Determination of Aqueous Nickel–Carbonate and Nickel–Oxalate Complexation Constants

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An ion-exchange method was used to determine complexation constants for the Ni–oxalate and Ni–carbonate systems in a NaClO₄ background electrolyte. The Ni–oxalate data were interpreted in terms of a single Niox(aq) complex having log K_1 values for $\text{Ni}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{Niox(aq)}$ of 3.9 ± 0.1 (I.S. = 0.5 mol·L⁻¹ p[H] = 7.1) and 4.4 ± 0.1 (I.S. = 0.1 mol·L⁻¹ p[H] = 8.6) at $22 \pm 1^\circ\text{C}$. Specific ion-interaction theory (SIT) was used to obtain log $K_1^\circ = 5.17 \pm 0.05$ (95% confidence level and $\Delta\varepsilon = -0.23 \pm 0.15$) at I.S. = 0. The Ni–carbonate studies were carried out at p[H] values of 7.5, 8.5, and 9.6 in 0.5 mol·L⁻¹ NaClO₄/NaHCO₃ solutions. The NiCO₃(aq) species was the dominant complex in the $[\text{CO}_3^{2-}]$ concentration ranges studied at all three p[H] values. A log K_1 value for $\text{Ni}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{NiCO}_3(\text{aq})$ of 2.9 ± 0.3 was deduced at I.S. = 0.5 mol·L⁻¹. Extrapolating this value to zero ionic strength using the SIT approach yielded log $K_1^\circ = 4.2 \pm 0.3$ (95% confidence level and $\Delta\varepsilon = -0.26 \pm 0.04$). The data allowed upper bound values for the complexation constants for NiHCO_3^+ and $\text{Ni}(\text{CO}_3)_2^{2-}$ to be estimated, i.e., log $K^\circ < 1.4$ for $\text{Ni}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{NiHCO}_3^+$, and log $K_2^\circ < 2$ for $\text{NiCO}_3(\text{aq}) + \text{CO}_3^{2-} \rightleftharpoons \text{Ni}(\text{CO}_3)_2^{2-}$, respectively.

KEY WORDS: Nickel–carbonate; nickel–oxalate; ion exchange; aqueous complexes; thermodynamic data.

1. INTRODUCTION

Reliable thermodynamic data describing aqueous speciation are required in any work aimed at developing models for predicting the fate of trace metals in natural systems. In this respect, hydrolysis and carbonate complexation constants are of particular relevance. For most metals, generally well-established values are available for the former,^(1,2) but, for the latter, there are important reservations about the quality of some values, which have been accepted and used in many “reviewed” thermodynamic data bases.^(3–5)

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In an attempt to apply a sorption model for Ni uptake on montmorillonite to isotherm measurements on a bentonite,^(6,7) very good agreement between predicted and measured sorption values was found at pH = 7.0, but the model significantly under predicted the Ni uptake at pH = 8.2. The major complexing anions in the system were OH⁻ and HCO₃⁻/CO₃²⁻. The Ni-carbonate constants given in Mattigod and Sposito,⁽⁸⁾ which are widely accepted, were used in the modeling ($\log K_1^\circ = 6.87$ for $\text{Ni}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{NiCO}_3(\text{aq})$; $\log K^\circ = 2.14$ for $\text{Ni}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{NiHCO}_3^+$). The calculations indicated extensive formation of the NiCO₃(aq) complex at pH = 8.2, but virtually no carbonate complexation at pH = 7.0. Even when the estimated (lower) constants provided in Glaus *et al.*,⁽⁹⁾ $\log K_1^\circ = 5.2$, $\log K^\circ = 2.8$, were used the correspondence between calculated and measured sorption values at pH = 8.2 improved, but the differences were still substantial.⁽⁷⁾

Although the reason(s) for the discrepancies at pH = 8.2 could not be identified unambiguously, the suspicion that the problem lay with the Ni-carbonate constants was so strong that a study aimed at measuring them was undertaken.

Additional support for this supposition came from an extensive literature review on Ni carbonate complexation constants and their origins by Hummel and Curti.⁽⁵⁾ These authors conclude: "At the end of this adventure in the realm of thermodynamic data collections we are left with the sobering fact that until now all numbers found in the literature concerning nickel carbonate complexation are derived by various estimation procedures and none were actually measured. The estimated values published so far vary over more than four orders of magnitude. This is no longer a surprise since a close inspection of the individual estimation procedures revealed that the estimated values are based on shaky grounds, to say the least."

Ni is a potentially important environmentally toxic metal and a safety relevant radionuclide in radioactive waste disposal. Carbonate is ubiquitous in almost all natural groundwater systems and, consequently, having reliable data for the Ni carbonate complexes is not just desirable, but essential.

2. ION-EXCHANGE METHOD: ANALYSIS OF DATA

The technique chosen to determine the complexation of Ni with oxalate and carbonate species was an ion-exchange method.⁽¹⁰⁻¹³⁾ This method allows the stability constants for metal-ligand complexes to be determined by measuring the solid-liquid distribution ratio of the metal M in the absence (R_d°) and presence (R_d) of different concentrations of a ligand L (oxalate and carbonate). Usually trace-metal concentrations are employed (radioactive tracers) in a constant ionic strength medium.

In the absence of ligand L, the distribution of a metal M between an ion-exchange resin and a solution can be expressed by a distribution ratio

defined as:

$$R_d^o = [M^o]_{\text{sorb}}/[M^o]_{\text{sol}} \quad (1)$$

where $[M^o]_{\text{sorb}}$ is the amount of metal sorbed on the resin in $\text{mol}\cdot\text{kg}^{-1}$, and $[M^o]_{\text{sol}}$ is the concentration of metal in solution in $\text{mol}\cdot\text{L}^{-1}$. In the absence of any side reactions, the metal in solution is the uncomplexed aqua ion.

If side reactions, such as hydrolysis and/or complexation with a buffer [e.g. Tris, tris(hydroxymethyl)aminomethane, see later] play a role, then the concentration of the metal in solution is:

$$[M^o]_{\text{sol}} = [M^o] + \Sigma_x [M^o(\text{OH})_x] + \Sigma_y [M^o(\text{Tris})_y] \quad (2)$$

$$[M^o]_{\text{sol}} = [M^o] (1 + \Sigma_x \beta_x^H [H^+]^{-x} + \Sigma_y \beta_y^{\text{Tris}} [\text{Tris}]^y) = [M^o] A \quad (3)$$

where A is the term representing the aqueous speciation of M in the absence of ligand L . The stability constants refer to the reactions (charge is neglected for simplicity):

(The calculations of the A term for the side reactions of Ni with Tris and for the hydrolysis of Ni , together with their associated uncertainties, are presented in the Appendix.)

In the presence of the ligand L , the distribution ratio is:

$$R_d = [M]_{\text{sorb}}/[M]_{\text{sol}} \quad (4)$$

where $[M]_{\text{sorb}}$ is the amount of metal sorbed on the resin in $\text{mol}\cdot\text{kg}^{-1}$ in the presence of ligand L , and $[M]_{\text{sol}}$ is the total concentration of metal in solution in $\text{mol}\cdot\text{L}^{-1}$. If L forms ML and ML_2 complexes and, in addition, a protonated complex MHL , the total concentration of metal in solution is:

$$[M]_{\text{sol}} = [M] + [ML] + [MHL] + [ML_2] + \Sigma_x [M(\text{OH})_x] + \Sigma_y [M(\text{Tris})_y] \quad (5)$$

$$[M]_{\text{sol}} = [M] (K_1^L [L] + K_1^L K^{\text{HL}} [H] [L] + K_1^L K_2^L [L]^2 + A) \quad (6)$$

The stability constants refer to the reactions

When the sorption is linear (low metal concentrations, $\approx 10^{-8} \text{ mol}\cdot\text{L}^{-1}$, and low fractional occupancies) the distribution ratio is constant, i.e.,

$$[M^o]_{\text{sorb}}/[M^o] = [M]_{\text{sorb}}/[M] \quad (7)$$

Combining Eqs. (1), (3), (4), (6), and (7) and rearranging gives:

$$(R_d^\circ/R_d - 1)A/[L] = K_1^L(1 + K^{HL}[H] + K_2^L[L]) \quad (8)$$

The contribution of the different complexes can be analyzed by plotting the experimental data as $\log(R_d^\circ/R_d - 1) + \log A - \log[L]$ vs. $\log[L]$.

1. If the complexes ML and/or MHL predominate, the data should plot on a horizontal line at constant pH. If ML is the dominant complex, this line represents the stability of the ML complex, i.e., $\log(R_d^\circ/R_d - 1) + \log A - \log[L] = \log K_1^L$.

2. The contribution of ML and MHL can only be deconvoluted if data measured at different p[H] are compared. If the complex MHL predominates at a certain low p[H], these data will also plot on a horizontal line, but at significantly higher values than the data measured at higher p[H].

$$\log(R_d^\circ/R_d - 1) + \log A - \log[L] = \log K_1^L + \log(1 + K^{HL}[H])$$

If the complex MHL predominates at two different p[H] values studied, the data should be separated by the difference in p[H], i.e.,

$$\log(R_d^\circ/R_d - 1) + \log A - \log[L] = \log K_1^L + \log K^{HL} - p[H]$$

If all data obtained at different pH values plot on the same horizontal line, the complex MHL is a minor species in the range of measurements and only an upper limit of the MHL complexation strength can be estimated from such data, i.e., $\log K^{HL} < p[H]_{\min}$, where $p[H]_{\min}$ is the lowest p[H] investigated.

3. If the complex ML_2 predominates in a region of high ligand L concentrations the measured values at constant p[H] start to increase with increasing L concentration

$$\log(R_d^\circ/R_d - 1) + \log A - \log[L] = \log K_1^L + \log(1 + K_2^L[L])$$

The start point of this increase in terms of $\log[L]$ determines $\log K_2^L = -\log[L]$. At higher L concentrations, the measured values should increase with a slope of unity:

$$\log(R_d^\circ/R_d - 1) + \log A - \log[L] = \log K_1^L + \log K_2^L + \log[L]$$

3. MATERIALS AND METHODS

3.1. Preparation of Dowex 50W X-4 Resin

The cation-exchange resin used in all tests was Dowex 50W X-4. Of the wet resin 10g, originally in the H^+ - form (capacity ~ 21 equiv-kg $^{-1}$), were converted to the Na^+ form by washing twice with 0.25 L of 0.1 mol-L $^{-1}$ NaOH, followed by three equilibrations with 0.1 mol-L $^{-1}$ NaClO $_4$. Finally the resin was dried at 50°C after rinsing with deionized water to remove the salt solution.

Fig. 1. Recorded pH values, pHr, plotted against acid and base solutions of known H^+ concentrations (p[H]) in 0.5 M NaClO_4 .

3.2. p[H] Values

All pH measurements were carried out on a Metrohm 691 pH meter using Metrohm double junction pH electrode. The electrode was calibrated in 0.5 mol-L^{-1} NaClO_4 solutions containing known concentrations of HNO_3 or NaOH (Fig. 1). Linear regression for the data yields $\text{p[H]} = (0.999 \pm 0.005) \text{pHr} + (0.02 \pm 0.07)$. In all further data evaluations, the measured pHr is taken to be the corresponding p[H] value with an uncertainty of ± 0.1 log units.

3.3. Preparation of Standard ^{63}Ni -Labeled Solutions

Stock solutions of NaHCO_3 and NaClO_4 each at 0.5 mol-L^{-1} were made up using Fluka high-purity chemicals ($>99.7\%$ pure). Mops [3-(N-morpholino) propanesulfonic acid] buffer was added to both solutions at a concentration of 2×10^{-3} mol-L^{-1} and the p[H] adjusted to 7.5 by adding 1 mol-L^{-1} HNO_3 .

Immediately after preparation, aliquots of the fresh stock solutions were mixed in appropriate proportions in 200-ml volumetric flasks to give a range of NaHCO_3 concentrations between 5×10^{-3} and 0.5 mol-L^{-1} at a constant I.S. = 0.5 mol-L^{-1} . Each solution was then transferred to polyethylene bottles, labeled with ^{63}Ni (Amersham, UK), at $\sim 10^{-8}$ mol-L^{-1} and the bottles sealed with screw caps. These standard labeled solutions were then left overnight to stabilize. The p[H] values of the stock solutions remained stable.

Similar procedures were used to prepare ^{63}Ni -labeled standard solutions at p[H] values of 8.6 (Tris buffer) and 9.6 {Ches [3-(cyclohexylamino) ethanesulfonic acid] buffer} except that 1 mol-L^{-1} NaOH was used to adjust the p[H] . At $\text{p[H]} = 8.5$, 27 ml of 1 mol-L^{-1} NaOH was added to the NaHCO_3 solution and at $\text{p[H]} = 9.6$, 220 ml 1 mol-L^{-1} NaOH. The buffer was used to accurately set the pH of the perchlorate solutions.

In addition, standard ^{63}Ni -labeled sodium oxalate/perchlorate solutions were prepared at ionic strengths of 0.1 and 0.5 mol-L^{-1} and p[H] values of 8.6 (Tris buffer, $2 \times 10^{-3} \text{ mol-L}^{-1}$) and 7.1 (Mops buffer, $2 \times 10^{-3} \text{ mol-L}^{-1}$), respectively. The oxalate concentrations ranged between 10^{-5} and $2.5 \times 10^{-2} \text{ mol-L}^{-1}$.

The reason that the well-behaved and much studied Ni-oxalate system was also included in the investigations, particularly the measurements at 0.5 mol-L^{-1} , was to gain confidence in the application of the ion-exchange method to the more experimentally demanding Ni-carbonate system.

3.4. Ni Sorption Experiments on Dowex

Aliquots, 30 ml, of the standard ^{63}Ni -labeled solutions were added to known quantities of Dowex resin in polypropylene centrifuge tubes. Screw caps were fitted to the centrifuge tubes, which were then shaken end-over-end for at least 24 hr at $22 \pm 1^\circ\text{C}$. (Kinetic experiments showed that sorption equilibrium was reached within a few hours.) After this time, the samples were centrifuged (1 hr at $95000 g$ max.), 5-ml aliquots taken for radioassay, and counted together with standards from the original labeled solutions. ^{63}Ni was measured by liquid scintillation counting (Canberra Packard Tri-Carb 2250 CA) using Instagel (Packard) as a scintillation cocktail.

Distribution ratios at the different ligand concentrations were calculated from

$$R_d = \frac{A_{\text{in}} - A_{\text{final}}}{A_{\text{final}}} \cdot \frac{V}{m} \quad (9)$$

where: A_{in} = initial activity, A_{final} = final activity, V = volume (L), and m = mass of solid (kg).

The sorption of Ni on batches of Dowex resin nominally prepared in the same manner varied somewhat from batch to batch. Consequently, R_d° values and sorption values in the presence of a specific complexing ligand were always determined on the same chemically prepared batch of Dowex resin.

Some preliminary Ni sorption experiments were performed with solutions containing up to 0.1 mol-L^{-1} Na bicarbonate ($\text{p[H]} = 8.6$; I.S. = 0.1 mol-L^{-1}). A reliable analysis of these data could not be carried out because the effects of nickel carbonate complexation in this range of bicarbonate concentration were too weak to extract any meaningful data from these measurements. (These data provided a first

Table I. Summary of Ni Sorption Data on Dowex 50W X-4 Exchange Resin in the Presence of Oxalate in I.S. = 0.1 mol-L⁻¹ Na₂Ox/NaClO₄ Solutions^a

Added Na ₂ Ox (mol-L ⁻¹)	log[ox ²⁻] (mol-L ⁻¹)	<i>R</i> _d (L·kg ⁻¹)
1.0 × 10 ⁻⁵	-5.00	1589
		1493
1.0 × 10 ⁻⁴	-4.00	810
		1001
1.0 × 10 ⁻³	-3.00	124
		134
1.5 × 10 ⁻³	-2.82	95
		99
		91
		76
2.5 × 10 ⁻³	-2.60	68
		49
1.5 × 10 ⁻²	-1.82	3.3
		8.4
		3.7
		3.3
2.5 × 10 ⁻²	-1.60	7.6
		4.3

^ap[H] = 8.6; solid to liquid ratio = 6.7 g·L⁻¹, Tris = 0.002 mol-L⁻¹,
*R*_d^o = 1741 ± 288 L·kg⁻¹ (mean of 6 measurements).

indication that the Ni-carbonate complexation constant was probably significantly weaker than the generally accepted values mentioned in Section 1).

4. RESULTS AND DATA ANALYSIS

4.1. Nickel-Oxalate Data

4.1.1. Results

*R*_d^o values of 1741 ± 288 and 77.6 ± 7.8 L·kg⁻¹ were determined for Ni sorption on the Dowex resin in 0.1 and 0.5 mol-L⁻¹ NaClO₄ background electrolytes, respectively. The results from the sorption experiments carried out in the presence of different oxalate concentrations under the condition of constant total ionic strength are presented in Tables I and II. The relative uncertainties on the individual *R*_d data points were taken to be the same as for the *R*_d^o values.

4.1.2. Nickel Oxalate Complexation Studied at p[H] 7.1 in 0.5 mol-L⁻¹ NaClO₄

According to the ongoing NEA review of simple organic ligands (W. Hummel, pers. commun.) there is no need to consider complexes, such as NaOx⁻, explicitly in

Table II. Summary of Ni Sorption Data on Dowex 50W X-4 Exchange Resin in the Presence of Oxalate in I.S. = 0.5 (mol-L⁻¹) Na₂ox/NaClO₄ Solutions

Added Na ₂ ox (mol-L ⁻¹)	log[ox ²⁻] (mol-L ⁻¹)	R _d (L·kg ⁻¹)
2.0 × 10 ⁻⁵	-4.70	64.3
		63.7
		66.1
6.0 × 10 ⁻⁵	-4.22	55.6
		48.9
		50.0
1.0 × 10 ⁻⁴	-4.00	40.7
		43.1
		40.7
2.0 × 10 ⁻⁴	-3.70	27.7
		28.2
		29.7
6.0 × 10 ⁻⁴	-3.22	13.6
		15.1
		13.9
1.0 × 10 ⁻³	-3.00	8.2
		12.2
		8.5
2.0 × 10 ⁻³	-2.70	3.9
		3.8
		3.7
5.0 × 10 ⁻³	-2.30	0.9
		1.4
		0.9
7.0 × 10 ⁻³	-2.15	0.1
		1.9
		0.3
1.0 × 10 ⁻²	-2.00	1.2
		0.8
		0.3

^ap[H] = 7.1; solid to liquid ratio = 20 g-L⁻¹; Mops = 0.002 mol-L⁻¹,
R_d⁰ = 77.6 ± 7.8 L·kg⁻¹ (mean of 6 measurements).

speciation models. The sodium oxalate interaction is taken care of as a specific ion interaction within the scope of the Specific Ion Interaction Theory (SIT) approach adopted here.⁽¹⁴⁾ In the pH range considered in this study, the protonation of oxalate is also negligible. Finally, nickel is used in trace concentrations ($\approx 10^{-8}$ mol-L⁻¹) and, hence, oxalate complexes can be neglected in the mass balance of oxalate, i.e., the total analytical concentration of [Na₂ox] equals the concentration of free oxalate [ox²⁻].

Fig. 2. Nickel–oxalate results at $p[H] = 7.1$ in 0.5 M NaClO_4 .

As mentioned above, the protonation of oxalate is negligible at $p[H] 7.1$ and, therefore, the NiHox^+ complex is not expected to form. The dominant complex is NiOx(aq) , and potentially Ni(ox)_2^{2-} at high oxalate concentration.

The Mops buffer does not form complexes with nickel,⁽¹⁵⁾ and at $p[H] 7.1$ nickel hydrolysis is negligible; thus $\log A = 0$.

The uncertainty in $\log(R_d^o / R_d - 1) - \log[\text{ox}^{2-}]$ originates primarily from the uncertainty in the values of R_d^o and R_d . The uncertainty in $[\text{ox}^{2-}]$, the total analytical concentration of $[\text{Na}_2\text{Ox}]$, is considered to be negligible in comparison.

A typical analytical window can be seen in Fig. 2. At the lowest oxalate concentrations studied, the concentration of nickel oxalate complexes becomes very low; R_d approaches R_d^o and the resulting overall uncertainty increases. At the highest oxalate concentrations studied, the nickel oxalate concentrations become so high that the distribution ratio R_d becomes very low. Hence, the scatter in the data points and their associated uncertainties increase.

Considering the scatter in the data and their uncertainties at high oxalate concentration, the formation of a Ni(ox)_2^{2-} , under these experimental conditions, cannot be identified. All data plot essentially along a horizontal line and, consequently, have been interpreted in terms of a single NiOx(aq) complex. A weighted average of all data yields $\log K_1 = 3.91$ for $\text{Ni}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{NiOx(aq)}$ (solid line in Fig. 2) with an uncertainty of ± 0.03 (95% confidence level). However, this uncertainty is estimated solely from the uncertainties associated with individual data points. Considering the scatter in the data points, a more realistic uncertainty is ± 0.10 (dotted lines in Fig. 2).

In summary, a $\log K_1 = 3.9 \pm 0.1$ in $0.5 \text{ mol-L}^{-1} \text{ NaClO}_4$ is obtained.

4.1.3. Nickel Oxalate Complexation Studied at $p[\text{H}]$ 8.6 in $0.1 \text{ mol-L}^{-1} \text{ NaClO}_4$

Tris was used as a buffer in these experiments. Tris forms complexes with nickel and at $p[\text{H}] = 8.6$, nickel hydrolysis cannot be completely neglected. Considering a Tris concentration of 0.002 mol-L^{-1} at $p[\text{H}]$ 8.6 and nickel hydrolysis, a side-reaction term $\log A = 0.28(+0.30, -0.09)$ is obtained (see Appendix). The asymmetric uncertainty stems from the second nickel hydrolysis constant. Only if the value at the maximum extent of its uncertainty range is used, does a significant contribution to A result at $p[\text{H}] = 8.6$.

The total uncertainty of $\log(R_d^\circ/R_d - 1) + \log A - \log[\text{ox}^{2-}]$ arises from the uncertainty in the determination of R_d° and R_d and the uncertainty in A .

In Fig. 3, the same effects with respect to the analytical window at the lowest and highest oxalate concentrations as seen in Fig. 2 are present. In addition, the asymmetric uncertainty due to the second nickel hydrolysis constant can also be seen at all intermediate values.

As in the previous case the formation of a $\text{Ni}(\text{ox})_2^{2-}$ cannot be confirmed. All of the data plot essentially along a horizontal line and have been interpreted in terms of a single complex $\text{Ni}(\text{ox})\text{aq}$. A weighted average of all data yields $\log K_1 = 4.4 \pm 0.1$ (solid and dotted lines in Fig. 3) at $0.1 \text{ mol-L}^{-1} \text{ NaClO}_4$.

Fig. 3. Nickel-oxalate results at $p[\text{H}] = 8.6$ in 0.1 M NaClO_4 .

4.1.4. Comparison with Literature Data

There are several published values with which to compare the results given here. McAuley and Nancollas⁽¹⁶⁾ determined nickel oxalate complexation by a precise electrochemical method at millimolar ionic strengths. The results were extrapolated to zero ionic strength by McAuley and Nancollas using the Davies equation with a coefficient of 0.2.⁽¹⁷⁾ The result at 25°C and I.S. = 0 is $\log K_1^\circ = 5.16 \pm 0.01$. Considering the uncertainty added by extrapolating to zero ionic strength, a realistic 95% confidence level for their constant is considered to be ± 0.05 .

Murai *et al.*⁽¹⁸⁾ used a solvent extraction technique to study nickel oxalate complexation. In 1 mol-L⁻¹ NaClO₄ at 25°C, they obtained a $\log K_1 = 3.7$. Considering their experimental method, a 95% confidence level of ± 0.2 is estimated.

Van Loon and Kopajtic⁽¹⁹⁾ used a similar ion-exchange method to the one applied in this study. The result obtained in 0.11 mol-L⁻¹ NaClO₄ at 20°C was $\log K_1 = 4.3 \pm 0.1$ (95% confidence level).

Comparing these values with the results given here, a SIT plot of ($\log K_1 + 8D$) versus I_m , where $D = 0.509$, $I_m(1 + 1.5\sqrt{I_m})$ and I_m is the molal ionic strength [see Grenthe *et al.*⁽¹⁴⁾] reveals that the current results fit well with the previously determined values (Fig. 4). A weighted linear regression of all oxalate data shown in Fig. 4 gives $\log K_1^\circ = 5.17 \pm 0.05$ at I.S. = 0 (95% confidence level) and $\Delta\varepsilon = -0.23 \pm 0.15$.

Fig. 4. SIT plot of nickel-oxalate complexation data.

Table III. Summary of Ni Sorption Data on Dowex 50W X-4 Exchange Resin in the Presence of Carbonate in I.S. = 0.5 mol-L⁻¹ NaHCO₃/NaClO₄ Solutions^a

Added NaHCO ₃ (mol-L ⁻¹)	log[CO ₃ ²⁻] (mol-L ⁻¹)	R _d (L·kg ⁻¹)
1.0 × 10 ⁻¹	-3.12	64.6
	-3.17	53.2
	-3.10	54.4
1.5 × 10 ⁻¹	-2.98	50.1
	-2.98	53.0
	-2.98	58.8
2.0 × 10 ⁻¹	-2.88	28.6
	-2.78	28.9
	-2.86	25.8
2.5 × 10 ⁻¹	-2.79	31.7
	-2.81	28.5
	-2.82	31.4
3.0 × 10 ⁻¹	-2.72	35.5
	-2.70	33.5
	-2.70	48.1
3.5 × 10 ⁻¹	-2.66	37.8
	-2.65	30.4
	-2.67	31.1
4.5 × 10 ⁻¹	-2.51	23.9
	-2.53	22.7
	-2.54	23.7

^ap[H] = 7.5; solid to liquid ratio = 10 g-L⁻¹; Mops = 0.002 mol-L⁻¹; R_d⁰ = 88.0 ± 3.3 L·kg⁻¹ (mean of 9 measurements).

4.2. Nickel Carbonate Data

4.2.1. Results

R_d⁰ values were determined at a series of (high) NaClO₄ concentrations covering the range of Na concentrations used in the experiments. The results from the sorption experiments carried out in the presence of different total inorganic carbon concentrations and pH values are presented in the Tables III–V, together with the corresponding R_d⁰ values. The relative uncertainties in the individual R_d data points were taken to be the same as for the R_d⁰ values.

4.2.2. Nickel Carbonate Complexation Studied at p[H] 7.5 in 0.5 mol-L⁻¹ NaClO₄/NaHCO₃

The Mops buffer does not form complexes with nickel,⁽¹⁵⁾ and at p[H] 7.5 the nickel hydrolysis is negligible; thus, log A = 0. The concentration of [CO₃²⁻] was calculated from the total analytical concentration of [NaHCO₃] and the measured

Table IV. Summary of Ni Sorption Data on Dowex 50W X-4 Exchange Resin in the Presence of Carbonate in 0.5 (mol-L⁻¹) NaHCO₃/NaClO₄ Solutions (I.S. in the range 0.5 to 0.56 mol-L⁻¹^a)

Added NaHCO ₃ (mol-L ⁻¹)	log[CO ₃ ²⁻] (mol-L ⁻¹)	R _d (L·kg ⁻¹)
5.0 × 10 ⁻²	-2.53	94.3
		90.0
1.0 × 10 ⁻¹	-2.22	65.4
		66.4
2.0 × 10 ⁻¹	-1.92	36.5
		36.9
3.0 × 10 ⁻¹	-1.75	25.1
		23.9
4.0 × 10 ⁻¹	-1.62	17.4
		17.5
5.0 × 10 ⁻¹	-1.52	14.6
		15.4

^ap[H] = 8.5; solid to liquid ratio = 33.3 g·L⁻¹, Tris = 0.004 mol-L⁻¹, R_d^o = 169.8 ± 7.9 L·kg⁻¹ (mean of 6 measurements).

p[H] using:⁽²⁰⁾

and SIT to extrapolate these values to I.S. = 0.5 mol-L⁻¹ NaClO₄/NaHCO₃ with the interaction parameters⁽¹⁴⁾ $\varepsilon(\text{H}^+, \text{HCO}_3^-) \approx \varepsilon(\text{H}^+, \text{ClO}_4^-) = 0.14 \pm 0.02$, $\varepsilon(\text{CO}_3^{2-}, \text{Na}^+) = -0.08 \pm 0.03$, $\varepsilon(\text{HCO}_3^-, \text{Na}^+) = 0.00 \pm 0.02$, and $\varepsilon[(\text{CO}_2(\text{aq}), \text{NaClO}_4/\text{NaHCO}_3)] = 0$.

Complexes, such as NaCO₃⁻ or NaHCO₃(aq), were not considered explicitly in the speciation calculations since sodium carbonate and bicarbonate effects were included in SIT.

The uncertainty in $\log(R_d^\circ/R_d - 1) - \log[\text{CO}_3^{2-}]$ originates from the uncertainty in measurements of R_d° and R_d . The uncertainty in p[H] (± 0.10) propagates directly to the uncertainty in $\log[\text{CO}_3^{2-}]$. By comparison, the uncertainties arising from extrapolating carbonate stability constants to I.S. = 0.5 mol-L⁻¹ NaClO₄/NaHCO₃ with SIT are negligible. Thus the uncertainty in $\log[\text{CO}_3^{2-}]$ is ± 0.10 and ± 0.18 in $\log(R_d^\circ/R_d - 1) - \log[\text{CO}_3^{2-}]$.

4.2.3. Nickel Carbonate Complexation Studied at p[H] 8.5 in 0.5 mol-L⁻¹ NaClO₄/NaHCO₃

In the original set-up of the experiments, 0.004 mol-L⁻¹ Tris was used to buffer the pH of the system. However, the experimental results revealed that only

Table V. Summary of Ni Sorption Data on Dowex 50W X-4 Exchange Resin in the Presence of Carbonate in 0.5 mol-L⁻¹ NaHCO₃/NaClO₄ Solutions (I.S. in the range 0.5 to 0.9 mol-L⁻¹^a)

Added NaHCO ₃ (mol-L ⁻¹)	log[CO ₃ ²⁻] (mol-L ⁻¹)	R _d (L·kg ⁻¹)
2.5 × 10 ⁻²	-1.95	53.9
		69.4
		62.7
1.0 × 10 ⁻¹	-1.35	22.6
		33.3
		32.1
1.5 × 10 ⁻¹	-1.17	19.9
		18.9
		17.6
2.0 × 10 ⁻¹	-1.05	15.2
		14.2
		16.1
2.5 × 10 ⁻¹	-0.96	10.6
		10.3
		10.0
3.0 × 10 ⁻¹	-0.88	7.8
		7.6
		7.9
4.0 × 10 ⁻¹	-0.76	2.6
		2.9
		2.8
4.5 × 10 ⁻¹	-0.72	2.5
		2.4
		2.6
5.0 × 10 ⁻¹	-0.65	2.7
		1.6
		2.3

^ap[H] = 9.6; solid to liquid ratio = 40 g·L⁻¹ Ches = 0.002 mol-L⁻¹, R_d⁰ = 115.1 ± 17.5 L·kg⁻¹ (mean of 6 measurements).

data measured at NaHCO₃ concentrations of 0.05 mol-L⁻¹ and higher showed significant complexation effects. Only these data have been used in subsequent analyses. In this concentration region the system is buffered by HCO₃⁻/CO₃²⁻ (6% [CO₃²⁻] in the system) and the effect of Tris can be neglected concerning pH buffering.

A side-reaction term log A = 0.42(+0.18, -0.10) was calculated, taking into account nickel/Tris complexes and nickel hydrolysis. The uncertainties in log A and log [CO₃²⁻] and, in addition, the uncertainty in the determination of R_d^o and R_d, results in an overall uncertainty of +0.27 and -0.20 for the term log(R_d^o/R_d - 1) + log A - log[CO₃²⁻].

Fig. 5. Summary of nickel-carbonate measurements.

4.2.4. Nickel Carbonate Complexation Studied at $p[H]$ 9.6 in $0.5 \text{ mol-L}^{-1} \text{ NaClO}_4/\text{NaHCO}_3$

The Ches buffer does not form complexes with nickel. The side-reaction term $\log A$ was calculated to be 0.96 with a relatively high uncertainty of $(+1.15, -0.74)$ due to the uncertainties in nickel hydrolysis, especially the second hydrolysis constant. The uncertainty in the calculated $\log [\text{CO}_3^{2-}]$ value was estimated to be ± 0.06 . Considering these uncertainties and those in the determinations of R_d^o and R_d , a minimum uncertainty of $+1.3$ and -0.9 in $\log(R_d^o/R_d - 1) + \log A - \log [\text{CO}_3^{2-}]$ was calculated. Compared with the other similar experiments, this experimental set-up created some additional uncertainty in data analysis since the ionic strength varied from 0.5 to 0.9 mol-L^{-1} with increasing bicarbonate concentration. Note that the pK values appropriate to relationships between the concentrations of carbonate, bicarbonate, and pH are $\sim 9.7 \pm 0.1$, even as the ionic strength varies between 0.5 and 0.9 mol-L^{-1} .

4.2.5. Summary of Carbonate Data

The data measured at $p[H]$ 7.5, 8.5, and 9.6 are plotted together in Fig. 5. As can be seen, all the data for $\log [\text{CO}_3^{2-}] < -0.8$ plot on a horizontal line, and

considering their uncertainty ranges, there is no significant difference between data measured at $p[H]$ 7.5, 8.5, and 9.6. Hence, it is concluded that $NiCO_3(aq)$ is the dominant complex in this concentration range [Section 2, paragraph 1]. A weighted mean of all data yields $\log K_1 = 2.94 \pm 0.04$. The weighted uncertainty results solely from the uncertainties in the individual experimental points and the large number of data. Considering the scatter in the data and the systematic effects discussed above, a more realistic value for this constant is considered to be $\log K_1 = 2.9 \pm 0.3$ at $0.5 \text{ mol-L}^{-1} \text{ NaClO}_4$ (dotted lines in Fig. 5).

Direct comparison of this constant with the one obtained for nickel oxalate under identical experimental conditions reveals that nickel carbonate complexation is one order of magnitude weaker than nickel oxalate complexation.

SIT can be used to extrapolate the $NiCO_3(aq)$ constant to zero ionic strength. Considering the specific ion-interaction parameters⁽¹⁴⁾ $\varepsilon(Ni^{2+}, ClO_4^-) \approx \varepsilon(Co^{2+}, ClO_4^-) = 0.34 \pm 0.03$, $\varepsilon(CO_3^{2-}, Na^+) = -0.08 \pm 0.03$, and $\varepsilon[NiCO_3(aq), NaClO_4] = 0$ gives $\Delta\varepsilon = -0.26 \pm 0.04$. Within the uncertainty range, the $\Delta\varepsilon$ constant is identical with the one derived from the weighted regression of the oxalate data ($\Delta\varepsilon = -0.23 \pm 0.15$). From the viewpoint of chemical systematics, this should be expected for similar reactions, such as oxalate and carbonate complexation with nickel, and, hence, adds to the confidence in using SIT to extrapolate a single data point to zero ionic strength. The result is:

This value is at the lower end of the range $4 < \log K_1^\circ < 5.5$ estimated by Hummel and Curti.⁽⁵⁾

Within the uncertainty of the measured values, there is no difference in the data obtained at $p[H]$ 7.5 and 8.5. The conclusion is, therefore, that the complex $NiHCO_3^+$ is a minor species over the entire $p[H]$ and concentration ranges studied here (Section 2, paragraph 2). Only an estimate for an upper bound value for its stability constant can be given, i.e., $\log K < 7.5$ for $NiCO_3(aq) + H^+ \rightleftharpoons NiHCO_3^+$. This isocoulombic reaction is expected to exhibit a very weak dependence on ionic strength and, hence, at I.S. = 0, $\log K^\circ < 7.5$.

Considering the reaction

and the carbonate reaction

then for

a $\log K^\circ < 1.4$ is calculated.

This upper limit also compares well with the range of $1 < \log K^\circ < 2$ estimated by Hummel and Curti.⁽⁵⁾ It may be speculated that $\log K^\circ \approx 1$, i.e., the value at the lower end of the expectation range is in agreement with $\log K_1^\circ$, which is also found to be at the lower end of its expectation range.

At the highest carbonate concentrations encountered in this study, the data seem to indicate a systematic increase (Fig. 5). Unfortunately, the precision of the data measured at $p[H]$ 9.6 is severely hampered by the large uncertainties in the hydrolysis constants. The good overall consistency of the data measured at different $p[H]$ values indicates that the nickel hydrolysis constants might be less uncertain than anticipated from the poor data they are derived from. However, this argument cannot be used in a circular way to diminish the uncertainty of the nickel hydrolysis constants and then subsequently claim that these more precise hydrolysis data prove the overall consistency of the carbonate data.

All that can be concluded in the present situation is that the data indicate the formation of a $\text{Ni}(\text{CO}_3)_2^{2-}$ complex at high carbonate concentrations (Section 2, paragraph (3), but due to the large uncertainty in the nickel hydrolysis data, only an estimate for an upper bound for this stability constant can be given (dashed line in Fig. 5):

The isocoulombic reaction is expected to exhibit a very weak dependence on ionic strength and, hence, $\log K_2 \approx \log K_2^\circ$. This upper bound also compares well with the range estimated by Hummel and Curti:⁽⁵⁾

$$\log K_2^\circ < \log K_1^\circ - 2, \text{ i.e., } \log K_2^\circ < 2.2$$

5. SUMMARY

A procedure based on the ion-exchange method was used to determine complexation constants for the Ni-oxalate and Ni-carbonate systems. Part of the reason for including the well-behaved and much studied Ni-oxalate system in these investigations, particularly the measurements at the higher I.S., was to gain confidence in the application of the ion-exchange method to the more experimentally demanding Ni-carbonate system.

The Ni-oxalate experiments were carried out at total ionic strengths of 0.5 and 0.1 mol-L⁻¹ at $p[H]$ values of 7.1 and 8.6, respectively, in background electrolytes of NaClO₄ for oxalate concentrations in the range 10⁻⁵ and 2.5×10^{-2} mol-L⁻¹. The data were interpreted in terms of a single $\text{Ni}(\text{ox})(\text{aq})$ complex. [At high oxalate concentration no evidence for the formation of a $\text{Ni}(\text{ox})_2^{2-}$ could be found under the experimental conditions used.]

The values of $\log K_1$ measured at I.S. of 0.5 and 0.1 mol-L⁻¹ were 3.9 ± 0.1 and 4.4 ± 0.1 , respectively. These NiOx(aq) complexation constants were in good agreement with literature values. Specific ion-interaction theory (SIT) was used to obtain $\log K_1^\circ = 5.17 \pm 0.05$ (95% confidence level and $\Delta\varepsilon = -0.23 \pm 0.15$) at I.S. = 0.

Preliminary studies on nickel carbonate complexation using the cation-exchange method were carried out at p[H] 8.6 in 0.1 mol-L⁻¹ NaClO₄/NaHCO₃ solutions. However, the effects of complexation on nickel exchange were so weak in the accessible range of bicarbonate concentrations that meaningful data could not be derived from these measurements. Hence, the studies focused on experiments carried out at higher I.S. in which the NaHCO₃ concentration ranged up to 0.5 M. In the experiments performed at a p[H] of 7.5, a constant I.S. of 0.5 mol-L⁻¹ in the NaClO₄/NaHCO₃ solutions was maintained. At p[H] values of 8.5 and 9.6 this was not possible at the highest NaHCO₃ concentrations and the I.S. ranged up to 0.56 and 0.9 mol-L⁻¹, respectively.

The data measured at p[H] 7.5, 8.5 and 9.6 were plotted together in a $\log(R_d^\circ/R_d - 1) + \log A - \log[\text{CO}_3^{2-}]$ vs. $\log[\text{CO}_3^{2-}]$ plot. All of the data for $\log[\text{CO}_3^{2-}] < -0.8$ lay on a horizontal line and, considering their uncertainty ranges, there was no significant difference between the data measured at the different p[H] values. This implied that NiCO₃(aq) was the dominant complex in the $[\text{CO}_3^{2-}]$ concentration range studied (section 2, paragraph (i)).

A $\log K_1 = 2.9 \pm 0.3$ was deduced for NiCO₃(aq) complexation constant at I.S. = 0.5 M. This value for the nickel carbonate complexation constant is one order of magnitude weaker than the corresponding nickel oxalate constant. Extrapolating the NiCO₃(aq) constant to zero ionic strength using the SIT approach, yielded $\log K_1^\circ = 4.2 \pm 0.3$ (95% confidence level and $\Delta\varepsilon = -0.26 \pm 0.04$).

Although the data did not allow complexation constants for NiHCO₃⁺ and Ni(CO₃)₂²⁻ to be determined directly, they did allow upper bound values to be estimated i.e., $\log K^\circ < 1.4$ and $\log K_2^\circ < 2$, respectively, which are in good agreement with the values at the lower end of the expected ranges given by Hummel and Curti.⁽⁵⁾

Errors are discussed at length in the text. The main sources of uncertainty in the measurements and data analysis arose from the uncertainty in the determinations of R_d° and R_d and the uncertainty in $\log A$ (see Eqs. 5 and 6), which was primarily due to the relatively poorly known nickel hydrolysis constants.

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APPENDIX

The appendix contains a description of the derivation of the side-reaction terms for Ni complexation with Tris buffer and for the hydrolysis of Ni.

Tris Buffer

Nickel forms complexes with Tris and thus a side reaction A with Tris has to be considered

$$A = 1 + \beta_1^{\text{Tris}}[\text{Tris}] + \beta_2^{\text{Tris}}[\text{Tris}]^2$$

The mass balance for Tris in a system with trace concentrations of nickel is

$$[\text{Tris}]_{\text{total}} = [\text{Tris}] + [\text{HTris}^+] = [\text{Tris}](1 + K^{\text{Tris}}[\text{H}^+])$$

$$[\text{Tris}] = [\text{Tris}]_{\text{total}} / (1 + K^{\text{Tris}}[\text{H}^+]) = [\text{Tris}]_{\text{total}} / (1 + 10^{\log K - \text{p}[\text{H}]})$$

The following equilibria are needed for calculating A :

These are all isocoulombic reactions with minimal dependence on temperature and ionic strength. In fact, the above values, recommended by Smith and Martell⁽²¹⁾ for 0.1 mol-L⁻¹ I.S., are within their uncertainty ranges also valid for 0.5 mol-L⁻¹ I.S. as an inspection of published data shows.⁽²²⁻²⁵⁾

$[\text{Tris}]_{\text{total}} \text{ (mol-L}^{-1}\text{)}$	$\text{p}[\text{H}]$	$\log A$
0.002	8.6 ± 0.1	0.24 ± 0.06
0.004	8.5 ± 0.1	0.41 ± 0.09

Nickel Hydrolysis

Nickel forms hydroxo complexes which may become important at pH values higher than 8. Thus a side-reaction A with hydroxide has to be considered

$$A = 1 + \beta_1^{\text{H}}[\text{H}^+]^{-1} + \beta_2^{\text{H}}[\text{H}^+]^{-2} + \beta_3^{\text{H}}[\text{H}^+]^{-3}$$

These equilibria at I.S. = 0 [Plyasunova *et al.*⁽²⁶⁾] are required to calculate A :

As discussed by Hummel and Curti,⁽⁵⁾ the second and third nickel hydrolysis constant are associated with large uncertainties, which, at present, cannot be

decreased due to a lack of suitable experimental data. The large uncertainty, especially of the second hydrolysis constant, propagates into the side-reaction A at $p[H]$ values above 8.

Using SIT with interaction constants taken from Plyasunova *et al.*,⁽²⁶⁾ the above equilibrium constants can be extrapolated to 0.1 and 0.5 mol-L⁻¹ NaClO₄ and used to calculate A and its associated uncertainties:

I.S. (mol-L ⁻¹)	$p[H]$	$\log A$	$\log A$ (hydrolysis + Tris)
0.5	7.5 ± 0.1	0.002 (+0.006, -0.001)	
0.5	8.5 ± 0.1	0.04 (+0.24, -0.03)	0.42 (+0.18, -0.10)
0.1	8.6 ± 0.1	0.07 (+0.37, -0.06)	0.28 (+0.30, -0.09)
0.5	9.6 ± 0.1	0.96 (+1.15, -0.74)	

Note that the pronounced asymmetry in the uncertainties in $\log A$ are caused by the large uncertainty in the second nickel hydrolysis constant. If the maximum value of its uncertainty range is used, a significant side-reaction value for $\log A$ results, even at $p[H]$ 8.6. If the minimum value is used, the $\log A$ term becomes small, even at $p[H]$ 9.6.

This large uncertainty in the hydrolysis constants adds a large and systematic uncertainty to measurements at $p[H]$ 9.6 and adds significant uncertainty to measurements at $p[H]$ 8.6. Only at $p[H]$ 7.5 does the uncertainty in the nickel hydrolysis constants have no influence on the experimental results.