CHEMICAL SCIENCES

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S.V. Ivanov, Dr.Sci. (Chemistry)

CHEMICAL DISSOLUTION OF NICKEL (II) OXIDE AND HYDROXIDE IN AMINO ACID SOLUTIONS

NAU Institute of Ecology and Design, e-mail: tech@nau.edu.ua

Simulation experimenting has been used to analyze thermodynamics of chemical dissolution of nickel (II) oxide and hydroxide in solutions containing various amino acids. Allowance for complexation, protonation and hydrolysis processes has been found to be a must for adequate description of chemical processes.

Introduction

The electrochemical oxidation of nickel accompanied by the formation of a film consisting of nickel oxide-hydroxide compounds at the electrode-electrolyte boundary [1; 2]. The formation of a film denotes the presence of a new electrode-film-electrolyte system [3]. The electrochemical process mechanism is determined by the physicochemical properties of a film: its chemical stability towards the electrolyte, especially the kind of ligand.

Kinetics of dissolution of oxides and hydroxides of metals depend on physicochemical properties of both oxides and solutions, e.g. on their concentration, acidity, redox potential, availability of complexation agents [4]. The study of this process in aqueous solutions allowed the determination of compound dependence of oxide dissolution rate on solution acidity, which many researchers tended to relate to a complicated mechanism of the process and its possible variation to occur on varying solution acidity. However, more logic seems to exist in interpreting this dependence in terms of the processes of interaction between particles existing in aqueous phase [5]. Addition to the solution of anions forming the complexes with metal ion of oxide or hydroxide being dissolved can notably accelerate dissolution [4]. Nevertheless, the rate of dissolution of nickel (II) and (III) oxides in complexons that form with nickel (II) and (III) ions stable complexes [6] decreases with the increase in ligand concentration [4].

Methods

As ligands [L], analyzed herein are the following amino acids: glycine, α- and β-alanine, valine, serine, leucine, asparagine, aspartic acid, phenylalanine and histidine. These ligands were selected because of the fact that complexing agents of protein origin were used in chemical and electrochemical deposition and dissolution of nickel. In particular, electrochemical behaviour of nickel (II) glycinate complexes of various composition was most comprehensively studied [7–11].

Dissolution of nickel (II) oxide and hydroxide in aqueous media can be represented as follows:

$$NiO + 2\,H^{+} \rightleftharpoons Ni^{2+} + H_2O\,; \qquad (1)$$

$$Ni(OH)_2 + 2\,H^{+} \rightleftharpoons Ni^{2+} + 2\,H_2O. \qquad (2)$$

Variation in Gibbs energy of such processes occurring in the conditions other than standard [12] is

$$\frac{\Delta G}{2{,}3RT} = \lg \frac{C_{Ni^{2+}}}{K_S[H^{+}]^2}\,, \qquad (3)$$

where K_S is the constant of equilibrium of processes (1) and (2); $C_{Ni^{2+}}$ is the total concentration of nickel (II) ions in the solution.

Equations (1) and (2) are valid only in the case of a high acidity of reaction medium which allows a complete suppression of hydrolysis, and if no complexing ligands are present in reaction medium [13]. It is due to the fact, with the decrease in acidity of reaction medium, nickel (II) ions being formed as result of processes (1) and (2) are subjected to hydrolysis that can be written in the following fashion:

$$Ni^{2+} + n\,H_2O \rightleftharpoons Ni(OH)_n^{2-n} + n\,H^{+}\,, \qquad (4)$$

where $n = 1–4$.

Here, allowance should be made for formation of bi- and tetranuclear particles [13]:

$$2Ni^{2+} + H_2O \rightleftharpoons [Ni_2OH]^{3+} + H^{+}; \qquad (5)$$

$$4Ni^{2+} + 4\,H_2O \rightleftharpoons [Ni_4\,(OH)_4]^{4+} + 4\,H^{+}. \qquad (6)$$

Given complexing agents in reaction medium, nickel (II) ions enter into appropriate reactions of complex formation. Depending upon the conditions (components ratio and their absolute concentrations), nickel complexes can be formed with the amino acids under consideration, varying in composition and, hence, molecular organization, while amino acids proper are subjected to protonation or deprotonation [6].

To allow for these factors acting concurrently and varying in nature, it has been proposed [14] to introduce into equation (3) a correction factor to quantitatively describe hydrolysis and complexation. Then equation (3) can be written in the following fashion:

$$\frac{\Delta G}{2{,}3RT} = \lg\frac{C_{Ni^{2+}}}{\alpha K_S[H^+]^2}.$$

Given no amino acids in the solution and, hence, complexation, only hydrolysis of nickel (II) ions occurs, and the factor above is subject to the following expression

$$\alpha = 1 + \sum_{i=1}^{n} K_i[H^+]^{-i} + 2K_{21}[Ni^{2+}][H^+]^{-i} +$$

$$+4K_{44}[Ni^{2+}][H^+]^{-4}, \qquad (7)$$

where K_i is the constant of equilibrium in processes of type (4); K_{21} and K_{44} are the constants of equilibrium of processes (5) and (6), respectively; $[Ni^{2+}]$ is the equilibrium concentration of nickel (II) ions in the solution governed by the following equation:

$$[Ni^{2+}] = \frac{C_{Ni^{2+}}}{\alpha}.$$

The right term of equation (7) allows for the formation in the solution of mononuclear complexes; the third term and the last do it for binuclear and tetranuclear complexes, respectively.

On adding amino acids to the solution, the complexation processes occur; therefore an additional term appears in equation (7) to allow for contribution of these processes, and equation (7) becomes as follows:

$$\alpha = 1 + \sum_{i=1}^{n} K_i[H^+]^{-i} + 2K_{21}[Ni^{2+}][H^+]^{-i} +$$

$$+4K_{44}[Ni^{2+}][H^+]^{-4} + \sum_{j=1}^{m} \beta_j[L]^j, \qquad (8)$$

where m is determined by the composition of the complex being formed.

It is 2 for aspartic acid, phenylalanine and histidine, and 3 for the remaining amino acids under analysis; [L] is the ligand equilibrium concentration in the solution determined by the equation

$$[L] = \frac{C_L}{1 + \sum_{k=1}^{p} \beta_k^H [H^+]^k}, \qquad (9)$$

where C_L is total ligand concentration in the solution.

The changes in Gibbs energy were calculated for total concentration of nickel (II) ions equal to $1 \cdot 10^{-3}$ to 1 mol/l and Ni:L ratio within 1:1 to 1000 in the 1 to 13 pH range.

To calculate the constants β_i of nickel complexes with amino acids β_k^H of amino acids.

Equations (8) and (9) were taken from [8], and K_i, K_{21} and K_{44} of nickel hydroxocomplexes from [14].

Results and Discussion

Fig. 1 shows the results of calculation experiment for solutions not containing amino acids.

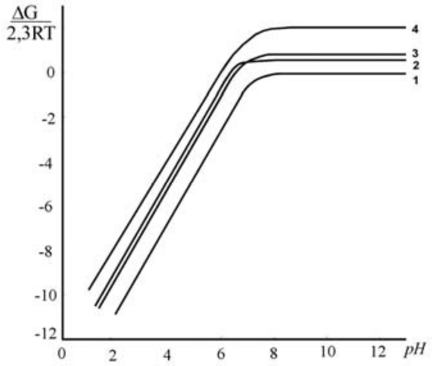

Fig. 1. Dependence of Gibbs energy of NiO (*1, 2*) and $Ni(OH)_2$ (*3, 4*) dissolution in aqueous solution containing $1 \cdot 10^{-3}$ mol/l (*1, 3*) and $5 \cdot 10^{-2}$ mol/l (*2, 4*) of nickel (II) ions upon solution acidity

In the scope of the approach proposed, at $\Delta G > 0$, nickel (II) oxide and hydroxide are thermodynamically stable, while at $\Delta G < 0$, they become dissolved. Thermodynamic stability of nickel (II) hydroxide exceeds that of nickel (II) oxide, with the total concentration of nickel in acid solutions increasing, it increases, while in alkaline solutions it becomes constant.

On adding various amino acids to the solution, dependencies vary significantly (fig. 2, 3). Here, variation of amino acids concentration in the solution, as compared with the change in nickel content, brings about a considerably higher effect on Gibbs energy. It follows from fig. 2 that amino acids under consideration can be divided into two groups with regard to their effect on thermodynamic stability of nickel (II) oxide and hydroxide. The first group includes aspartic acid and phenylalanine which do not reduce Gibbs energy in the range of alkaline solutions.

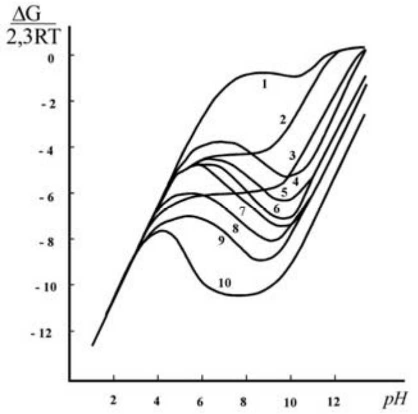

Fig. 2. Dependence of Gibbs energy of NiO dissolution in aqueous solution containing $5 \cdot 10^{-3}$ mol/l nickel (II) ions and β-alanine (*1*), phenylalanine (*2*), α-alanine (*3*), aspartic acid (*4*), glycine (*5*), valine (*6*), leucine (*7*), serine (*8*), asparagine (*9*) and histidine (*10*) at the 1:50 ratio upon solution acidity

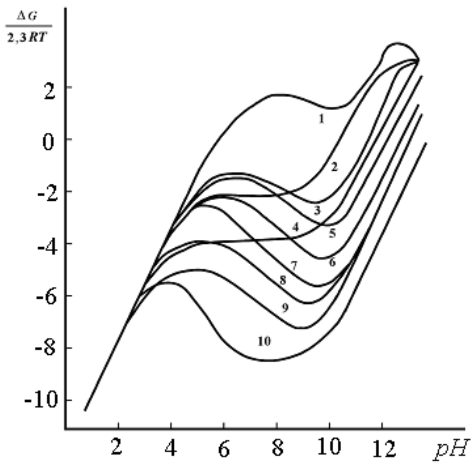

Fig. 3. Dependence of Gibbs energy of $Ni(OH)_2$ dissolution in aqueous solution containing $5 \cdot 10^{-2}$ mol/l nickel (II) ions and *β*-alanine (*1*), phenylalanine (*2*), valine (*3*), α-alanine (*4*), aspartic acid (*5*), glycine (*6*), leucine (*7*), serine (*8*), asparagine (*9*) and histidine (*10*) at the 1:50 ratio upon solution acidity

The second group comprises all remaining amino acids that cause a distinct minimum on the ΔG/2,3RT – pH curve in the pH range. The analysis of complexation of these amino acids with nickel (II) ions shows [6] that aspartic acid and phenylalanine do not form three-ligand complexes. This is brought about by various causes which will not be considered herein. Thus, the minimum on the ΔG/2,3RT – pH curve is determined by the formation of three-ligand complexes of nickel (II). The influence of histidine on thermodynamic stability of nickel (II) oxide and hydroxide requires a special consideration because three-ligand complexes with nickel (II) ions are not formed despite a minimum observed on the curves under discussion [6].

The Gibbs energy minimum is, probably, caused by the fact that histidine forms the most stable complexes with nickel (II) ions (as compared with the other amino acids). Their constant $K^{NiL}_{NiL_2}$ is approxi-mately 2 to 4 times higher than similar constants of the other complexes; therefore, the process of formation of such complexes will dominate over all other processes occurring in the given condition in the solution. Typical curves ΔG/2,3RT – pH of dissolution of nickel (II) oxide and hydroxide in solution containing amino acids of the 1st and 2nd groups are given in fig. 4, 5, the solution containing serine and phenylalanine being examples. On these curves, four specific sections can be distinguished for the following pH ranges: 1 to 3, 3 to 8, 8 to 10, 10 to 13.

In section I of the ΔG/2,3RT – pH curve, thermodynamic stability of nickel (II) oxide and hydroxide decreases with the increase in pH. Here, the change in amino acid concentration and nature of amino acid do not practically affect this magnitude. This is caused by transition of amino acids from a dipolar zwitter-ion form to that of a monopolar cation taking practically no part in complexation since solution pH at which the transition above occurs corresponds precisely to the pH range of this section of the dependence under analysis [15]. In section II of the ΔG/2,3RT – pH curve, given serine in the solution, a maximum is observed (fig. 4), while Gibbs energy does not vary if phenylalanine is in the solution (fig. 5).

Amino acids in the pH range corresponding to this section of the curve exist in a stable form of dipolar zwitter-ion. Solution pH at which Gibbs energy maximum is observed, shifts to the acid solution range with the increase in ligand content (fig. 4, *a*). The range wherein constant Gibbs energy increase with the increase in ligand content is observed (fig. 5, *a*).

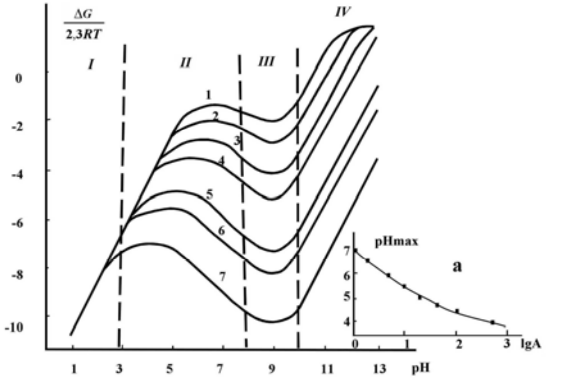

Fig. 4. Dependence of Gibbs energy of NiO dissolution in aqueous solution containing $1 \cdot 10^{-2}$ mol/l nickel (II) ions and serine at the 1:1 ratio (1), 1:2 (*2*), 1:5 (*3*), 1:10 (*4*), 1:50 (*5*), 1:100 (*6*), 1:500 (*7*) upon solution acidity:

a – dependence of solution pH at which maximum is observed on the ΔG/2,3RT – pH curve, on excess (A) ligand

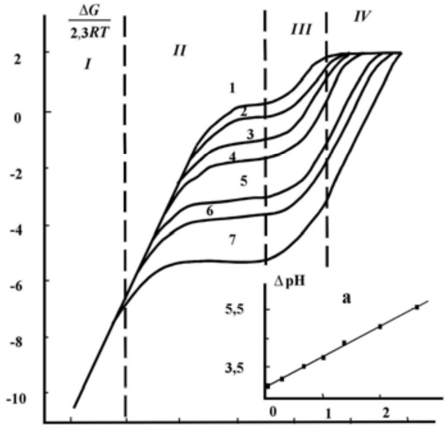

Fig. 5. Dependence of Gibbs energy of $Ni(OH)_2$ dissolution in aqueous solution containing $1 \cdot 10^{-2}$ mol/l nickel (II) ions and phenylalanine at the 1:1 ratio (*1*), 1:2 (*2*), 1:5 (*3*), 1:10 (*4*), 1:50 (*5*), 1:100 (*6*), 1:500 (*7*) upon solution acidity:

a – dpendence of solution pH at which constant Gibbs energy is observed on the ΔG/2,3RT – pH curve, on excess (A) ligand

It should be emphasised that thermodynamic parameters of dissolution of nickel (II) oxide and hydroxide in solution containing various amino acids, in the pH range of the ΔG/2,3RT – pH curve, do not depend on the constant K_{NiL}, $K_{NiL_2}^{NiL}$ or β_{NiL_2}, nor on constants β_{HL} or β_{H_2L}. At same time, a distinct dependence of Gibbs energy $\beta_{NiL_2}/\beta_{H_2L}$ ratio (fig. 6).

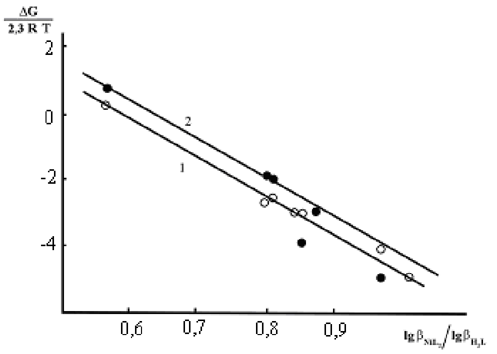

Fig. 6. Dependence of Gibbs energy of NiO dissolution in aqueous solution containing various acids at pH 5 (*1*) and 7 (*2*) upon the $\beta_{NiL_2}/\beta_{H_2L}$ parameter

With the $\beta_{NiL_2}/\beta_{H_2L}$ parameter increasing, stability of the nickel compounds lessens. This can be attributed to a concurrent occurrence of several reactions in the solutions in the given conditions, these reactions bringing about complex equilibria. The influence of any specific process (formation of complex particles or protonation of functional groups of an amino acid) is not dominant. Concurrent allowance for these processes is made through the use of the $\beta_{NiL_2}/\beta_{H_2L}$ parameter as a measure of their effect on dissolution on the whole. In section III of the ΔG/2,3RT – pH curve, Gibbs energy of dissolution of nickel (II) oxide and hydroxide in solutions containing the 1st group of amino acids shift toward positive values with the decrease in solution acidity (fig. 5). The increase in the total concentration of nickel (II) ions in the solution brings about an opposite effect. Given the 2nd group of amino acids in the solution, in the solution, in the pH range of this section a minimum of thermodynamic stability of nickel compounds is observed (fig. 4). Gibbs energy, at solution pH at which the minimum above is observed, depends linearly on the $\beta_{NiL_3}/\beta_{H_2L}$ ratio (fig. 7). With the $\beta_{NiL_3}/\beta_{H_2L}$ parameter increasing, thermodynamic stability of nickel compounds decreases.

The absolute value of the difference between maximum Gibbs energy (II section) and minimum Gibbs energy (III section) depends upon the $K_{NiL_3}^{NiL_2}$ constant. Therefore, the run of the ΔG/2,3RT – pH curve in the 8 to 10 pH range is governed by the

$NiL_2 + L \rightarrow NiL_3$

process (changes are omitted), on the one hand, and, on the other hand, by protonation of amino acid amino group. In IV section of the ΔG/2,3RT – pH curve, thermodynamic stability of nickel (II) oxide and hydroxide abruptly rises (fig. 4, 5), right up to the end of their dissolution (ΔG reverses its sign). Under these conditions, amino acids exist exclusively in the form of a monopolar anion which readily forms complexes with nickel (II) ions. Gibbs energy depends on the NiL_3 constant (fig. 8).

The increase in β_{NiL_3} results in abrupt increase in thermodynamic stability of nickel (II) oxide and hydroxide. Also, in such highly-alkaline media the formation of mixed-ligand complexes [16] is possible, containing one or two hydroxogroups. Because of the absence of valid data on stability constants for these complexes, this factor was not allowed for in the experiments.

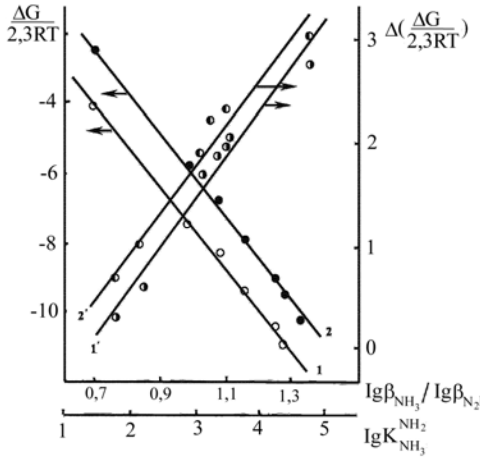

Fig. 7. Dependence of Gibbs energy (*1,2*) and its variation (*1′,2′*) NiO (*1,1′*) and $Ni(OH)_2$ (*2,2′*) dissolution in aqueous solution containing $5 \cdot 10^{-2}$ mol/l of nickel (II) ions and various amino acids at the 1:100 ratio upon the $\beta_{NiL_3}/\beta_{H_2L}$ parameter and constant $K_{NiL_3}^{NiL_2}$ (*1′,2′*)

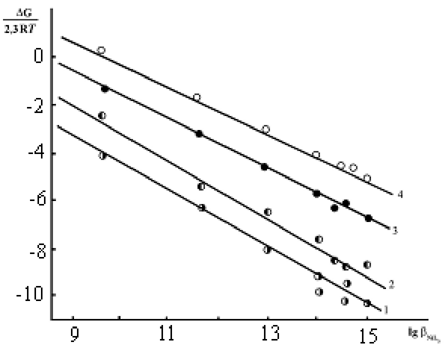

Fig. 8. Dependence of Gibbs energy of NiO (*1, 3*) and $Ni(OH)_2$ (*2, 4*) dissolution in aqueous solution containing $5 \cdot 10^{-2}$ mol/l of nickel (II) ions and various amino acids at the 1:100 ratio (at pH 10 (*1, 2*) and 12 (*2, 4*)) upon the β_{NiL_3} constant

Conclusion

The results of this research allow the conclusion about expediency of a thermodynamic approach to estimation of possibility for chemical reactions which is useful for understanding and controlling electrochemical dissolution of metals.

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С.В.Іванов

Хімічне розчинення оксиду та гідроксиду нікелю в розчинах амінокислот

Методом математичного моделювання досліджено процеси хімічного розчинення оксиду та гідроксиду нікелю (II) у розчинах амінокислот. Показано, що при pH 3–8, коли амінокислоти існують у формі цвіттер-іону, термодинамічна стабільність сполук нікелю лінійно залежить від співвідношення констант $\beta_{NiL_2}/\beta_{H_2L}$. При pH 8–10 спостерігається мінімум енергії Гіббса. Його величина лінійно залежить від співвідношення констант $\beta_{NiL_2}/\beta_{H_2L}$, а відносне її зниження визначається величиною константи $K_{NiL_3}^{NiL_2}$. При pH>10 термодинамічна стабільність сполук нікелю лінійно зменшується зі збільшенням константи β_{NiL_3}. У зв'язку з цим для адекватного опису процесу розчинення потрібне врахування процесу комплексоутворення, протонування і гідролізу.

С.В.Иванов

Химическое растворение оксида и гидроксида никеля в растворах аминокислот

Методом математического моделирования исследован процесс химического растворения оксида и гидроксида никеля (II) в растворах аминокислот. Показано, что при pH 3–8, когда аминокислоты существуют в форме цвиттер-иона, термодинамическая стабильность соединений никеля линейно зависит от отношения констант $\beta_{NiL_2}/\beta_{H_2L}$. При pH 8–10 наблюдается минимум энергии Гиббса. Его величина линейно зависит от отношения констант $\beta_{NiL_2}/\beta_{H_2L}$, а относительное его снижение определяется величиной константы $K_{NiL_3}^{NiL_2}$. При pH>10 термодинамическая стабильность соединений никеля линейно уменьшается с ростом константы β_{NiL_3}. В связи с этим для адекватного описания процесса растворения необходим учет процесса комплексообразования, протонирования и гидролиза.