

Extraction of metals under Galvani potential control

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ABSTRACT

Galvani potential established by a common ion at an interface between two immiscible electrolyte solutions (ITIES) can serve as a driving force and catalyse various biphasic reactions. Using potential determining ions provides a means to scale-up electrochemical processes at the ITIES from the laboratory, analytical scale - at least - to the preparative scale without relying on electrodes and an external power source. However, research on the applications of this phenomenon has been rather scarce. In this work, the effect of Galvani potential on the extraction of various metals with diphenylthiocarbazone (Dithizone) dissolved in 1,2-dichlorobenzene (DCB) was investigated using conventional 4-electrode cell cyclic voltammetry (CV) and extraction experiments in which the Galvani potential at the ITIES was controlled by a common ion. Especially, in the case of metals that do not spontaneously form a complex with the ligand, extraction was not detectable in the CV within the potential window provided by the supporting electrolytes. However, the extraction experiments show that the Galvani potential does enhance the extraction rate of these metals significantly, which indicates that the established potential exceeds the potential window of the CVs. Some of the metals were found to have affinity to the potential determining ions, and negative effect of additional electrolytes in the water phase on the extracted fraction was observed, which will have to be taken into account if potential determining ions were applied in extraction.

KEYWORDS: liquid-liquid interface, Galvani potential, metal extraction

INTRODUCTION

The history of modern electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) is now almost 50 years long. After the initial work by Guastalla and Gavach in the late 1960s and early 1970s (see [1] for references), the next advance was the introduction of the four-terminal potentiostat by the Prague group [2]. Since then various aspects of the structure and thermodynamics of the ITIES as well as charge transfer kinetics has been addressed, mainly using the analogy of ion transfer across the solution interface to electron transfer at solid electrodes. As it is well-known, an ITIES can be either polarizable or non-polarizable. The former interface usually is the “working” interface, providing a potential window of up to 1 V, depending on the organic solvent and the electrolytes, while the latter is utilized as a liquid junction in order to have a reversible reference electrode in an aqueous phase.

Most of the work is carried out at the polarizable oil-water interface utilizing the concept of the four-terminal potentiostat. The non-polarizable interface and the distribution potential created by a common ion, as analysed already in 1983 by Melroy and Buck [3], have been utilized as the driving force of charge transfer across the ITIES rather rarely. In an early study by Cunnane *et al.* [4], electron transfer between tin diphthalocyanine in 1,2-dichloroethane (1,2-DCE) and an aqueous ferro-ferricyanide couple was observed, run by the

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common ions tetraethyl ammonium (TEA⁺) or tetrapropyl ammonium (TPrA⁺). Later, potential control by a common ion has been utilized in electrocatalysis. Lahtinen *et al.* [5] used aqueous Pd and Au colloids to catalyse the dehalogenization of 2-bromoacetophenone with decamethyl ferrocene (DMFc) as the electron donor and tetramethyl ammonium (TMA⁺) as the potential determining ion; Pt and Pd nanoparticles created *in-situ* at the ITIES catalyzed hydrogen evolution with DMFc as the electron donor and ammoniumtetrakis-(pentafluorophenyl)borate (TB⁻) as the potential determining ion [6]. Biomimetic oxygen reduction at the ITIES with the potential control by a common ion has received a lot of interest [7-10] where ferrocenes are most often used as electron donors and (metallo)porphyrines as catalysts. The progress of the reaction can be verified by the UV spectrum of ferrocene/ferrocenium and by the formation of H₂O₂. All these experiments prove that the Galvani potential difference across the ITIES, created with a common ion is, indeed – although not directly measurable – a real physical quantity which can run charge transfer across the phase boundary.

Assisted ion transfer across the ITIES is also studied extensively, as Girault has reviewed in [11]. In addition to obvious cases where a ligand that is specific to a particular ion in the aqueous phase is added in the oil phase, such as valinomycin and K⁺ [12], the base electrolytes in the oil phase also can act as an ionophore. It has been claimed that the reported standard transfer potentials of some alkali metal cations are too low because their transfer is assisted by the base electrolytes [13]. Studying solvent extraction of heavy or rear earth metals seems a self-evident application area for ITIES but so far the studies have mostly been limited to the polarizable interface. Schiffrin and co-workers have reported electroassisted transfer of Cu²⁺ to 1,2-DCE using a tetradentate phosphorus-nitrogen ligand [14] and the transfer of Cd²⁺, Co²⁺, Cu²⁺, Mn²⁺, Ni²⁺, Zn²⁺ to 2-heptanone and 2-octanone with a terpyridine ligand [15, 16]; also the transfer of Au and Pt chlorocomplexes to 1,2-DCE and methyl isobutyl ketone (MIBK) was observed even without a ligand in the organic phase [17], apparently due to ion-pairing with the organic phase cation.

The EPFL group has studied the transfer of divalent heavy metal cations assisted by cyclic thioether ligands [18].

As valuable as the studies at the polarizable water-oil interfaces are, they cannot be used in practical separation processes because the interfacial area remains very small, and electrochemical instrumentation is required. Using a common ion to fix the Galvani potential between the aqueous and oil phases provides a means to scale-up electrochemistry at the ITIES from the laboratory – if not to the industrial – to the preparative scale. There are only a couple of studies known to us where this paradigm has been applied. Schiffrin *et al.* have reported the transfer of Cu²⁺, Ni²⁺ and Cd²⁺ from the aqueous phase to 1,2-DCE with TMA⁺ or TEA⁺ as the potential determining ion and 4,7-dimethyl-[1,10]-phenanthroline or terpyridine as the ligand; they also succeeded in separating Cu²⁺, Cd²⁺ and Ni²⁺ [19].

In this communication we report the transfer of Cu²⁺, Ni²⁺ and Co²⁺ from the aqueous phase to 1,2-dichlorobenzene (DCB), fixing the Galvani potential with a common anion. Also, we perform analogous cyclic voltammograms in the traditional 4-electrode setup. We used the commercial ligand Diphenylthiocarbazone, Dithizone. Also Di-(2-ethylhexyl)-phosphoric acid (D2EHPA) that have recently been successfully used in the separation of metals of Li ion batteries [20] was tried, but it did not show any Galvani potential dependence of the extraction efficiency. Furthermore, we also show that similarly to the reduction of Pt and Pd [6], two-phase reduction of Cu²⁺ is possible with the potential determining ion.

2. THEORY

When an ion *i* is at equilibrium between the aqueous (*w*) and an organic (*o*) phase the Nernst-Donnan equation states that

$$\frac{a_i^o}{a_i^w} = \exp\left[\frac{z_i F}{RT} (\Delta_o^w \phi - \Delta_o^w \phi_i^0)\right] \quad (1)$$

In Eq. (1), *a_i* is the activity of the ion, *z_i* its charge number, $\Delta_o^w \phi_i^0$ its standard transfer potential and $\Delta_o^w \phi$ the Galvani potential difference between

the phases; R , T and F have their usual significance. Adding a common ion in the phases does not, however, solely define $\Delta_o^w\phi$ because in a shake-flask experiment all the ions in the system distribute between the phases in a varying extent. Realizing that the values of the standard transfer potentials are not very accurately known, we omit the activity coefficients of the ions and consider their minor contribution to be included in the values of $\Delta_o^w\phi_i^0$. Hence, considering the mass balance, the concentration of ion i in water becomes,

$$c_i^w = \frac{c_i^{w,0} + r \cdot c_i^{o,0}}{1 + r \cdot \exp\left[-\frac{z_i F}{RT} (\Delta_o^w\phi - \Delta_o^w\phi_i^0)\right]} \quad (2)$$

where $c_i^{x,0}$ is the initial concentration of i in phase x and $r = V^o/V^w$, i.e. the volume ratio of the phases. As Kakiuchi has shown [21], $\Delta_o^w\phi$ can be calculated from the electroneutrality condition $\sum_i z_i c_i^w = 0$ which imposes electroneutrality also in the oil phase. The calculation, however, requires the values of $\Delta_o^w\phi_i^0$ of all distributing ions; their estimation thus presents another task.

The equations above assume free ions but ion-pairing takes place in the organic phase. Experiments clearly show that protons are distributed in oil because the pH of the aqueous phase changes during mixing with oil. Considering the ion-pairing theories of Bjerrum or Fuoss [22], a proton hardly exists as a free ion but is paired with an organic phase anion (here most of the time, with the potential determining anion TB⁻). Similarly, a metal cation to be extracted is bound to the extracting ligand. In the case of Dithizone, it is suggested that it donates a proton to balance charges. The metal-ligand stoichiometry is not a trivial question which further complicates the analysis of the results.

3. MATERIALS AND METHODS

3.1. Chemicals

Ultrapure water (Millipore Milli-Q, specific resistivity 18.2 M Ω cm) was used to prepare the aqueous

phases throughout the experiments. 1,2-dichlorobenzene (1,2-DCB, Sigma-Aldrich, anhydrous, 99%) was used as the organic phase. Lithium tetrakis(pentafluorophenyl)borate (LiTB) *n*-etherate (Boulder Scientific Company), bis(triphenylphosphoranylidine)ammonium chloride (BACl, 97%, Sigma-Aldrich), sodium tetraphenylborate and tetrabutylammonium chloride, tetraethylammonium chloride (TEACl, Sigma-Aldrich, 98%) and decamethylferrocene (DcMeFc, Sigma-Aldrich) were used as received. Bis(triphenylphosphoranylidine) ammonium tetrakis(pentafluorophenyl)borate (BATB) was prepared by metathesis and recrystallized in acetone, as described in literature [23]. Tetrabutylammonium tetraphenylborate (TBATPB) was prepared similarly, but in recrystallization a mixture of acetone and Milli-Q water (1:9) was used. Diphenylthiocarbazone (Dithizone, ACS reagent grade, Sigma-Aldrich) was used as received. Stock solutions of the brines were prepared by dissociating hydrated CuCl₂ (Merck, pa.) and NiSO₄ (Merck, pa.), CuSO₄ (Merck, pa.), CoSO₄ (Merck, pa.), FeSO₄ (Merck, pa.), ZnSO₄ (Sigma, pa.), Li₂SO₄ (Sigma-Aldrich, ACS reagent grade) and H₂PtCl₆ to HCl and H₂SO₄ solutions. The acid solutions were prepared by diluting 1.0 M HCl and 0.5 M or 1.0 M H₂SO₄ (VWR, AVS TITRINORM[®]) to Milli-Q water.

3.2. Methods

The cyclic voltammetry measurements were carried out using an Autolab 4-electrode potentiostat PGSTAT100 (Echochemie, the Netherlands) at an ambient temperature (22 °C) in aerobic conditions. The 4-electrode glass cell used in the electrochemical liquid-liquid metal transfer experiments was a generous gift from Prof. Z. Samec from J. Heyrovský Institute of Physical Chemistry, Prague. The interfacial area in the cell was 0.159 cm². The structure of the electrochemical cells used in the measurements is presented in Scheme 1. Dithizone was dissolved into the organic phase and 10 mM BATB was added as the supporting electrolyte in the organic phase. The cation (BA⁺) was common for the reference aqueous phase and the organic phase and therefore determines the Galvani potential between them. The transfer of Cu²⁺ was measured in chloride or sulphate media. The reference

| | | | | |
|-----------|------------|------------|---|-----------|
| Ag AgCl | 1 mM BACl | 10 mM BATB | 5 mM Li ₂ SO ₄ | Pt |
| | | Dithizone | H ₂ SO ₄ CuSO ₄ | |
| | Ref. water | Organic | Water | |
| Ag AgCl | 1 mM BACl | 10 mM BATB | 5 mM LiCl | AgCl Ag |
| | | Dithizone | HCl CuCl ₂ | |
| | Ref. water | Organic | Water | |

Scheme 1. Electrochemical four-electrode cell used for CV-measurements. Pt electrode was used with sulphate-based electrolyte and Ag|AgCl with chloride solutions.

| Organic phase | Water phase |
|---------------|--|
| BATB | BACl |
| Dithizone | HCl |
| | MCl ₂ /H ₂ PtCl ₆ |
| | LiCl |
| | H ₂ SO ₄ |
| | MSO ₄ |
| | Li ₂ SO ₄ |

Scheme 2. Initial compositions of the water and organic phase in the shake-flask experiments with chloride or sulphate medium. Two possible aqueous phase compositions are indicated with the dashed line.

electrode was Pt when sulphate electrolyte was used and Ag|AgCl in chloride solutions. The scan rate was varied from 10 to 100 mV/s and the ohmic drop was compensated by positive feedback. The potential was converted to the Galvani scale using the transfer wave of TEA⁺ with the value of $\Delta_o^w \phi_{\text{TEA}^+}^0 = 116$ mV.

The shake-flask experiments were carried out by placing 5 ml of the organic phase and 5 ml of the aqueous phase in a flask which was shaken for 45 s. The compositions of the phases are shown in scheme 2. The phases were allowed to separate and the aqueous phase was recovered. The initial and final metal concentrations in water were analysed with atomic absorption spectrometry (AAS) or inductively coupled plasma optical emission spectrometry (ICP-OES). The initial and final pH of the water phase was measured with Mettler Toledo SevenEasy pH meter. The extracted

fraction was calculated by dividing the change of the metal concentration in the water phase by the initial metal concentration and the Galvani potential at the ITIES was estimated by solving it from electroneutrality, mass balance and electrochemical equilibrium equations as shown in Appendix.

Light scattering experiments were carried out with Malvern Zeta-Sizer apparatus (Nano Sizer, Malvern, UK).

4. RESULTS AND DISCUSSION

4.1. Electrochemical measurements

Figure 1a shows the effect of Dithizone on Cu²⁺ transfer. Adding Dithizone to the organic phase causes Cu²⁺ peak to emerge at -190 mV. It can also be seen that the addition of Dithizone causes the potential window to shrink at both limits. Furthermore, the peak separation of the TEACl

peak and its reverse peak becomes less than 59 mV when Dithizone is added to the organic phase. This is probably attributed to a film formation at the liquid-liquid interface. The Randles-Ševčík analysis of the peak sweep rate dependency is shown in Figure 1b and it yields a value for diffusion coefficient $2 \cdot 10^{-7} \text{ cm}^2/\text{s}$ which is much less than that in water ($7 \cdot 10^{-6} \text{ cm}^2/\text{s}$). Hence, it appears that current is not limited by the transfer of Cu^{2+} from water to oil but, for example, the transfer of the metal complex from the ITIES to bulk solution or the partial limitation of the complexation reaction itself.

Cu^{2+} transfer has a negative dependence on the LiCl concentration. As shown in Figure 1c, the current peak decreases from 33 to $6.5 \mu\text{A}/\text{cm}^2$ as the LiCl concentration increases from 10 mM to 1 M. This is probably attributed to the increased amount of chlorocomplexes which hinder the complex formation with Dithizone. Increasing the LiCl concentration also shifts the Cu^{2+} peak to more negative potentials. Similar experiments were conducted with Li_2SO_4 as the supporting electrolyte. Increasing the concentration of Li_2SO_4 has a synergic effect on the transfer, increasing the peak current to almost 2.5-fold. Increasing the

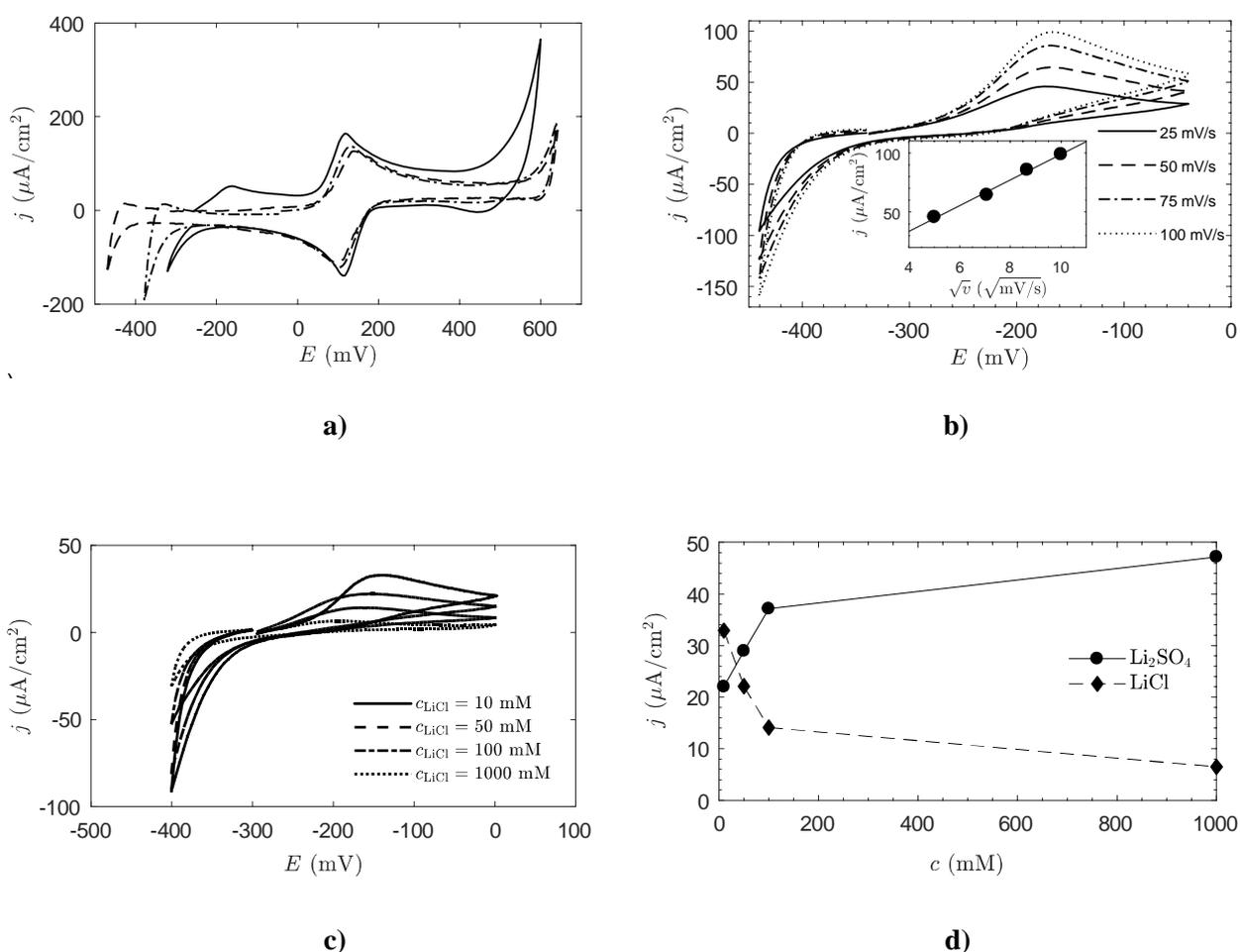


Figure 1. a) Cyclic voltammogram showing the effect of Dithizone on Cu^{2+} transfer; $v = 50 \text{ mV/s}$, $c_{\text{Cu}} = 50 \text{ mM}$ and $c_{\text{TEACl}} = 1 \text{ mM}$. The reversible peak at 120 mV is that of TEA⁺ and the peak at -190 mV is due to Cu^{2+} transfer. b) Sweep rate dependency of the Cu^{2+} transfer peak. c) The effect of LiCl on Dithizone assisted Cu^{2+} transfer with $v = 25 \text{ mV/s}$ and $[\text{Cu}^{2+}] = 1 \text{ mM}$. d) Current peaks as a function of the concentration of LiCl (diamonds) and Li_2SO_4 (circles); $v = 25 \text{ mV/s}$.

concentration of Li_2SO_4 from 10 mM to 1 M increases pH from ca. 2.3 to 3.9, implying that the ability of Dithizone to exchange protons to Cu^{2+} is enhanced. The effects of LiCl and Li_2SO_4 on Cu^{2+} transfer are compared in Figure 1.

Whereas the Dithizone-assisted transfer of Cu^{2+} could be observed in cyclic voltammograms, Co^{2+} or Ni^{2+} did not produce any reproducible peak, which implies that the facilitated transfer either takes place outside of the potential window or does not take place at all.

4.2. Extraction experiments

The extraction experiments were performed with Cu^{2+} , Co^{2+} and Ni^{2+} . The extraction of Cu^{2+} was the most facilitated and, contrary to voltammetry, was also independent of Cl^- concentration. The presence of sulphate did not restrict the extraction either. At pH 2, the concentration of Li_2SO_4 or LiCl was raised up to 1.0 M, but the extracted fraction still remained at 100%. When the ligand to metal ratio was 5:1, the extracted fraction was practically 100% without the use of any potential determining salts. When the ratio was lowered to 2:1, the extracted fraction dropped to ca. 50%, which implies the complexation reaction $\text{Cu}^{2+} + 2\text{DH} \rightarrow \text{CuD}_2 + 2\text{H}^+$. The ease of Cu^{2+} transfer can also be seen from the transfer peak of Cu^{2+} in the cyclic voltammogram. The peak has a relatively negative half-wave potential. Therefore, the Galvani potential threshold could be overcome without the help of potential determining ions, i.e. the extraction is spontaneous.

Co^{2+} extraction with Dithizone was much weaker than that of Cu^{2+} . Ligand-to-cobalt ratio 1:1 results in the extracted fraction of 6.1% at the initial pH 2. However, addition of potential determining ions to the organic and water phases increased the metal extraction significantly. As Figure 2 shows, the potential determining salts alone are able to extract Co^{2+} but combining potential determining ions with the ligand shows clear synergistic effect caused by the established Galvani potential. Extraction of Co^{2+} is also more susceptible to pH than other metals, and the most optimal initial pH is between 3 and 4. At pH 2, the extracted fraction remains under 10%, even under the established positive Galvani potential. The stoichiometry was determined by extracting excess concentration of Co^{2+} (22.6 mM) with

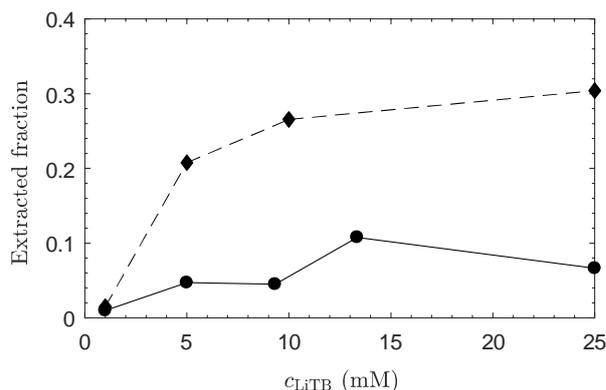


Figure 2. The extracted fraction of Co^{2+} from sulphate solution as a function of LiTB concentration in the aqueous phase; no ligand added to the organic phase (circles), and with ligand (diamonds). The initial ligand and Co^{2+} concentrations were 5 mM each. The initial pH of the aqueous phase was 4.

5 mM Dithizone in a Galvani potential regime where the cobalt transfers to the organic phase. The Co^{2+} concentration in the aqueous was lowered by 2.2 mM, which indicates that the complexation stoichiometry was the same as with Cu^{2+} : $\text{Co}^{2+} + 2\text{DH} \rightarrow \text{CoD}_2 + 2\text{H}^+$.

The effect of the potential determining salts on the Dithizone-assisted Ni^{2+} extraction was more pronounced than that of Cu^{2+} or Co^{2+} . Without fixing the Galvani potential difference across the ITIES, the extracted fraction of Ni^{2+} remained virtually zero when varying the ligand-to-metal ratio between 0.1 and 5 (pH 4). The inability of Dithizone to extract Ni^{2+} without the potential determining ions was also confirmed by increasing the contact time of the organic 5 mM Dithizone solution with the aqueous 5 mM NiSO_4 solution to 20 hours. Again, the extraction ratio was barely detectable (ca. 3%). When Ni^{2+} was extracted into the organic phase containing 5 mM Dithizone without BATB, while having 0–25 mM LiTB dissolved in the water phase (pH 3), the extraction resulted in an extracted fraction of less than 20%. The lack of potential determining ion in the organic phase results in poorly determined Galvani potential at the ITIES and, therefore, it was predictable that the extraction would not result into synergistic effect.

Fixing the Galvani potential with 0.1 mM BATB in the organic phase and any concentration of

LiTB in the aqueous phase, the extracted fraction remained under the detection limit when Dithizone was not added in the organic phase. Only the addition of Dithizone with a sufficiently high positive Galvani potential difference across the ITIES made Ni^{2+} to transfer to the organic phase. The results of the nickel extraction experiments with 5 mM Dithizone are recorded in Table 1. The extracted fraction is somewhat dependent on the pH of the aqueous phase, as shown in Figure 3a. This is probably due to the HTB complex formation at excess proton concentrations. Extracted fraction data converted to the Galvani potential scale is shown in Figure 3b. The details of the calculations are given in the Appendix. Similarly to Cu^{2+} and Co^{2+} extraction, in a suitable Galvani potential regime, Dithizone seems to extract Ni^{2+} in the same 1:2 Ni-ligand stoichiometry.

Examination of Table 1 reveals several interesting features. First, at the lowest LiTB concentration, the analysis of ionic equilibria (see Appendix) resulted in negative or extremely low aqueous TB^- concentrations, which is due to the high sensitivity of the bisulphate equilibrium to smallest errors in the pH measurements in the dilute solutions. Alternatively, our assumption of Li^+ or sulphate species not partitioning into oil is not strictly correct. At LiTB concentrations

higher than 1 mM this problem disappears. Yet, in all cases, a substantial fraction of TB^- is transferred from water to oil upon mixing.

The second finding is that protons are also transferred from water to oil, except at the lowest acid concentration of $5.0 \mu\text{M}$ (pH ~ 5) where the increase of the proton concentration must be due to Dithizone that exchanges protons to nickel cations. At higher acid concentrations this process is shadowed by the transfer of protons to oil, associating with TB^- in oil. The detailed analysis of the proton equilibria is also presented in Appendix.

Figure 3a shows the calculated Galvani potential differences as a function of the aqueous LiTB concentration. The standard value of the TB^- transfer potential was taken as 660 mV. In Figure 3b the extracted fraction of nickel is shown as a function of the LiTB concentration.

As can be seen, the Galvani potential across the ITIES follows the LiTB concentration quite well, whereas the extracted fraction seems to be insensitive to it. Only the highest concentration of 5 mM rises monotonously as should be expected. However, it has to be emphasized that two-phase-multi-ion equilibria are rather complicated to evaluate and the smallest errors in the chemical analysis can shift them significantly.

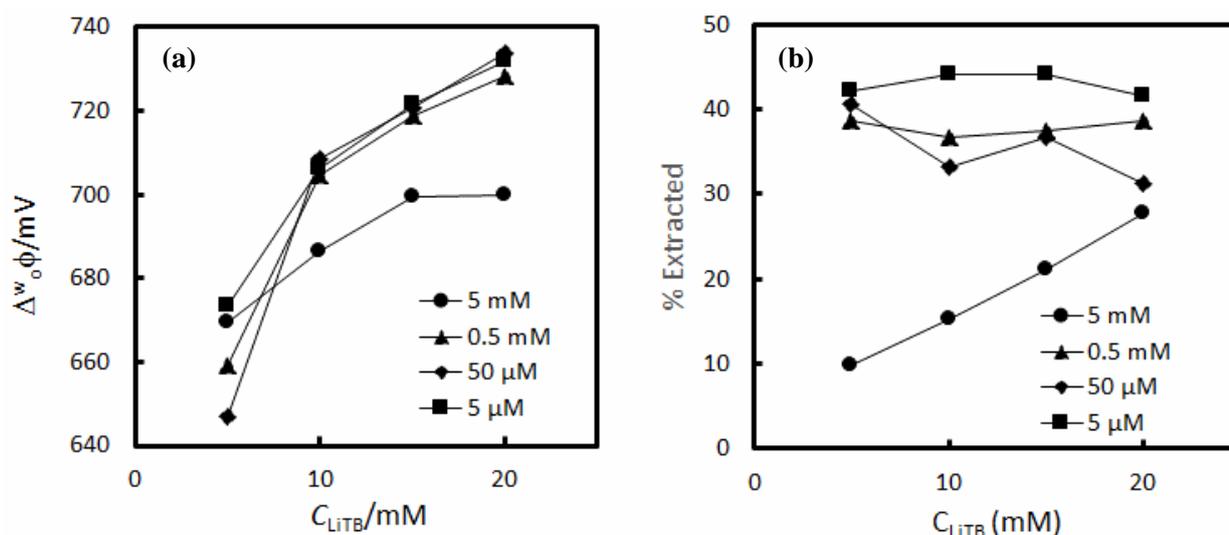


Figure 3. (a) Calculated Galvani potential difference in nickel extraction with varying concentrations of H_2SO_4 and LiTB; (b) extracted fractions as a function of the LiTB concentration with varying concentrations of H_2SO_4 .

Table 1. Results from the nickel extraction experiments; Dithizone concentration was 5.0 mM. Shadowed cells are experiments that produced unphysical parameter values in the calculations.

| [H ₂ SO ₄] = 5.0 mM, [NiSO ₄] = 4.517 mM | | Aqueous phase | | | | Aqueous phase | | | Galvani potential | |
|---|-----------------------|---------------|------------------------------------|------------------------------------|-----------------------|---|---|--|--|----------------------------------|
| [LiTB]/mM | [Ni] _f /mM | Δ[Ni]/mM | [H ⁺] ₀ /mM | [H ⁺] _f /mM | Δ[H ⁺]/mM | [HSO ₄ ⁻] _f /mM | [SO ₄ ²⁻] _f /mM | [TB ⁻ (w)] _f /mM | [TB ⁻ (o)] _f /mM | Δ ^w _o φ/mV |
| 1 | 4.291 | -0.226 | 7.586 | 6.761 | -0.825 | 3.786 | 5.731 | 1.096 | 0.001 | 835 |
| 5 | 4.074 | -0.443 | 8.511 | 4.266 | -4.246 | 2.800 | 6.717 | 1.180 | 0.819 | 669 |
| 10 | 3.830 | -0.687 | 6.457 | 3.162 | -3.294 | 2.247 | 7.270 | 4.035 | 1.446 | 686 |
| 15 | 3.567 | -0.950 | 8.128 | 2.239 | -5.890 | 1.708 | 7.809 | 7.047 | 1.512 | 700 |
| 20 | 3.261 | -1.256 | 6.457 | 1.122 | -5.335 | 0.940 | 8.577 | 9.551 | 2.012 | 700 |
| [H ₂ SO ₄] = 0.5 mM, [NiSO ₄] = 4.566 mM | | Aqueous phase | | | | Aqueous phase | | | Galvani potential | |
| [LiTB]/mM | [Ni] _f /mM | Δ[Ni]/mM | [H ⁺] ₀ /mM | [H ⁺] _f /mM | Δ[H ⁺]/mM | [HSO ₄ ⁻] _f /mM | [SO ₄ ²⁻] _f /mM | [TB ⁻ (w)] _f /mM | [TB ⁻ (o)] _f /mM | Δ ^w _o φ/mV |
| 1 | 3.292 | -1.274 | 0.776 | 1.514 | 0.737 | 0.653 | 4.413 | -0.382 | | |
| 5 | 2.800 | -1.766 | 0.776 | 0.363 | -0.413 | 0.174 | 4.892 | 1.005 | 1.035 | 659 |
| 10 | 2.885 | -1.681 | 0.776 | 0.209 | -0.567 | 0.101 | 4.964 | 5.948 | 1.053 | 704 |
| 15 | 2.851 | -1.715 | 0.776 | 0.123 | -0.653 | 0.060 | 5.006 | 10.753 | 1.086 | 719 |
| 20 | 2.800 | -1.766 | 0.776 | 0.117 | -0.659 | 0.058 | 5.008 | 15.643 | 1.101 | 728 |
| [H ₂ SO ₄] = 50 μM, [NiSO ₄] = 5.333 mM | | Aqueous phase | | | | Aqueous phase | | | Galvani potential | |
| [LiTB]/mM | [Ni] _f /mM | Δ[Ni]/mM | [H ⁺] ₀ /mM | [H ⁺] _f /mM | Δ[H ⁺]/mM | [HSO ₄ ⁻] _f /mM | [SO ₄ ²⁻] _f /mM | [TB ⁻ (w)] _f /mM | [TB ⁻ (o)] _f /mM | Δ ^w _o φ/mV |
| 1 | 4.004 | -1.329 | 0.074 | 0.724 | 0.650 | 0.356 | 5.027 | -0.678 | | |
| 5 | 3.169 | -2.164 | 0.078 | 0.051 | -0.026 | 0.027 | 5.356 | 0.650 | 1.076 | 647 |
| 10 | 3.561 | -1.772 | 0.074 | 0.028 | -0.047 | 0.014 | 5.369 | 6.398 | 0.973 | 708 |
| 15 | 3.374 | -1.959 | 0.072 | 0.026 | -0.047 | 0.013 | 5.370 | 11.020 | 1.028 | 721 |
| 20 | 3.663 | -1.670 | 0.074 | 0.028 | -0.047 | 0.014 | 5.369 | 16.602 | 0.942 | 734 |

Table 1 continued..

| [H ₂ SO ₄] = 5.0 μM, [NiSO ₄] = 4.602 mM | | Aqueous phase | | | Aqueous phase | | | Galvani potential | | |
|---|-----------------------|---------------|------------------------------------|------------------------------------|-----------------------|---|---|--|--|---------------------|
| [LiTB]/mM | [Ni] _f /mM | Δ[Ni]/mM | [H ⁺] ₀ /mM | [H ⁺] _f /mM | Δ[H ⁺]/mM | [HSO ₄ ⁻] _f /mM | [SO ₄ ²⁻] _f /mM | [TB ⁻ (w)] _f /mM | [TB ⁻ (o)] _f /mM | Δ ^w φ/mV |
| 1 | 3.561 | -1.041 | 1.000 | 0.661 | 0.660 | 0.279 | 4.328 | -0.152 | | |
| 5 | 2.662 | -1.940 | 1.549 | 0.309 | 0.307 | 0.135 | 4.472 | 1.554 | 0.929 | 673 |
| 10 | 2.566 | -2.036 | 2.089 | 0.129 | 0.127 | 0.057 | 4.550 | 6.104 | 1.007 | 706 |
| 15 | 2.574 | -2.028 | 1.905 | 0.123 | 0.121 | 0.055 | 4.552 | 11.111 | 1.006 | 722 |
| 20 | 2.685 | -1.917 | 2.399 | 0.081 | 0.079 | 0.036 | 4.571 | 16.274 | 0.985 | 732 |

In order to check the effect of the common ion on the extraction efficiency, TB^- was replaced with either tetraethylammonium (TEA^+) or PF_4^- ions. Figure 4 shows the expected behaviour, i.e. the standard transfer potential of these ions is too low to create a sufficiently positive Galvani potential across the ITIES to drive the extraction of nickel. The calculations were done similarly as in the case of TB^- but are not repeated here as no meaningful extraction could be detected. Figure 4 clearly tells that the nature of the potential determining ion is the main factor in the Galvani potential, not the concentration term in the Nernst equation.

Stripping experiments with Ni-loaded Dithizone in the organic phase were also attempted. The pH of the stripping solutions varied from 1 to 5. Stripping was also attempted by polarizing the water phase negatively by adding 5 mM BACl to the aqueous solution. Stripping solution with pH 3 yielded the best result in which 5 ml of the water phase stripped 33% of nickel from 5 ml of the organic phase. Other stripping solutions yielded zero stripping percentage; nickel is not transferred to the negatively polarized water phase either.

Potential determining ions can interact or even associate with other ions that are present in the water phase. This can effectively affect the Galvani potential, as it reduces the activity of the potential determining ion in the water phase.

Figure 5 shows the effect of Li_2SO_4 on Ni^{2+} transfer with the initial LiTB concentration in the water phase of 5 mM which, according to the extraction data in Figure 3, would be sufficient to assist the metal extraction. It should be mentioned that at the highest Li_2SO_4 concentrations (250 and 500 mM) the water phase turned cloudy, which probably indicates precipitation of LiTB due to the high salting-out capability of Li_2SO_4 [24]. At these concentrations, the extracted fraction is significantly lower than that without additional salt in the aqueous phase. Furthermore, the extracted fraction seems to be more tolerant to the presence of Li_2SO_4 at higher pH. The behaviour shown in Figure 5 thus is opposite to that shown in Figure 1d due to the presence of LiTB in the aqueous phase.

In some cases, potential determining ions have a tendency to behave as a ligand and form complexes with the metal dissolved in the water phase without the help of an additional ligand. Behavior of this kind is shown in Figure 6 that shows the extraction of hexachloroplatinate in shake-flask experiments with no ligand in the organic phase. The extracted fraction was proportional to the TBACl concentration, and the highest extracted fractions were reached at the highest TBACl concentrations. Curiously, the extracted fraction remained relatively low when there was no HCl in the water phase and TBATPB

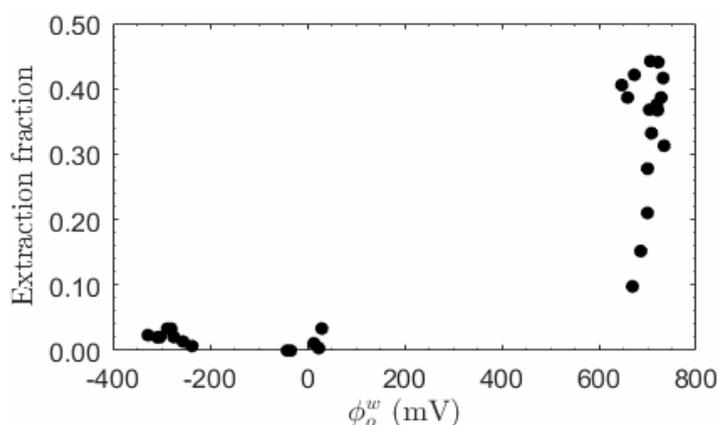


Figure 4. The extraction data plotted as a function of Galvani potential calculated from electrochemical equilibrium, mass balance and electroneutrality equations. Different Galvani potential regimes were achieved using different common ions with different standard transfer potentials, $\Delta_o^w \phi^0$.

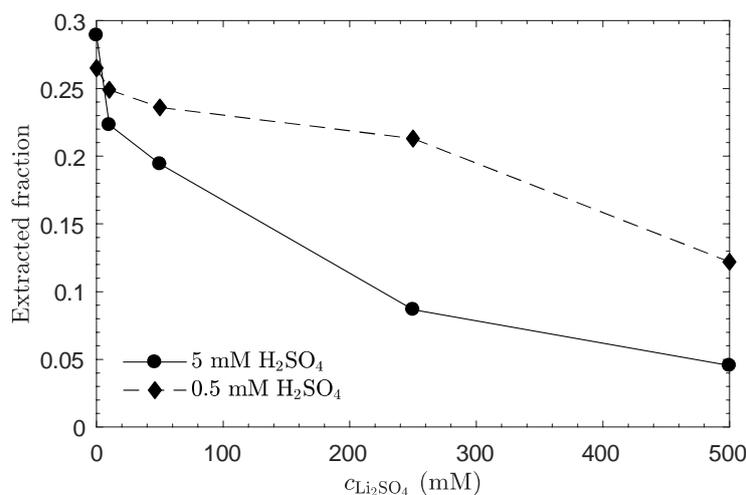


Figure 5. The effect of Li_2SO_4 on Galvani potential driven Ni^{2+} extraction with 5 mM Dithizone. The initial LiTB concentration was 5 mM and BATB concentration in the organic phase was 0.1 mM. The pH of the water phase was set with either 0.5 or 5 mM H_2SO_4 .

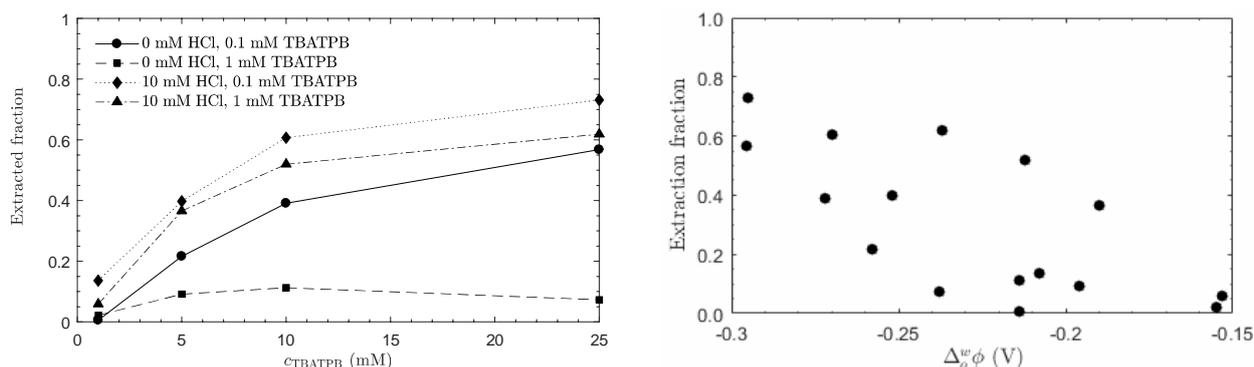


Figure 6. Extracted fraction of PtCl_6^{2-} at 0 and 10 mM HCl at various TBATPB concentrations, and extracted fractions converted to Galvani potential scale.

concentration was 1 mM, as contrast to similar experiment in which TBATPB concentration was 0.1 mM. Converting the extraction data to the Galvani potential scale shows a slight trend towards higher extracted fraction at lower Galvani potentials, and the extracted fraction grows at Galvani potentials less than 0.18 V which coincides well with the PtCl_6^{2-} half-wave potential measured previously (0.18 V, [17]).

4.3. Two-phase reduction

As mentioned in INTRODUCTION, Galvani potential fixed with a common ion can also drive electron transfer across the water-oil interface.

We made a very simple proof-of concept shake-flask experiment where aqueous $\text{H}_2\text{SO}_4\text{-CuSO}_4$ solution (both 5 mM) was brought into contact with an organic (DCB) solution containing 0.1 mM BATB and 5 mM decamethylferrocene (DcMeFc) as the electron donor. Upon mixing the solutions overnight barely nothing happened, only the yellow color of DcMeFc turned pale green due to its oxidation by atmospheric oxygen, see left panel in Figure 7. Adding LiTB in the aqueous phase, the organic phase turned immediately to dark green, indicative of the oxidation of ferrocenes [7-10] (right panel). A light scattering measurement from the organic phase sample



Figure 7. Left: A flask containing DcMeFc in DCB is mixed overnight in the beaker with the aqueous CuSO_4 solution. Pale green color indicates a partial oxidation of DcMeFc by atmospheric oxygen. Right: Adding LiTB in the aqueous phase turns yellow color immediately to dark green.

showed nanoparticles of the diameter of ca. 200 μm . A similar kind of an experiment was carried out by Aslan *et al.* [25], who deposited Cu nanoparticles first at the interface with the 4-electrode set-up, and then proved the hydrogen evolution reaction by using DcMeFc as the electron donor. We are going to study the two-phase reduction of metals in a subsequent paper.

5. CONCLUSION

In this study, four-electrode cyclic voltammetry was used to detect ligand-assisted metal extraction at the ITIES. As majority of the studied metals had a high standard transfer potential, the transfer could not be detected within the potential window enabled by the supporting electrolytes. However, the shake-flask experiments presented in this study prove the concept that a Galvani potential established by potential determining salts can have a synergistic effect on metal extraction. In order to attain the synergistic effect, the Galvani potential must be well-established and the presence of the potential determining salt is required in both the water and organic phases. It has to be reminded that the effect of Galvani potential on the extraction rate is highly case-dependent and it also has to be taken into account that the potential determining salts on their own tend to have some affinity to the metal that are being extracted. This may result into precipitation

or potential determining salt induced metal extraction. The association of the metal ions with the potential determining ions in the water phase also complicates the metal analysis with AAS or ICP-OES, since the analyses of the unfiltered samples showed considerable uncertainty. Furthermore, we have shown that the presence of other electrolytes in the water phase may prevent the synergistic effect of the potential determining salts, which is likely to be due to the salting-out effect of Li^+ . This is relevant when hydrometallurgical applications for this phenomenon are considered, since leached solutions often contain other salts.

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CONFLICT OF INTEREST STATEMENT

There are no conflicts of interest.

APPENDIX

Analysis of the ionic equilibria

After the equilibrium has settled, the aqueous phase contains the following ions: Li^+ , H^+ , Ni^{2+} , HSO_4^- , SO_4^{2-} and TB^- . In order to keep the problem reasonably calculable, we assume that neither Li^+ nor sulphate species partition into the oil phase; it is also assumed that BA^+ is not present in the aqueous phase. We denote Li^+ as species 1, H^+ as

species 2, Ni^{2+} as species 3, HSO_4^- as species 4, SO_4^{2-} as species 5 and TB^- as species 6. Hence:

$$c_1 = 2[\text{Li}_2\text{SO}_4] + [\text{LiTB}]; \text{ known} \quad (\text{A1})$$

$$c_2 = 10^{-\text{pH}}; \text{ known} \quad (\text{A2})$$

$$c_3; \text{ known (measured)} \quad (\text{A3})$$

$$c_4 + c_5 = [\text{Li}_2\text{SO}_4] + [\text{H}_2\text{SO}_4] + [\text{NiSO}_4] \\ = c_T; \text{ known} \quad (\text{A4})$$

$[\text{Li}_2\text{SO}_4]$, $[\text{LiTB}]$, $[\text{H}_2\text{SO}_4]$ and $[\text{NiSO}_4]$ are the initial concentrations in the aqueous phase; c_T denotes the total sulphate concentration. The dissociation equilibrium of bisulphate is

$$K_a = \frac{c_2 c_5}{c_4} = \frac{c_2 (c_T - c_4)}{c_4} \Rightarrow c_4 = \frac{c_2 c_T}{c_2 + K_a} \quad (\text{A5})$$

The concentration of TB^- can now be calculated from the electroneutrality condition:

$$c_6 = c_1 + c_2 + 2c_3 - c_4 - 2c_5 = \\ c_1 + c_2 + 2c_3 + c_4 - 2c_T \quad (\text{A6})$$

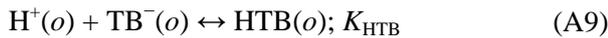
The Galvani potential difference across the water-oil interface can be calculated from the Nernst-Donnan equation

$$\Delta_o^w \phi = \Delta_o^w \phi_{\text{TB}^-}^0 - \frac{RT}{F} \ln \left(\frac{c_6^o}{c_6} \right) \quad (\text{A7})$$

where we have neglected the activity coefficients because of the uncertainty of the exact values of the ion-pairing constants in oil (see below) as well the standard transfer potential of TB^- from oil to water. The concentration of free TB^- in oil is obtained considering its mass balance. Initially, it is added as LiTB in the aqueous phase and BATB in the oil phase. The mass balance reads

$$[\text{LiTB}] + [\text{BATB}] = c_6 + c_{\text{TB}^-}^o + c_{\text{HTB}}^o + c_{\text{BATB}}^o \quad (\text{A8})$$

The ion-pairing equilibria considered are



$$K_{\text{HTB}} = \frac{c_{\text{HTB}}^o}{c_{\text{H}^+}^o c_{\text{TB}^-}^o} \Rightarrow c_{\text{HTB}}^o = K_{\text{HTB}} c_{\text{H}^+}^o c_{\text{TB}^-}^o \quad (\text{A11})$$

$$K_{\text{BATB}} = \frac{c_{\text{BATB}}^o}{c_{\text{BA}^+}^o c_{\text{TB}^-}^o} \Rightarrow c_{\text{BATB}}^o = K_{\text{BATB}} c_{\text{BA}^+}^o c_{\text{TB}^-}^o \quad (\text{A12})$$

Again, we neglect the activity coefficients due to the uncertainty of the association constants. The mass balance of TB^- now becomes

$$[\text{LiTB}] + [\text{BATB}] = \\ c_6 + c_{\text{TB}^-}^o \left(1 + K_{\text{HTB}} c_{\text{H}^+}^o + K_{\text{BATB}} c_{\text{BA}^+}^o \right) \quad (\text{A13})$$

Electroneutrality in the oil phase states that $c_{\text{BA}^+}^o = c_{\text{TB}^-}^o - c_{\text{H}^+}^o$. In order to find the proton concentration in oil, its mass balance must also be considered. Protons come from aqueous sulphuric acid and Dithizone in oil. Thus:

$$c_{2,0} + c_{\text{DH},0}^o = c_2 + c_{\text{H}^+}^o + c_{\text{DH},f}^o + c_{\text{HTB}}^o \\ = c_2 + c_{\text{DH},f}^o + c_{\text{H}^+}^o \left(1 + K_{\text{HTB}} c_{\text{TB}^-}^o \right) \\ c_{\text{H}^+}^o = \frac{(c_{2,0} - c_2) + (c_{\text{DH},0}^o - c_{\text{DH},f}^o)}{1 + K_{\text{HTB}} c_{\text{TB}^-}^o} \quad (\text{A14}) \\ = \frac{\Delta c_2 + \Delta c_{\text{DH}}^o}{1 + K_{\text{HTB}} c_{\text{TB}^-}^o} = \frac{\Delta c_2 + 2\Delta c_3}{1 + K_{\text{HTB}} c_{\text{TB}^-}^o}$$

The subscripts ‘‘0’’ and ‘‘f’’ refer to the initial and final concentrations, respectively. We assume above that a nickel ion binds to two ligands, releasing two protons. The final equation from which $c_{\text{TB}^-}^o$ is calculated looks a bit complex but is easily solved numerically:

$$[\text{LiTB}] + [\text{BATB}] = \\ c_6 + c_{\text{TB}^-}^o \left(1 + K_{\text{BATB}} c_{\text{TB}^-}^o + \frac{(K_{\text{HTB}} - K_{\text{BATB}})(\Delta c_2 + 2\Delta c_3)}{1 + K_{\text{HTB}} c_{\text{TB}^-}^o} \right) \quad (\text{A15})$$

From the Bjerrum theory, noticing that the closest approach of H^+ and TB^- is less than that of BA^+ and TB^- , we can estimate that $K_{\text{BATB}} \approx 1000 \text{ M}^{-1}$ and $K_{\text{HTB}} \approx 3000 \text{ M}^{-1}$. Our calculation is

semi-quantitative, yet reflecting the trend when we vary the concentration of LiTB in the aqueous phase.

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