Speciation of the nickel(II) complexes with oxalic and malonic acids studied in 1.0 mol dm⁻³ NaCl at 25°C

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In this article, we present the results of the speciation of the binary nickel(II)-oxalic acid (H_2L) and nickel(II)-malonic acid (H_2L) systems studied by electromotive forces measurements emf (H) using $1.0\,\mathrm{mol\,dm^{-3}}$ NaCl as the ionic medium at 25°C. The experimental data were analyzed by a computational least-squares program LETAGROP/FONDO, a version of the LETAGROP program, written to analyze regular formation function and reduced formation functions, taking into account the hydrolysis of the nickel(II) cation and the acid base reactions of the ligands which were kept fixed during the analysis. In the nickel(II)-oxalic acid system the complexes $[NiHL]^+$, $[NiL]$, $[Ni(OH)L]^-$, and $[NiL_2]^{2-}$ were observed and for the nickel(II)-malonic acid system the complexes $[NiHL]^+$, $[NiL]$, $[Ni(OH)L]^-$, and $[Ni(OH)_2L]^{2-}$ were detected. The stability constants were determined and the species distribution diagrams as a function of pH are briefly discussed.

Keywords: Nickel(II) complexes; Oxalic acid; Malonic acid; Potentiometric studies; Speciation

1. Introduction

Oxalic acid, the simplest organic diacid, is a strong acid in its first stage of dissociation due to the proximity of the second carboxylic group. The dianion, oxalate, is a good reducing agent and an excellent ligand in coordination chemistry. Many metal ions form insoluble precipitates with oxalate, a prominent example is calcium oxalate, which is the primary component of the most common type of kidney stone. Oxalic acid is moderately toxic (LD_{50} rat = 375 mg kg⁻¹) because calcium oxalate precipitate can block the renal capillaries, and prevent its absorption by the body. For this reason, lactating women and growing children eating large amounts of foods rich in oxalates is not recommended [1]. Oxalate is a bidentate ligand, forming five-membered chelate rings.

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Malonic acid (propanedioic acid), $CH_2(COOH)_2$ is important because of its widespread use in organic synthesis, since it has properties similar to those of ethyl acetonate. When malonic acid is heated above its melting point, it loses one carboxylic group with evolution of CO_2. Malonate is a bidentate ligand, forming six-membered chelate rings.

Similar to other toxic heavy metal ions, toxicity of Ni(II) is determined mainly by pH and its speciation. Its uptake and transport can be promoted by complex formation with natural and anthropogenic ligands in soils, water, and biofluids. Therefore, it is of interest to understand the mechanisms and pathways of the formation of soluble nickel(II) complexes with natural and anthropogenic ligands [2]. We considered this investigation of the Ni(II) complexes with oxalic and malonic acids because nickel(II) commonly occurs in industry and the information observed in the database [3, 4] of these two systems is too old; we wanted to re-investigate these systems with the new computational methodology that we have in our laboratory.

2. Experimental

2.1. *Reagents*

$NiCl_2 \cdot 6H_2O$ (Merck p.a.), sodium oxalate (Na_2ox) (Merck 99%), malonic acid (H_2mal) (Merck p.a.), $Na_2EDTA \cdot 2H_2O$ (Merck p.a.), and bromopyrogallol Red (Merck p.a.) as indicator in order to standardize the nickel(II) stock solution were used without purification. The HCl and NaOH solutions were prepared using $100.0\,mmol\,dm^{-3}$ Titrisol Merck ampoules. The NaOH solution was standardized against potassium hydrogen phthalate (Merck p.a., recrystallized and dried at $120°C$) using phenolphthalein as indicator, and the HCl solution was standardized with NaOH solution of known concentration [5]. The solutions were prepared using triply glass-distilled water, boiled before preparation of the solutions in order to remove dissolved CO_2. To prevent hydrolysis of the $NiCl_2$ stock solution, it contained $100\,mmol\,dm^{-3}$ HCl. $NiCl_2$ is hygroscopic and must be weighed as fast as possible. For that reason it is necessary to standardize the $NiCl_2$ stock solution using a $Na_2EDTA \cdot 2H_2O$ solution ($0.01\,mol\,dm^{-3}$) in a buffer media (pH 10) and using bromopyrogallol Red as indicator [6]. The acidity of the $NiCl_2$ stock solution was determined by the Gran method [7].

Potentiometric measurements were carried out in aqueous solution using $1.0\,mol\,dm^{-3}$ NaCl as ionic medium. Nitrogen free O_2 and CO_2 were used.

2.2. *Methods*

Potentiometric measurements were done using a Thermo Orion model 520A pH meter, a Metrohm EA 876–20 titration vessel, and a Lauda Brikmann RM6 thermostat bath. The sealed 100 mL thermostated double-walled glass titration vessel was fitted with a combined Orion Ross 8102BN pH electrode with a titrant inlet, magnetic stirrer, and a nitrogen inlet with outlet tubes. The temperature was maintained at $(25.0 \pm 0.1)°C$ by constant circulation of water from the thermostat bath.

The emf (H) measurements were carried out by a REF//S/GE cell, where REF = Ag/AgCl/3.0 mol dm^{-3} KCl; S = equilibrium solution and GE = glass electrode. At 25°C, the emf (mV) of this cell follows the Nernst equation, $E = E^0 + jh + 59.16 \log h$, where h represents the free hydrogen ion concentration, E^0 is the standard potential, and j is a constant which takes into account the liquid junction potential [8]. The experiments were carried out as follows: a fixed volume of 0.100 mol dm^{-3} HCl was titrated with successive additions of 0.100 mol dm^{-3} NaOH until near neutrality in order to get the parameters E^0 and j. Then, aliquots of the ligands under study were added and finally an aliquot of the nickel(II) stock solution was added; the titration was continued with 0.100 mol dm^{-3} NaOH. The measurements were done using a total metal concentration, $M_T = 2$–3 mmol dm^{-3} and ligand : metal molar ratios $R = 1$, 2, 4, and 10.

The Ni^{2+}-H$_2$L systems were studied according to the reaction scheme:

$$p\mathrm{H_2O} + q\mathrm{Ni}^{2+} + r\mathrm{H_2L} \rightleftharpoons [\mathrm{Ni}q(\mathrm{OH})p(\mathrm{H_2L})r]^{2q-p} + p\mathrm{H}^+, \beta_{p,q,r},$$

where H$_2$L represents oxalic and malonic acids, $[\mathrm{Ni}q(\mathrm{OH})p(\mathrm{H_2L})r]^{2q-p}$ is the (p, q, r) complex, and β_{pqr} is the respective stability constant.

The potentiometric data were analyzed using LETAGROP/FONDO [9, 10] in order to minimize the function $Z_B = (h - H)/M_T$, where Z_B is the average number of moles of H$^+$ dissociated per mole of metal, H is the total (analytical) concentration of H$^+$, h represents the concentration in equilibrium of H$^+$, and M_T represents the total (analytical) concentration of nickel(II). The Z_{Bfondo} function is:

$$Z_{\mathrm{Bfondo}} = \frac{h - H - Kwh^{-1} - \sum p\beta_{pr}h^p h_n l^r - \sum p\beta_{pq}m^q h^{-p}}{M_T - \sum q\beta_{pq}m^q h^{-p}}.$$

With this analysis we do a subtraction of the total average number of moles of protons dissociated and extract the contributions of the metal hydrolysis and the acid base reactions of the ligand, so what remains is the contribution of the number of moles of proton dissociated due to the complex reactions.

Equilibria corresponding to the formation of the hydroxo complexes of nickel(II) were considered in the calculation of the stability constants of the complexes. [Ni(OH)$_2$], $\log \beta_{1,-2} = -17.02(4)$ [11] is the hydrolytic species observed in the pH range studied. The stability constants of the nickel(II) hydroxo complex and the acidity constants of the ligands were kept fixed during the analysis. The aim was to find a complex or complexes giving the lowest sum of the errors squared, $U = \sum(Z_B^{\mathrm{exp}} - Z_B^{\mathrm{calc}})^2$ and $U = \sum(Z_{\mathrm{Bfondo}}^{\mathrm{exp}} - Z_{\mathrm{Bfondo}}^{\mathrm{calc}})^2$; the fittings were done by testing different (p, q, r) combinations.

The species distribution diagrams were done with the computer program HYSS [12], yielding β_{pqr} values, which are summarized in tables 1 and 2.

3. Results

3.1. *Ionization constants of the studied ligands*

The ionization constants (table 3) in 1.0 mol dm^{-3} NaCl are in good agreement with the literature values, considering the differences in ionic strength and ionic medium [3, 4].

Table 1. Stability constants (log β_{pqr}) of the Ni(II)-oxalic acid system studied in 1.0 mol dm^{-3} NaCl at 25°C.

Equilibria	log β_{pqr} Z_B	log β_{pqr} Z_Bfondo
$Ni^{2+} + H_2L \rightleftharpoons [NiHL]^+ + H^+$	3.41(2)	3.41(2)
$Ni^{2+} + H_2L \rightleftharpoons [NiL] + 2H^+$	0.96(2)	0.96(3)
$Ni^{2+} + H_2L \rightleftharpoons [Ni(OH)L]^- + 3H^+$	−8.49(6)	−8.48(6)
$Ni^{2+} + 2H_2L \rightleftharpoons [NiL_2]^{2-} + 4H^+$	−0.78(1)	−0.77(3)
Dispersion (σ)	0.033	0.035

Values in parentheses are standard deviations [$3\sigma(\log \beta_{pqr})$] on the last significant figure.

Table 2. Stability constants (log β_{pqr}) of the Ni(II)-malonic acid system studied in 1.0 mol dm^{-3} NaCl at 25°C.

Equilibria	log β_{pqr} Z_B	log β_{pqr} Z_Bfondo
$Ni^{2+} + H_2L \rightleftharpoons [NiHL]^+ + H^+$	3.64(5)	3.64(5)
$Ni^{2+} + H_2L \rightleftharpoons [NiL] + 2H^+$	1.19(3)	1.19(3)
$Ni^{2+} + H_2L \rightleftharpoons [Ni(OH)L]^- + 3H^+$	−3.12(4)	−3.12(4)
$Ni^{2+} + H_2L \rightleftharpoons [Ni(OH)_2L]^{2-} + 4H^+$	−12.0(1)	−12.0(1)
Dispersion (σ)	0.075	0.075

Values in parentheses are standard deviations [$3\sigma(\log \beta_{pqr})$] on the last significant figure.

Table 3. Acidity constants (log β_{p1}) of oxalic acid and malonic acid in 1.0 mol dm^{-3} NaCl at 25°C.

Equilibria	log β_{p1}	pK_a
Oxalic acid		
$H_2L \rightleftharpoons HL^- + H^+$	−1.098(5)	1.098
$H_2L \rightleftharpoons L^{2-} + 2H^+$	−4.641(5)	3.543
Dispersion (σ)	0.007	
Malonic acid		
$H_2L \rightleftharpoons HL^- + H^+$	−2.576(3)	2.576
$H_2L \rightleftharpoons L^{2-} + 2H^+$	−7.544(5)	4.968
Dispersion (σ)	0.006	

Values in parentheses are standard deviations [$3\sigma(\log \beta)$] on the last significant figure.

3.2. *Nickel(II) complexes*

3.2.1. Nickel(II)-oxalic acid system.   Figure 1(a) gives the Z_B(pH) data, figure 1(b) the Z_Bfondo(pH) data, and figure 2 presents the species distribution diagram for this system considering the following conditions: $M_\mathrm{T} = 3$ mmol dm^{-3} and molar ratio $R = 4$, taking into account the stability constants summarized in table 1.

3.2.2. Nickel(II)-malonic acid system.   Figure 3(a) gives the results of the Z_B(pH) analysis, figure 3(b) the results of the Z_Bfondo(pH) analysis performed with LETAGROP/FONDO, and figure 4 presents the species distribution diagram for the following conditions: $M_\mathrm{T} = 3$ mmol dm^{-3} and molar ratio $R = 4$ for this system, considering the stability constants summarized in table 2.
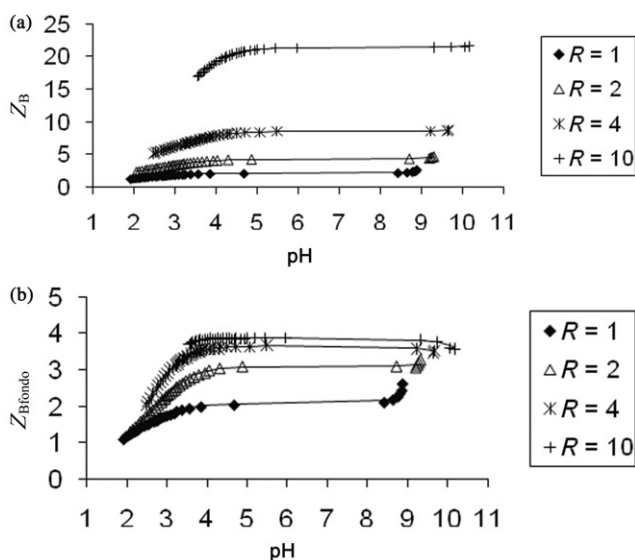
Figure 1. (a) Z_B(pH) and (b) Z_{Bfondo}(pH) data of the Ni(II)-oxalic acid system studied in $1.0\,mol\,dm^{-3}$ NaCl at 25°C.
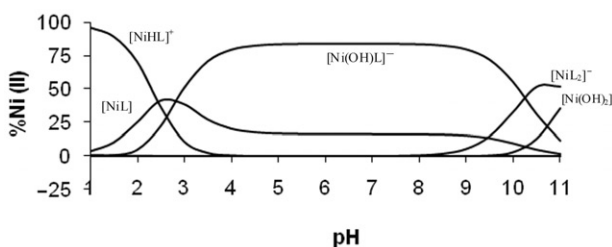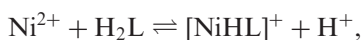

Figure 2. Species distribution diagram of the Ni(II)-oxalic acid system at $M_T = 3\,mmol\,dm^{-3}$ and molar ratio $R = 4$.

4. Discussion

The potentiometric data analysis of the nickel(II)-oxalic acid system performed with LETAGROP/FONDO [9] indicates the formation of the mononuclear complexes $[NiHL]^+$, $[NiL]$, $[Ni(OH)L]^-$, and $[NiL_2]^{2-}$. Good agreement between the experimental data (dotted curve) and the model (continuous line) can be observed in figure 1(a) and (b); the stability constants are summarized in table 1. Because of deprotonation of the ligand, when we do the Z_{Bfondo} analysis subtracting the metal hydrolysis contribution and the deprotonation of the ligand (figure 1b) for the molar ratio $R = 4$ and 10, the values of Z_{Bfondo} go from 1 to 3 in the pH range 2–3.5, indicating liberation of 1, 2, and 3 moles of proton per mol of metal. This forms a plateau in the pH range 3.5–10, indicating liberation of 4 moles of proton per mol of metal. The following reactions explain the behavior of figure 1(a) and (b):
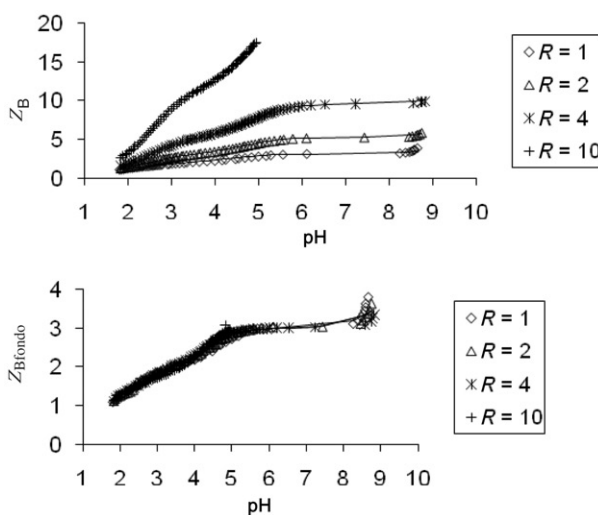
$$Ni^{2+} + H_2L \rightleftharpoons [NiHL]^+ + H^+,$$

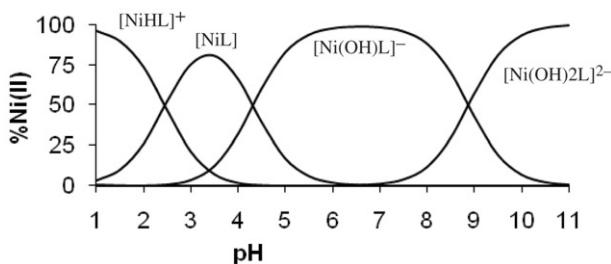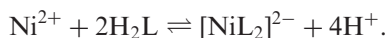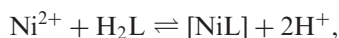Figure 3. (a) Z_B(pH) and (b) Z_{Bfondo}(pH) data of the Ni(II)-malonic acid system studied in $1.0\,mol\,dm^{-3}$ NaCl at 25°C.

Figure 4. Species distribution diagram of the Ni(II)-malonic acid system at $M_T = 3\,mmol\,dm^{-3}$ and molar ratio $R = 4$.

$$Ni^{2+} + H_2L \rightleftharpoons [NiL] + 2H^+,$$

$$Ni^{2+} + H_2L \rightleftharpoons [Ni(OH)L]^- + 3H^+,$$

$$Ni^{2+} + 2H_2L \rightleftharpoons [NiL_2]^{2-} + 4H^+.$$

The species distribution diagram for this system considering the experimental conditions $M_T = 3\,mmol\,dm^{-3}$ and a molar ratio $R = 4$ is given in figure 2. [NiHL]$^+$ and [NiL] are formed in the range $1 < pH < 3$, [Ni(OH)L]$^-$ is formed in 80% in the range $3 < pH < 10$, and [NiL$_2$]$^{2-}$ is abundant at pH > 10.

The analysis of the potentiometric data of the nickel(II)-malonic acid system shows the formation of [NiHL]$^+$, [NiL], [Ni(OH)L]$^-$, and [Ni(OH)$_2$L]$^{2-}$, as in the previous case, good agreement between the experimental data (dotted curve) and the model

(continuous line) can be observed in figure 3(a) and (b); the respective stability constants are summarized in table 2. We detect $[Ni(OH)_2L]^{2-}$ instead of $[NiL_2]^{2-}$, different from the nickel(II)-oxalic acid system. In figure 3(b), for the Z_{Bfondo} analysis the value goes from 1 to 4, and all the curves have the same values, because the complexes formed have the same concentration no matter the molar ratio employed. Inclusion of $[NiL_2]^{2-}$ gave worse fitting. In the literature [3, 4], for the nickel(II)-oxalic acid system only $[NiL]$ and $[NiL_2]^{2-}$ are reported; we observed these two complexes and $[NiHL]^+$ and $[Ni(OH)L]^-$. For the nickel(II)-malonic acid system $[NiHL]^+$, $[NiL]$, and $[NiL_2]^{2-}$ are reported; we could not detect $[NiL_2]^{2-}$ and we observe the hydrolytic products of the $1:1$ complex $[Ni(OH)L]^-$ and $[Ni(OH)_2L]^{2-}$. Data analysis was performed with the regular Z_B and Z_{Bfondo} functions, and we obtained the same stability constants with these two functions. The Z_{Bfondo} function gave us a better idea of the complexes formed in solution.

The species distribution diagram for the nickel(II)-malonic acid system at $M_T = 3 \, \text{mmol dm}^{-3}$ and $R = 4$ is presented in figure 4. $[NiHL]^+$ is important at $1 < \text{pH} < 2.5$, $[NiL]$ is formed in 80% in the range $2.5 < \text{pH} < 4$, $[Ni(OH)L]^-$ is the most abundant species at pH 4–9 and $[Ni(OH)_2L]^{2-}$ is more abundant at pH > 9.

5. Conclusions

Analysis of the potentiometric data shows the formation of mononuclear complexes with composition $1:1$ and $1:2$ in the nickel(II)-oxalic acid system, with protonated $[NiHL]^+$, a neutral $[NiL]$, and the hydrolytic product $[Ni(OH)L]^-$ in the two systems. Additionally, $[Ni(OH)_2L]^{2-}$ in the nickel(II)-malonic acid system was detected. The results of the Z_{Bfondo} analysis permit us to have a more realistic idea above the complexes formed in aqueous solution.

Acknowledgments

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