Thermodynamic Modeling of Poorly Complexing Metals in Concentrated Electrolyte Solutions: An X-Ray Absorption and UV-Vis Spectroscopic Study of Ni(II) in the NiCl₂-MgCl₂-H₂O System

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Abstract

Knowledge of the structure and speciation of aqueous Ni(II)-chloride complexes is important for understanding Ni behavior in hydrometallurgical extraction. The effect of concentration on the first-shell structure of Ni(II) in aqueous NiCl₂ and NiCl₂-MgCl₂ solutions was investigated by Ni K edge X-ray absorption (XAS) and UV-Vis spectroscopy at ambient conditions. Both techniques show that no large structural change (e.g., transition from octahedral to tetrahedral-like configuration) occurs. Both methods confirm that the Ni(II) aqua ion (with six coordinated water molecules at $R_{\text{Ni-O}} = 2.07(2) \, \text{Å}$) is the dominant species over the whole NiCl₂ concentration range. However, XANES, EXAFS and UV-Vis data show subtle changes at high salinity ($> 2 \, \text{mol kg}^{-1} \, \text{NiCl}_2$), which are consistent with the formation of small amounts of the NiCl⁺ complex (up to $0.44(23) \, \text{Cl}$ at a Ni-Cl distance of $2.35(2) \, \text{Å}$ in $5.05 \, \text{mol kg}^{-1} \, \text{NiCl}_2$ solutions). At high Cl:Ni ratio in the NiCl₂-MgCl₂-H₂O solutions, small amounts of [NiCl₂]⁰ are also present. We developed a speciation-based mixed-solvent electrolyte (MSE) model to describe activity-composition relationships in NiCl₂-MgCl₂-H₂O solutions, and at the same time predict Ni(II) speciation that is consistent with our XAS and UV-Vis data and with existing literature data up to the solubility limit, resolving a long-standing uncertainty about the role of chloride complexing in this system.

Introduction

One of the most challenging tasks in the extractive metallurgy of nickel from ores or Ni-containing industrial wastes is its separation from Co and Cu [1,2]. Pospiech and Walkowiak [3] developed a separation method by taking advantage of the different tendency between Ni and
Co to form complexes with the chloride ion [4,5]. Further development of these ionic exchange methods to remove trace Cu/Co from Ni chloride aqueous solutions require a profound understanding of the formation of Ni(II)-chloride complexes in NiCl₂ aqueous solution.

A number of studies investigated Ni(II) aqueous solutions in the presence of excess Cl⁻ ions (Cl⁻/Ni²⁺ >> 2) under a wide range of conditions using different techniques; a summary is given in Table 1. Most of these investigations [5–12] agree that the octahedral NiCl⁺ and [NiCl₂]₀ species are formed at ambient temperature. Other divalent transition metals such Cu(II) [13–15], Co(II) [4] and Zn(II) [16] form anionic tetrahedral-like MCl₄⁻—complexes in the presence of a large excess of HCl or LiCl at room-temperature. In contrast, the anionic [NiCl₃(H₂O)]⁻ complex with tetrahedral-like configuration appears to be the highest order Ni(II) chloro-complex in aqueous solutions, and was observed only at elevated temperature [5].

The role and extent of chloride complexing in stoichiometric concentrated Ni(II) chloride solutions (Cl⁻/Ni = 2) remains controversial [17–26]. There is broad agreement that the 6-fold-water-coordinated Ni(II) ion is the dominant complex in NiCl₂ solutions up to high concentrations (4 mol L⁻¹), a result supported by extended X-ray absorption fine structure (EXAFS) measurements [19,20,23], neutron diffraction measurements [22,24], and first principle molecular dynamics simulations [26]. However, some studies emphasize the existence of small but significant amounts of inner-sphere complexes in concentrated NiCl₂ solutions. For example, on the basis of X-ray diffraction (XRD) studies, Magini [21] suggested the existence of about 8% NiCl⁺ complex in a 3.12 mol kg⁻¹ NiCl₂ solution, and Waizumi et al. [25] reported 0.4 Cl⁻ in the first coordination shell of Ni(II) at the solubility limit (5.06 mol kg⁻¹ NiCl₂). A recent Ni L₂,3- edge X-ray absorption near edge structure (XANES) study showed less than ~10% Cl⁻ in the first coordination shell in a 1.5 mol L⁻¹ NiCl₂ solution [17]. However, the data show evidence for a distortion of the complex from octahedral symmetry, which was interpreted to reflect the presence of solvent-shared ion pairs.

### Table 1. Previous studies on aqueous Ni(II) halide complexes in aqueous solutions.

| Method                     | T, P and salinity range* | Cl⁻/Ni²⁺ ratio (Y) range | Species identifieda | Ref.   |
|----------------------------|--------------------------|--------------------------|---------------------|--------|
| X-ray absorption spectroscopy | 25–434°C, 400–600 bar, 0 m < Cltot < 7.68 m, Ntot = 0.2 m | 0.28 ≤ Y ≤ 42 | Octa-[Ni(H₂O)₆]²⁺, Octa-[Ni(H₂O)₅Cl]⁺, Octa-[NiCl₂(H₂O)₄]₀, Td-[NiCl₂(H₂O)₂]₀, Td-[NiCl₃(H₂O)]⁻ | [5]    |
| UV-Vis spectrophotometry    | 26–250°C, 0.1 kbar, Cltot ≤ 3 m, 0.05 ≤ Ntot ≤ 0.1 m | 20 ≤ Y ≤ 54 | Ni²⁺, NiCl⁺, [NiCl₂]₀, [NiCl₃]⁻ | [10]   |
| EXAFS                      | 25°C, P_sat. 2 M ≤ Cltot ≤ 10 M, Ntot = 2 M | 2 ≤ Y ≤ 5 | Octa-[Ni(H₂O)₆]²⁺, Octa-[NiCl₂(H₂O)₄]₀ | [9]    |
| X-ray diffraction          | 25°C, P_sat. 4 M ≤ Cltot ≤ 6 M, Ntot = 2 M | 2 ≤ Y ≤ 5 | Octa-[Ni(H₂O)₆]²⁺, Octa-[NiCl₂(H₂O)₄]₀, Octa-[NiCl₃(H₂O)₂]₀ | [11]   |
| UV-Vis spectrophotometry    | 25–320°C, P_sat. 0 m ≤ Cltot ≤ 11 m | Y > 10 | Octa-[Ni(H₂O)₆]²⁺, Octa-[NiCl₂(H₂O)₄]₀, Octa-[NiCl₃(H₂O)₂]₀ | [6]    |
| UV-Vis spectrophotometry    | 25°C, P_sat. 0.12 M ≤ Cltot ≤ 13.7 M, Ntot = 0.06 M | 1 ≤ Y ≤ 228 | [Ni(H₂O)₆]²⁺, [NiCl₂(H₂O)₄]₀, [NiCl₃(H₂O)₂]₀ | [12]   |
| Polarography and UV-Vis spectrophotometry | 25°C, P_sat. 1 M ≤ Cltot ≤ 13.9 M, Ntot = 0.03 M | 33 ≤ Y ≤ 463 | Ni(H₂O)₂Cl⁺ | [8]    |
| UV-Vis spectrophotometry    | 25°C, P_sat. 0.12 M ≤ Cltot ≤ 12.5 M, Ntot = 0.06 M | 1 ≤ Y ≤ 208 | [NiCl⁺]⁺, [NiCl₂]₀ | [7]    |

* m is molality and M is molarity.

a Complex geometries: Octa: octahedral; Td: tetrahedral.

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Some XRD studies were also carried out on NiBr₂ solutions to help resolve the ambiguities regarding the structure of NiCl₂ solutions [27,28], as the Ni-Br distance is longer than the Ni-Cl distance, and Br⁻ is a stronger X-ray scatter than Cl⁻. The results indicated the formation of strong inner-sphere complexes, with 0.29(3) Br coordinated to Ni(II) in a 2 mol·L⁻¹ solution; this suggests that chloro-complexes exist in concentrated solutions of NiCl₂ [27].

In this study we used a combination of X-ray absorption spectroscopy (XAS) and UV-Vis spectrophotometry to provide a molecular-level understanding of the effect of concentration on the speciation and structure of Ni(II)-chloride complexes in NiCl₂ and NiCl₂-MgCl₂ solutions at concentrations ranging from dilute to the solubility limit at ambient temperature. A speciation-based mixed-solvent electrolyte (MSE) thermodynamic model is used to provide a speciation model that is consistent with most existing experimental and theoretical data on NiCl₂-MgCl₂ solutions. The results of our study can be used to predict Ni(II) behavior in high concentration brines for hydrometallurgical processing.

**Experimental**

**Sample Preparation**

NiCl₂·6H₂O(s), NiSO₄·6H₂O(s) and MgCl₂·6H₂O(s) (99.8% purity) from Sinoreagent, China, were used as XAS standards and for solution preparation. All Ni(II) solutions were prepared gravimetrically and made freshly before the experiments. The sample solutions were prepared by dissolving NiCl₂·6H₂O(s) in doubly deionized water. For the UV-Vis spectroscopic measurement, two series of solutions were prepared by gravimetrically mixing (i) deionized water with a 4.65 mol·kg⁻¹ NiCl₂ stock solution (NiCl₂-H₂O system); and (ii) a 5.72 mol·kg⁻¹ MgCl₂ + 0.05 mol·kg⁻¹ NiCl₂ stock solution with a 0.05 mol·kg⁻¹ NiCl₂ stock solution (NiCl₂-MgCl₂-H₂O system). The chloride concentrations in the stock solutions were checked using the Ag chloride gravimetric method [76]. To suppress the hydrolysis of Ni(II), ~0.001 mol·kg⁻¹ hydrochloric acid (HCl(l), Sinoreagent, China, AR) was added to all the Ni-Cl and Ni-Mg-Cl solutions; spectrographic measurements of acidified and non-acidified solutions were identical. The compositions of both systems were listed in the S1 and S2 Tables. In order to establish a reference free of Ni(II)-chloride complexes at different ionic strengths, two Ni(II) perchlorate solutions (0.05 and 4.46 mol·kg⁻¹) were prepared by mixing hexahydrate Ni(ClO₄)₂·6H₂O (Sinoreagent, China, AR) with deionized water.

**XAS measurement and analysis**

The coordination environment of Ni(II) in solutions containing 1, 2, 4 and 5.05 mol·kg⁻¹ NiCl₂ was characterized using XAS data obtained at the XAS beamline of the 1.5–2.2 GeV Beijing Synchrotron Radiation Facility (BSRF). This beamline has a Si(111) double-crystal monochromator with an energy resolution of 1.25 eV at the Ni K-edge (8333.0 eV). Data on solutions and solid samples were acquired in transmission mode. The solutions were placed in a cell that consisted of a square-shaped Kapton spacer having a thickness from 125 to 605 μm; the higher concentration of solution, the shorter the path length that was used. The liquid samples were injected into the cell with a micro-syringe. For the solid samples, a layer of powder was placed on a flat Kapton substrate.

EXAFS data were analyzed using the HORAE package [29], with amplitude and phase shifts calculated using FEFF6 [30]. The fits were performed in R-space using $k^3$-weighting and a Hanning window. The fit parameters include the scale factor ($S_0^2$), the energy shift ($\Delta E_0$), the number of oxygen (water molecule, $N_O$) and chlorine (N_Cl) in the first coordination shell of Ni (II), the bond distances $R_O$ and $R_{Cl}$, and the Debye-Waller factors for the O and Cl atoms.
A value $S^2_0 = 0.83(7)$ was obtained from fitting the EXAFS spectra of the two solid standards; this value is in excellent agreement with previous studies (5,31), and was used for fitting all the samples.

UV-Vis measurements

Spectrophotometric measurements were carried out using a Shimadzu (Japan) UV-2550 double-beam spectrophotometer at room temperature. Sample solutions of the NiCl$_2$-H$_2$O and NiCl$_2$-MgCl$_2$-H$_2$O systems were placed in 1 and 10 mm rectangular quartz cells, respectively. Dual-beam mode was used with the reference cell containing deionized water. The data were baseline-corrected using measurements of two water-filled cuvettes. Spectra were recorded at a 1.0 nm interval over the range 300–850 nm, and the absorbance range was typically between 0 and 3 absorbance units. The experimental error was estimated by multiple scans (5 times) of two solutions with 0.1 and 4 mol·kg$^{-1}$ NiCl$_2$. The difference between these repeat spectra was generally less than 0.002–0.005 absorbance units.

The raw UV-Vis and XAS data are provided in the supporting information (S1–S10 Tables).

Results and Discussion

XAS investigation

**XANES analysis.** Fig 1 shows the XANES spectra (Raw spectral data was collected in S1–S4 Tables) for the NiSO$_4$·6H$_2$O(s) and NiCl$_2$·6H$_2$O(s) reference compounds, which contain octahedral [Ni(H$_2$O)$_6$]$^{2+}$ and [NiCl$_2$(H$_2$O)$_4$]$^{2+}$ moieties [32], respectively. The main spectral differences between the two spectra are: (i) presence of a shoulder at ~8340 eV attributed to the 1$s$ to 4$p$ transition [31] in NiCl$_2$·6H$_2$O(s) (feature A); (ii) a lowering of the intensity of the white line (feature B) and shift of its position by ~ -1.2 eV in NiCl$_2$·6H$_2$O(s) relative to NiSO$_4$·6H$_2$O(s); as well as (iii) reduced intensity of the oscillation in the 8360 to 8420 eV region in NiCl$_2$·6H$_2$O(s) (features C and D in Fig 1).

The Ni K-edge XANES spectra (Raw spectral data was collected in S5–S8 Tables) of solutions with various NiCl$_2$ concentrations at room temperature are plotted in Fig 2 with the XANES spectra calculated by Tian et al. [5] using ab initio XANES simulations for the NiO$_6$ and NiO$_5$Cl clusters. The spectra of the four solutions are similar and show features that are characteristic for octahedral transition metal complexes [5,31,34]. A slight decrease (9.7%) of the white line intensity and a subtle energy shift (0.4 eV) of the white line to lower energy (feature B in Fig 2) are observed as the NiCl$_2$ concentration increases from 1 to 5.05 mol·kg$^{-1}$. Therefore, the changes affecting the white line region of the solution spectra are analogous with the difference of XANES spectra of the two solid reference compounds and are consistent with some Cl entering the first coordination sphere of Ni(II) upon increasing salt concentration. Similar spectral changes are confirmed by the XANES simulations of Ni clusters (Fig 2). In addition, the XANES calculations show that the differences in features C and D observed for the solid standards are due to second-shell contributions. The only significant difference between the experimental and simulated spectra lies in the pre-edge peak intensity (feature around 8332 eV), which is associated with a 1$s$→3$d$ photoelectron transition and is sensitive to the local geometry of the Ni site [5,35,36]. There is no change observed in the experimental spectra (inset in Fig 2), whereas the XANES simulations predict an increase in intensity of this pre-edge upon replacement of a water molecule by a chloride ion in the Ni(II) coordination sphere. Tian et al. [5] similarly failed to confirm this feature experimentally. Overall, the XANES data are consistent with octahedral Ni(II) aqua complexes being present over the whole NiCl$_2$ concentration range, with minor amounts of chloride complexing taking place at high salt concentration.
EXAFS analysis. The Ni K-edge EXAFS \( k \)- and R-space spectra for the two solid standards and the four solutions are shown in Fig 3. The small amount of replacement of water molecules by chloride ions upon increasing NiCl\(_2\) concentration is clearly shown by the phase shift in the imaginary part of the EXAFS Fourier transform (arrow in Fig 3c). In the final analysis, Ni(II) coordination was constrained to be 6, consistent with the result of octahedral configuration obtained from XANES data; the fitting results are listed in Table 2. For all solutions, the refined Ni-O bond distances are 2.07(2) Å, which is consistent with earlier studies [31,37]. For the 1 and 2 mol·kg\(^{-1}\) NiCl\(_2\) solutions, the fully hydrated ([Ni(H\(_2\)O)\(_6\)]\(^{2+}\)) model reproduced well the experimental \( k \)-space and R-space EXAFS spectra. The effect of replacing one of the water molecules with a chloride ligand on the fit quality (reduced chi-square, \( \chi^2 \) [38]) of the 2 mol·kg\(^{-1}\) NiCl\(_2\) solution is illustrated in Fig 4a. The absolute minimum of \( \chi^2 \) is located at 0 chloride, and the residuals increase slowly with addition of Cl, resulting in a large uncertainty at the 90% confidence level. In contrast, \( \chi^2 \) shows a minimum at 0.44 Cl for the 5.05 mol·kg\(^{-1}\) NiCl\(_2\) corresponding to the “deepest” depression with an uncertainty of +/- 0.23 Cl (Fig 4b). As expected, the Cl ion resides at a longer distance than O (\( R_{\text{Ni-Cl}} = 2.35(2) \) Å vs. \( R_{\text{Ni-O}} = 2.07(2) \) Å) due to the larger hard-sphere radius. These results are close to those obtained using XRD by Waizumi et al. [25]; for a 5.06 mol·kg\(^{-1}\) NiCl\(_2\) solution, these authors reported \( N_{\text{Ni-O}} = 5.6 \pm 0.2 \) and \( R_{\text{Ni-O}} = 2.06(2) \) Å; and \( N_{\text{Ni-Cl}} = 0.4 \pm 0.2 \) and \( R_{\text{Ni-Cl}} = 2.37(2) \) Å.
UV-Vis spectroscopy investigation

**Qualitative analysis of UV-Vis spectra.** The baseline-corrected room-temperature spectra (Raw spectral data was collected in S9 and S10 Tables) for both sets of solutions, one with systematically increasing NiCl₂ concentration and the other containing constant Ni(II) (0.05 mol·kg⁻¹) but systematically increasing the MgCl₂ concentration, are presented in Fig 5a and 5b, respectively. The spectra show two characteristic absorption features at 350–500 and 600–800 nm. With increasing NiCl₂ concentration, the absorbance increases and the spectra display a systematic red-shift: the band in the range of 350–500 nm shifts from ~393 to ~405 nm (arrow A in Fig 5a), and the bands in the 600–800 nm range (arrows B and C in Fig 5a) shifts from ~720 to ~737 nm and ~656 to ~670 nm, respectively. These features become more pronounced for the Ni-Mg-Cl system at higher MgCl₂ concentration, with the ~393 nm band shifting up to ~415 nm (inset in Fig 5b) and the ~720 band shifting to ~770 nm. The shoulder at ~654 nm becomes weaker (arrow B in Fig 5b, almost vanishing) at the higher chloride concentration. To check the effect of ionic strength on the UV-Vis spectra, solutions of 0.05 and 4.46 mol·kg⁻¹ Ni(ClO₄)₂ were measured (inset in Fig 5a). No shift of the peak position was observed, and the molar absorbance coefficients remained nearly constant. Deviations from the Beer-Lambert law at high salinity [75,40] can be due to the influence of the dielectric constant of the medium on the absorption.
Fig 3. Ni K-edge $k^2$-weighted EXAFS (a), and the amplitude (b) and imaginary part (c) of their Fourier transforms of the two solid compounds and four NiCl$_2$ solutions. The dot line is the position of Ni-O and Ni-Cl peaks.

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of light by a particular complex [41], or to changes in the electronic structure of the complex induced by changes in the structure of the solvent and in the outer coordination shells of the complex. These effects can be difficult to quantify. The Ni(II) perchlorate data in Fig 5a, however, clearly indicate that the structure of the Ni(II) aqua ion is not sensitive to changes in solvent structure as the salt concentration changes from 0.05 to 4.5 mol·kg⁻¹; this stable structure was also confirmed by the neutron diffraction study of Newsome et al. [42]. Consequently, the Beer-Lambert law appears to be obeyed up to high salinity in this system.

Ligand field theory can be used to describe the electronic absorption spectra of first row transition metal complexes. For the [Ni(H₂O)₆]²⁺ species at room temperature, the bands at

Table 2. Results of Ni EXAFS analysis of the Ni(II) first shell structure under ambient conditions.

| Composition of system | \(\Delta E_\text{O} (\text{eV})\) | Ni-O interaction | Ni-Cl interaction | k-range | R-range | R-factor | Ref. |
|-----------------------|-----------------------------|-------------------|-------------------|----------|---------|----------|------|
| NiSO₄·6H₂O™          | 2.68(1.00)                  | 2.0                | 2.02(2)           | 2.0      | 2.0    | 0.014    | This work |
| 2.00                  | –4.15(0.65)                 | 6.0                | 2.07(09)          | 7.1(8)   | 2.0    | 0.021    | This work |
| 4.00                  | –4.90(0.98)                 | 5.8                | 2.06(1)           | 4.8(7)   | 2.38(1) | 8.4(27)  | This work |
| 5.05                  | –3.46(0.93)                 | 5.6                | 2.08(1)           | 2.4(5)   | 2.35(2) | 7.3(21)  | This work |
| NiCl₂·6H₂O™          | –1.19(1.53)                 | 4.0                | 2.07(2)           | 9.2(2)   | 2.36(4) | 13.4(42) | This work |
| 3.12™                | -                           | 5.92               | 2.07(1)           | 0.08     | 2.44(1) | -         | [21] |
| 5.06™                | -                           | 5.6(2)             | 2.06(2)           | 0.4(2)   | 2.37(2) | -         | [25] |

The results for 3.12 and 5.06 mol·kg⁻¹ NiCl₂ solutions using X-ray diffraction [21,25] are also listed. The concentrations are expressed in molality (mol·kg⁻¹). Uncertainty limits are given in parentheses.

a Value fixed (not optimized) during refinements.

b Sum of number of O and Cl fixed to be equal to 6.

c Solid standard.

d Concentration in molarity (mol·L⁻¹) in references [21,25], converted to molality (mol·kg⁻¹).

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Fig 4. The distribution maps of analysis error of XAS spectra for 2 mol·kg⁻¹ (a) and 5.05 mol·kg⁻¹ (b) NiCl₂ solution as a function of number of Cl ligands. The gray area represents 90% confidence level.

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800–550 nm and ~500–350 nm are assigned to the $^{2}A_{2g} \rightarrow ^{3}T_{1g}$ and $^{3}A_{2g} \rightarrow ^{3}T_{1g}(P)$ transitions of the octahedral structure, respectively [10]. The spin-orbit coupling that mixes the $^{3}T_{1g}(F)$ and $^{1}E_{g}$ states results in the $^{3}A_{2g}$ to $^{3}T_{1g}$ transition band in the 800–550 nm range being split with a main peak at ~720 nm and a shoulder at ~656 nm [43], which is consistent with a splitting of approximately 18 eV (~68 nm) observed in the Ni L$_{2,3}$-edge XANES spectra [17].

The peak shift observed as a function of NiCl$_2$ and MgCl$_2$ concentrations reflects the progressive replacement of a H$_2$O ligand by a chloride ion around Ni(II) within the first coordination shell, because the $d$-$d$ splitting caused by the chloride ion is at lower energy than that produced by water [10]. Since the spectral changes observed via UV-Vis are mainly related to inner-sphere complexing, we performed a quantitative treatment of the UV-Vis dataset to retrieve species concentrations and thermodynamic properties of the Ni(II)-chloride complexes.

**Speciation model and activity coefficients calculations for quantitative analysis.** The quantitative treatment was based on the Beer-Lambert law, following the approach developed by Brugger et al. [13] and implemented in the BeerOz program [39]. The analysis deconvolutes the measured matrix of absorbances into spectra for individual absorbing species (molar absorptivity coefficients) present in solutions, and a matrix of concentrations of these species in each solution. The species concentrations are constrained by a thermodynamic model (mass action and mass balance equations) so that the analysis refines formation constants (log$_{10}$K) of aqueous Ni(II)-chloride complexes rather than actual species concentrations. The spectral dataset was restricted to the wavelengths over which peaks are present (350–550 nm and 580–850 nm). Prior to the analysis of the spectra, the usual molarity scale-based Beer’s law was converted to a molality absorbance by dividing a transfer factor, $f$, defined as a function of density of electrolyte [13,39], which was calculated in present study by the method as described in Zhang et al. [14].

Based on the analysis of XAS data above, two main Ni(II) species are present in NiCl$_2$ solutions: the fully hydrated aqua ion and the monochloro complex. Principal component analysis (PCA) [44] confirms that two species are required to explain the UV-Vis data for the pure NiCl$_2$ solutions within experimental error (Fig 6). In contrast, three species are required to explain the NiCl$_2$-MgCl$_2$-H$_2$O system dataset (Fig 6), suggesting that [NiCl$_2$]$^+$ may be present in
the solutions with the highest ionic strength. This is also consistent with the XAS results of Tian et al. [5]; consequently, the analysis was conducted using the Ni²⁺, NiCl⁺ and [NiCl₂]₀ species. The minor species H⁺ and [HCl]₀ were also included in the speciation model, with the formation constant of the neutral ion pair, [HCl]₀, taken from the result of Sverjensky et al. [45] (Table 3).

In order to calculate the distribution of species in concentrated NiCl₂ solutions, activity coefficients need to be available for all the species in the model. The “b-dot” equation developed by Helgeson and Kirkham [50] is a popular method for calculating activity coefficients, used for example by Liu et al. [10] in their UV-Vis study of Ni(II)-chloride complexes in chloride brines up to high temperature. This model is well suited for relatively dilute solutions (ionic strength ≤ 2 molal), though some studies extended the approach to higher salinities (10,1–15,40). The ion-interaction Pitzer model [51] is a popular semi-empirical approach used to describe the thermodynamics of concentrated electrolyte solutions. Originally, Pitzer’s model assumed full dissociation of electrolytes, but several authors [52–54] have introduced speciation-based extensions to the theory. In the present study, we implemented the speciation-based mixed-solvent electrolyte (MSE) model [55–57]. This comprehensive and self-consistent model has the following advantages: (i) it is a speciation-based model, taking complexation reactions explicitly into account; (ii) it provides a bridge to the Helgeson-Kirkham-Flowers

![Fig 6. Principal component analysis results for NiCl₂-H₂O and Ni-MgCl₂-H₂O system in 350–550 nm and 580–850 nm absorbance bands, respectively. The circle is calculated by $100 \times \sqrt{\frac{(x_{\text{calc}} - x_{\text{meas}})^2}{x_{\text{meas}}^2}}$, where $x_{\text{calc}}$ and $x_{\text{meas}}$ are the model and observed value, respectively. The gray area stands for the level of experimental error of 0.2%-0.5%.](doi:10.1371/journal.pone.0119805.g006)
(HKF) approach \cite{50,58}, so that predictions can be expanded over a wide range of pressures and temperatures; (iii) it covers the full concentration range from highly dilute to the solubility limit. The standard-state properties calculated from the model of Helgeson and Kirkham \cite{59} are based on the molality concentration scale and on the infinite-dilution reference state and result in large excess properties in concentrated solutions, whereas the activity coefficients in the MSE framework are based on the mole fraction scale and are symmetrically normalized (i.e., unit activity coefficients for \(x_i = 0\) and \(x_i = 1\)).

In the MSE model, the activity coefficient of any aqueous species \(k\) is expressed as a sum of three terms,

\[
\ln \gamma_k = \ln \gamma_k^{LR} + \ln \gamma_k^{MR} + \ln \gamma_k^{SR}
\]

where LR represents the long-range electrostatic interactions between ions at low concentrations, calculated using the Pitzer-Debye-Hückel expression \cite{55,60}; SR is the short-range contribution resulting from intermolecular interactions, calculated by the UNIQUAC equation \cite{61}. As ions are the dominant species in this study, the short-range term can be neglected \cite{62}. MR is an additional symmetrical second virial coefficient-type (middle-range) term, which represents primarily ionic interactions (i.e., ion-ion and ion-molecule) that are not

| Phase | Reaction | \(\log_{10}K/\log_{10}K_{sp}\) | MSE | Pitzer | HSC$\|$ | Ref. |
|-------|----------|------------------|-----|--------|---------|------|
| Solid | \(\text{MgCl}_2 \cdot 6\text{H}_2\text{O} = \text{Mg}^{2+} + 2\text{Cl}^- + 6\text{H}_2\text{O}\) | 4.4 (+0.2/−0.3) | 4.5 (+0.1/−0.2) | - | This work |
|       | - | - | 4.307*2 | - | [46] |
|       | - | - | 4.455 | - | [47] |
|       | \(\text{NiCl}_2 \cdot 6\text{H}_2\text{O} = \text{Ni}^{2+} + 2\text{Cl}^- + 6\text{H}_2\text{O}\) | 3.2 (+0.1/−0.2) | 3.1 (+0.2/−0.1) | - | This work |
|       | 3.133 | - | 3.180 | - | [48] |
|       | \(\text{NiCl}_2 \cdot 4\text{H}_2\text{O} = \text{Ni}^{2+} + 2\text{Cl}^- + 4\text{H}_2\text{O}\) | 3.9 (+0.1/−0.1) | 3.2 (+0.3/−0.1) | - | This work |
|       | 3.985 | - | 3.713 | - | [48] |
| Aqueous | \(\text{H}^+ + \text{Cl}^- = \text{HCl(aq)}\) | -0.711 | -0.63 | -0.43 | -0.32 | [45] |
|       | \(\text{Ni}^{2+} + \text{Cl}^- = \text{NiCl}^+\) | 0.09 (+0.05/−0.03) | - | - | - | [10] |
|       | - | -0.5 | -1.31 (+0.07/−0.07) | -2.0 (+0.2/−0.2) | -0.37 | [12] |
|       | \(\text{Ni}^{2+} + 2\text{Cl}^- = \text{[NiCl}_2^0\) | -6.6 (+0.5/−0.4) | -0.95 | -4.1 (+0.4/−0.4) | -4.5 (+0.5/−0.5) | This work |

The association constant of \([\text{HCl}]^0\) aqueous species used in the calculation is also listed. Uncertainty limits are given in parentheses.

* The solubility products were converted from mole fraction-scale in the literatures to molality-scale.

$\$ Value was calculated by Pitzer–Simonson–Clegg (PSC) model \cite{46}.

$\$ Values were calculated by HSC software (H = enthalpy, S = entropy, C = heat capacity) in literature \cite{48}.

$\$ The activity coefficient model assumed \(\gamma_{\text{ion}} = \gamma_{\pm,\text{ion}}\).

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accounted for by the LR term. The MR term is given by [55]

$$\ln\beta_{ij}^{MR} = \sum_i \frac{x_i \beta_{ij}(I_x)}{n_i} \sum_j x_j \frac{\partial \beta_{ij}(I_x)}{\partial n_j} + 2 \sum_i x_i \beta_{ii}(I_x)$$

(2)

where \(i\) and \(j\) represent aqueous species (ions or molecules), \(x\) is the mole fraction, \(n\) is the mole number and \(\beta_{ij}(I_x)\) are binary interaction parameters, which are assumed to be symmetric, i.e., \(\beta_{ij}(I_x) = \beta_{ji}(I_x)\), and \(\beta_{ii}(I_x) = 0\), and dependent on the ionic strength, with

$$\beta_{ij}(I_x) = b_{ij} + c_{ij}\exp(-\sqrt{I_x} + a_i)$$

(3)

where

$$b_{ij} = b_{0,ij} + b_{ij} T + \frac{b_{ij} T}{T} + b_{ij} T^2 + b_{ij}\ln T$$

(4)

$$c_{ij} = c_{0,ij} + c_{ij} T + \frac{c_{ij} T}{T} + c_{ij} T^2 + c_{ij}\ln T$$

(5)

For the final fit, the MSE MR parameters \(b_{0,ij}\) and \(c_{0,ij}\) (Table 4), the formation constants \(\log_{10}K(\text{NiCl}^+)\) and \(\log_{10}K(\text{NiCl}_2)^0\), and the molar absorptivity coefficients for NiCl\(^+\) and \([\text{NiCl}_2]^0\) were optimized by using non-linear least squares [39] to minimize the residual function \(\chi^2\),

$$\chi^2 = w_1 \sum_i \sum_j (\lambda_{\text{UV-Vis}} - \lambda_{\text{calc}})^2 + w_2 \sum_i \sum_j (\lambda_{\text{Act}} - \lambda_{\text{calc}})^2 + w_3 \sum_i (K_{\text{exp}} - K_{\text{calc}})^2$$

(6)

The experimental data consisted of the UV-Vis spectra data for 16 solutions with NiCl\(_2\) concentrations ranging from 0.1 to 4.53 mol kg\(^{-1}\), and for 23 solutions with a constant Ni(II) concentration (~0.05 mol kg\(^{-1}\)) with MgCl\(_2\) concentrations ranging from 0 to 5.72 mol kg\(^{-1}\) \((\lambda_{\text{UV-Vis}})\), together with the experimental mean activity coefficient data of NiCl\(_2\) solutions at room temperature \((\chi^2_{\text{Mean Activity}})\) [63], and the solubility data in the NiCl\(_2\)-MgCl\(_2\)-H\(_2\)O ternary system \((\chi^2_{\text{Solubility}})\) [64]. In Eq (6), \(V\) is the total number of wavelengths at which measurements were made, and \(U\) is the number of solutions. \(A_{\text{exp}}^v\) and \(A_{\text{calc}}^v\) are the measured and calculated absorbance at wavelength \(v\) for solution \(u\). \(w_1, w_2\) and \(w_3\) are weighting factors and are set as 0.5, 1.0 and 1.0, respectively, in the present study. \(\gamma_{\text{exp}}^i, j, k\) and \(\gamma_{\text{calc}}^i, j, k\) are the experimental and calculated mean activity coefficient of solution \(i\); the experimental activity coefficients show a deviation from ideal behavior at high concentration due to the formation of Ni(II)-chloride complexes [63], and can be described as a combination of an ideal stoichiometric activity coefficient, and

**Table 4. MSE middle-range ion interaction parameters in this study.**

| Species \(i\)     | Species \(j\)     | \(b_{0,ij}\)    | \(c_{0,ij}\)    |
|------------------|------------------|----------------|----------------|
| Ni\(^{2+}\)      | Cl\(^-\)         | -54.9768       | 69.0819        |
| NiCl\(^+\)       | Cl\(^-\)         | -28.5398       | -             |
| Ni\(^{2+}\)      | Mg\(^{2+}\)      | -33.8995       | 50.9434        |
| NiCl\(^+\)       | Mg\(^{2+}\)      | -6.8626        | -             |
| [NiCl\(_2\)]\(^0\) | Mg\(^{2+}\)      | -0.0984        | -             |
| Mg\(^{2+}\)      | Cl\(^-\)         | -82.4238       | 112.1769       |

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the effect of complexation. Aparicio and Elizalde [65] calculated the experimental mean stoichiometric activity coefficient for an electrolyte containing a significant amount of complexes (ZnCl₂ solutions), and their approach is used here:

\[ \gamma_{\text{calc}} = \left( \frac{m_+}{u_+} \right)^{1/2} \left( \frac{m_-}{u_-} \right)^{1/2} \]

where \( u_+ \) and \( u_- \) are the number of Ni\(^{2+}\) and Cl ions, whose activity coefficients are \( \gamma_+ \) and \( \gamma_- \) calculated by the MSE model, and \( m_+ \) and \( m_- \) are their respective equilibrium concentrations in molality; \( v = u_+ + u_- \); and \( m \) is the conventional total NiCl₂ concentration (in molal). The Mg\(^{2+}\)-Cl mixing parameters were refined from the mean stoichiometric activity and water activity data [66] (Table 5).

\[ K_{sp} = \left( a_{M^{2+}} a_{X^-} \right)^{a_+} \left( \gamma_{M^{2+}} m_{M^{2+}} \right)^{a_+} \left( \gamma_{X^-} m_{X^-} \right)^{-a_-} \]

\( K_{sp} \) is calculated by

where \( a \) is the activity, \( \gamma \) is the activity coefficient calculated by Eq (1), and \( m \) is the concentration in molality. In this work, the solid phases MgCl₂-6H₂O and NiCl₂-nH₂O \((n = 4, 6)\) in the ternary system NiCl₂-MgCl₂-H₂O at room temperature are involved for reproducing experimental solubility data [64].

Due to the low concentration of [NiCl₂]\(^0\) present in the solution, correlations among concentration and molar absorptivity coefficients [39,40], and the large number of parameters involved in the regression, a step-wise approach was required to obtain a self-consistent solution for the NiCl₂-MgCl₂-H₂O system: 1) refine the molar absorbance of the NiCl\(^+\) species, the formation constant of NiCl\(^+\), and the mixing parameters for the Ni\(^{2+}\)-Cl and NiCl\(^+\)-Cl interaction based on the NiCl₂-H₂O system spectrophotometric data. 2) The molar absorbance and formation constant of [NiCl₂]\(^0\) species were fixed using the results of step 1). 3) We then refined the molar absorbance and formation constant for [NiCl₂]\(^0\) species, as well as the \( b_{0, \text{NiCl}_2, \text{Mg}^{2+}} \) mixing parameter based on the NiCl₂-MgCl₂-H₂O system spectrophotometric data.

**Results of the quantitative analysis of UV-Vis data.** The analysis provides a good agreement between experimental and calculated spectra; for the 350–550 nm range, the largest differences (in absorbance unit) were 0.05 (NiCl₂-H₂O system) and 0.07 (NiCl₂-MgCl₂-H₂O system); and for the 580–850 nm range, 0.012 and 0.006, respectively. The regressed MSE ion interaction parameters are presented in Table 4, and the optimized formation constants of Ni (II)-chloride complexes and the solubility products of solids obtained from solid-liquid equilibrium data and spectral data are reported in Table 3 together with the comparison of \( \log_{10}K_{sp} / \log_{10}K \) values at 25°C from this work and the literature [7,10,12,46,47,48], respectively. The

| Systems                        | data type | Ref.  |
|-------------------------------|-----------|-------|
| MgCl₂-H₂O                     | \( a_{i_{\text{H}2O}} \), \( \gamma_{s} \) | [66]  |
| NiCl₂-H₂O                     | \( \gamma_{s} \) | [63]  |
| MgCl₂-NiCl₂-H₂O               | SLE**     | [64]  |

* Water activity data
** Solid liquid equilibrium data

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uncertainties of formation constants for NiCl\(^+\) and [NiCl\(_2\)]\(^0\) at the 90% confidence level are also listed; they are derived from residual maps as described in the literature [39]. The molar absorptivity spectra of individual Ni(II)-chloride complexes show a shift to lower energy (red-shift) with increasing substitution of chloride ions. We also conducted a fit in which we refined the molar absorptivity coefficients for the Ni(II) species; the refined molar absorptivity spectrum is close to the spectrum fixed from measurement of the Ni(ClO\(_4\))\(_2\) solution, indicating that the analysis method is reliable. There is a large increase in molar absorptivity from Ni\(^2+\) to NiCl\(^+\); the change in intensity between NiCl\(^+\) and [NiCl\(_2\)]\(^0\) was model-sensitive, which is attributed to the low concentration of this complex in the studied solutions. For the 580–850 nm region (Fig 7), the analysis only reveals a red-shift for the molar absorbance spectrum of [NiCl\(_2\)]\(^0\), but failed to provide a realistic molar absorptivity spectrum for this complex. The changes of the calculated spectra of each individual Ni(II) species are analogous with the results obtained for minor amounts of Ni(II) in NaCl solutions at elevated temperatures [10].

The formation constant of NiCl\(^+\) in this work is larger than that reported in the potentiometric study of Libus and Tialowska [49] and in the spectrophotometric studies of Bjerrum [7], Liu et al. [10] and Paatero and Hummelstedt [12], whereas that of the neutral [NiCl\(_2\)]\(^0\) complex is more negative than that reported by Liu et al. [10] (Table 3) but closer the values from Bjerrum [7] and Paatero and Hummelstedt [12]. The distributions of absorbing species in the NiCl\(_2\)-H\(_2\)O and NiCl\(_2\)-MgCl\(_2\)-H\(_2\)O solutions calculated with the new model show a larger percentage of the NiCl\(^+\) complex in the NiCl\(_2\)-MgCl\(_2\)-H\(_2\)O solutions (higher Cl/Ni ratio) compared to the NiCl\(_2\)-H\(_2\)O solutions, implying a stronger association in the former solutions (Fig 8a and 8c). In addition, the neutral complex [NiCl\(_2\)]\(^0\) can account up to ~38% Ni(II) in the MgCl\(_2\) solutions. For comparison, we calculated the distribution of Ni(II) species in NiCl\(_2\)-H\(_2\)O solutions using Liu et al. [10]'s model, in which the activities of the species are calculated using the “b-dot” equation (Fig 8b). The agreement is good at low NiCl\(_2\) concentrations (< 1 mol·kg\(^{-1}\) NiCl\(_2\)). However, the predictions diverge with increasing electrolyte concentration, with Liu et al. [10]'s model showing the neutral complex, [NiCl\(_2\)]\(^0\), playing an important role (up to ~30%) in pure NiCl\(_2\) solutions at high concentrations, while our model and UV-Vis data suggest that no significant [NiCl\(_2\)]\(^0\) is present (Fig 8a). This apparent contradiction is the result of
Fig 8. Distribution of Ni(II) species in NiCl$_2$-H$_2$O (a, b), and NiCl$_2$-MgCl$_2$-H$_2$O (c) solutions and average number of ligand in the first shell of Ni$^{2+}$ as a function of NiCl$_2$ solution concentration. In (a) and (c), the distributions of species are calculated with the formation constant and MSE parameters determined in this study (all lines); in (b), the distributions of species was calculated for NiCl$_2$ solutions using the model and parameters from literature [10]; In (a), the calculated average numbers of ligands in the first shell of Ni$^{2+}$ are compared with the number of ligands extracted by EXAFS (Cl ligand, empty circles with error bar; O ligand,
the poor description of activity-composition relationships in highly saline solutions in the HKF model. The experimental mean activity coefficient of NiCl₂ solutions is compared to the values calculated using the MSE parameters and the model of Liu et al. [10] in Fig 9. The mean activity coefficient calculated in this work agrees well with the experimental data [63], while Liu et al. [10]'s model only reproduces the data at low NiCl₂ concentrations (≤ 0.5 mol·kg⁻¹), with increasingly significant deviations occurring with increasing salt concentrations.

The solubility products from this work are mostly in agreement with the literature values [46–48]. The solubility isotherms calculated using the parameters from Tables 3 and 4 are displayed in Fig 10, and are consistent with the experimental values [64]. If ion association is neglected for the NiCl₂-MgCl₂-H₂O ternary system, the results are unsatisfactory as shown in the dashed line of Fig 10 using the Pitzer completely dissociated model (see [47,67] for details of calculation.)
procedure), although the solubility products of the solid phases are comparable in both models as tabulated in Table 3. Furthermore, the predicted water activity in the NiCl₂-H₂O system in this work is in excellent agreement with the literature value [63] (Fig 11). In the absence of Ni (II)-chloride complexing, the calculated water activity for pure NiCl₂ solutions deviated from the experimental values at high salt concentration (dotted line in Fig 11). The deviation occurs at higher concentration for NiCl₂ solutions than that for ZnCl₂ solutions (~2.5 mol kg⁻¹ vs ~0.05 mol kg⁻¹, respectively [65]); this is consistent with the smaller extent of chloro complex formation in Ni(II) chloride solution relative to Zn(II) chloride solutions [68–70]. We also attempted to fit the experimental mean activity coefficient of NiCl₂ solutions without considering the NiCl⁺ complex (dotted line in inset of Fig 9), with no significant decrease in fit quality.

The results of our speciation calculations confirm that the fully hydrated Ni(II) species is dominant in NiCl₂-H₂O solutions, with only a small amount of chloride anions replacing water within the first octahedral shell even in saturated NiCl₂ solutions under ambient conditions. This indicates that the capacity of Ni(II) to bind chloride is much weaker than Zn(II) [16,70], Cu(II) [13–15] and Co(II) [4]. The average numbers of inner-sphere chloride and oxygen (water molecule) ligands calculated based on our thermodynamic speciation model agree with the experimental results from EXAFS and XRD experiments [21,25] (Fig 8a). Note that the low proportion of NiCl⁺ (~30%, i.e. 0.3 Cl on average around Ni atoms) present in solution was detected by UV-Vis spectroscopy (red-shift) and XANES (subtle decrease of the intensity of the white line), but can easily be overlooked in the EXAFS data. Therefore, accurate results require the integration of results from a range of techniques and careful error analysis. We note that the apparent discrepancies in the literature—with some studies claiming no inner-sphere complexing in concentrated NiCl₂ solutions—are related to poor consideration of errors. In
addition, the molecular dynamics simulations of Xia et al. [26], used to dismiss the formation of ion pairs in concentrated NiCl₂ solutions, are inconclusive because the simulation times (19 ps) were short relative to the ligand exchange rates \( k_{\text{ex}} \), e.g. \( 3 \times 10^4 \) to \( 10^7 \) s\(^{-1}\) for M-Cl exchange (M = Au(III), Zn(II), Cd(II) [71–72]; \( 3.2 \times 10^4 \) s\(^{-1}\) for Ni-H\(_2\)O exchange at room temperature ([73]). Aziz et al. [17] observed a geometrical distortion of the Ni(II) coordination sphere with increasing NiCl₂ concentration (0.05 to 1.5 mol·L\(^{-1}\)) on the basis of L₂,₃-edge XANES spectra. They interpreted this distortion to reflect solvent-shared ion pairs rather than inner-sphere complexes, on the basis of a comparison with an unspecified NiCl₂\(\cdot n\)H\(_2\)O(s) solid in vacuum. However, in view of the uncertainty on the hydration state of the standard, and the low concentrations of the inner-sphere complex even in concentrated NiCl₂ solutions, Aziz et al. [17]'s L₂,₃-edge XANES data are consistent with the speciation proposed in this study. Indeed, more recent L-edge XANES spectroscopy studies have emphasized the sensitivity of this method to small amounts of ion pairing (e.g., [74]).

Conclusions
The Ni(II)-chloride interaction in aqueous solutions of NiCl₂·H₂O (Cl:Ni = 2) and NiCl₂·MgCl₂·H₂O systems (Cl:Ni from 2 to 230) was systematically investigated using XAS and UV-Vis spectroscopy at room temperature. All the evidence indicates that there is no large structural change (e.g., from octahedral to tetrahedral configuration) in these systems up to the solubility limit. The analysis confirms that the hexa-aqua Ni(II) complex is the major complex in all studied solutions. However, the subtle changes of XAS and UV-Vis spectra as a function of salinity indicate that a small amount of Ni(II)-chloride complexation occurs, with up to 0.44 (23) Cl in the first coordinated shell of Ni(II) at 5.05 mol·kg\(^{-1}\) at a Ni-Cl distance of 2.35(2) Å.
At high Cl:Ni ratio, small amounts of the \([\text{NiCl}_2]^0\) complex are also present. These results are consistent with existing literature.

We developed a self-consistent thermodynamic model, based on the comprehensive MSE framework, for predicting the speciation, mean activity coefficients, water activities, and mineral solubilities in Ni-Cl-Mg-H\(_2\)O solutions up to the solubility limits. The stability of the Ni(II)-chloride complexes was retrieved mainly from a quantitative analysis of the UV-Vis spectroscopic data. The obtained speciation model is consistent with existing XAS and XRD data, and can easily be extended to include further components.

**Supporting Information**

S1 Table. Compositions (in molal) of the 18 NiCl\(_2\)-H\(_2\)O solutions measured by UV-Vis.
(TXT)

S2 Table. Compositions (in molal) of the 23 NiCl\(_2\)-MgCl\(_2\)-H\(_2\)O solutions measured by UV-Vis.
(TXT)

S3 Table. XAS data for the NiCl\(_2\)-6H\(_2\)O\(_{(s)}\) standard.
(TXT)

S4 Table. XAS data for the NiSO\(_4\)-6H\(_2\)O\(_{(s)}\) standard.
(TXT)

S5 Table. XAS data for the 1 mol kg\(^{-1}\) NiCl\(_2\) solution.
(TXT)

S6 Table. XAS data for the 2 mol kg\(^{-1}\) NiCl\(_2\) solution.
(TXT)

S7 Table. XAS data for the 4 mol kg\(^{-1}\) NiCl\(_2\) solution.
(TXT)

S8 Table. XAS data for the 5 mol kg\(^{-1}\) NiCl\(_2\) solution.
(TXT)

S9 Table. Raw absorbance data for the NiCl\(_2\)-H\(_2\)O solutions.
(XLS)

S10 Table. Raw absorbance data for the NiCl\(_2\)-MgCl\(_2\)-H\(_2\)O solutions.
(XLS)

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**Author Contributions**

Conceived and designed the experiments: NZ DZ. Performed the experiments: NZ. Analyzed the data: NZ JB BE YN. Contributed reagents/materials/analysis tools: NZ JB BE YN. Wrote the paper: NZ JB BE YN DZ.

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