text{O})_2\text{Ak}^-]$ intermediate – complex. The removal of three water molecules occurring under the complex formation allows an electron to occupy one of the Ni^{2+} ion orbital and thus to transfer it to the Ni^+ reduced form. The central atom charge in the formed $[\text{Ni}^+(\text{H}_2\text{O})_2\text{Ak}^-]$ intermediate decreases to $+0.645$ (Table 2), and the charge localized on acrylate ion becomes equal -0.754 .

The process of reconstruction of primary coordination sphere of partially reduced nickel complexes is accompanied by complementary energy release

and thus is supposed to run fast.

The transfer of the secondary electron to the $[\text{Ni}^+(\text{H}_2\text{O})_2\text{Ak}^-]$ intermediate turned out to be performed in line with the pattern of the primary electron transfer. In this case, we observe its localization not on nickel orbital, either, but on vinyl fragment of acrylate ions (Table 2). The main difference is in the fact that the examination of structures with lower nickel coordination number revealed no preferred options concerning $[\text{Ni}^0(\text{H}_2\text{O})_2\text{Ak}^-]$ (Table 3).

At the same time, when searching for various option of the $[\text{Ni}^0(\text{H}_2\text{O})_2\text{Ak}^-]$ structure embodiment, we found out that the attraction of a negatively charged vinyl radical to a positively charged nickel atom completes a five-membered cycle, within which acrylate ion shows bidentate nature (Table 1, Figure 1, Structure D). The pattern of charge distribution in this cluster is an evidence of chelate type π -complexes formation. For the account of $d\pi$ - $\pi\pi$ interaction of nickel atoms with acrylate ion, a charge on Ni^0 and Ak^- ligands increases to $+1.159$ and -2.326 , respectively (Table 2).

The juxtaposition of energy of σ - and π -complexes formation (-90.0 kJ/mole for $[\text{Ni}^0(\text{H}_2\text{O})_2\sigma\text{-Ak}^-]$ and -107.1 kJ/mole for $[\text{Ni}^0(\text{H}_2\text{O})_2\pi\text{-Ak}^-]$ points out that the first one will act as an intermediate and the last one will represent an end product of double electron reduction of Ni^{2+} -complexes.

Since, except for $[\text{Ni}^0(\text{H}_2\text{O})_2\text{Ak}^-]$ -complexes, Ni^0 -complexes with Hak molecular form and σ - and π -coordination were identified as stable structures (Table 4), they are also able to compose reduction product of Ni^{2+} -complexes.

4. Conclusion

The juxtaposition of energetics of all the defined structures made it possible to create a framework of the process of Ni^{2+} -ions electroreduction over acrylic acid:

It is obvious that the impact of exposures embodied under nickel electrodeposition will modify correlation of the stated forms and thus exert influence on the nature of a formed metal phase over *en* – type unsaturated organic compounds.

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