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New methodology to measure low free indium (III) concentrations based on the determination of the lability degree of indium complexes. Assessment of $\text{In}(\text{OH})_3$ solubility product.

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Abstract

The vast industrial and consumer application of indium (solar cells, displays, etc.) risks its eventual leakage to the environment. Given the relevant role of speciation on the ecotoxicological effects of a certain total amount of indium, it is crucial to develop proper techniques to determine free concentrations of indium. The electroanalytical technique AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) has already proved useful in such a goal. However, the optimization of suitable deposition times in some conditions might be laborious. This work presents a new strategy, based on the technique ADLC (Accumulation under Diffusion Limited Conditions), to determine lability degrees, which apart from their intrinsic physicochemical interest -by comparing reaction kinetics with diffusion rates-, provide useful guidelines for AGNES deposition times. The suggested novel methodology is illustrated with: i) the computation of lability degrees of indium-oxalate complexes (unreported up to date) and ii) measuring free concentration of indium (for the first time as low as pmol L^{-1}) in precipitated solutions (i.e. containing precipitated indium hydroxide in the electrochemical cell). The method takes advantage of the fact that the addition of a suitable concentration of oxalate does not change the free indium concentration (which is buffered due to the existing precipitate at a fix pH), but creates a large amount of

labile and mobile indium complexes that contribute to the desired accumulation at very large gains (preconcentration factors). Results confirm the validity of the solubility product of indium hydroxide reported in the database NIST 46.7

Keywords: kinetics; diffusion-reaction; speciation; precipitation

1. Introduction

Indium is a trivalent amalgamating metal that has been widely used in alkali batteries and electronic devices. Indium alloys also have many industrial applications. For example, indium tin oxide (ITO) is a common alloy of In_2O_3 and tin-oxide (SnO_2) in a ratio of 90:10 (wt:wt) that serves as coating for solar cells, plasma and liquid crystal display (LCDs) [1, 2]. These vast applications of indium compounds justify that its world production has increased over the past 30 years, with potential impact on the environment and human health. It is, therefore, timely to study the chemistry and behaviour of indium (III), such as the evolution of its free concentration (i.e. the hexaquo complex) in a variety of aqueous matrices at different pH values.

Even at moderately acidic pH, indium solution chemistry is often dominated by its strong hydrolysis [3]. When the alkalinity of the system increases, indium hydroxide precipitates due to its extremely low solubility. This explains the low concentrations of free indium in the environment [1].

The precipitation of indium hydroxide $\text{In}(\text{OH})_3$ is ruled by the solubility product (of the corresponding activities)

$$K_{\text{sp}} = \{\text{In}^{3+}\} \{\text{OH}^-\}^3 \quad (1)$$

for which conflicting values (from $\log K_{\text{sp}} = -33.0$ to $\log K_{\text{sp}} = -39.8$) have been reported [3-5]. Orlov *et al*, [6] indicated a significant difference between the K_{sp} of the aged (log

$K_{sp} = -37.0$) and freshly precipitated solutions ($\log K_{sp} = -33.0$). Taking into account the recommended value of the reviewing work of Tuck in 1983 [4], the database NIST 46.7 adopts $\log K_{sp} = -36.9$. So, despite the investigations conducted (with most of the determinations dating from quite long time ago), there is still a lack of certainty about the solubility product of indium hydroxide.

The elucidation of an accurate K_{sp} value and many other issues depend on the capability of measuring free indium concentration. Potentiometry with recently developed Ion Selective Electrodes (ISE) [7, 8] measures free indium concentration, but their limit of detection is still not lower than submicromolar concentrations. Also a polymer imprinted sensor [9] and fluorescent probes [10, 11] have been reported to determine In^{3+} concentration with a detection limit of 4.7, 64 and 890 nmol L^{-1} , respectively. The retrieval of free metal concentrations from electroanalytical techniques such as Anodic Stripping Voltammetry (ASV), Scanned Stripping ChronoPotentiometry (SSCP) or Adsorptive Cathodic Stripping Voltammetry (AdCSV) is hampered with difficulties in interpretation [12] worsened by hydrolysis and the formation of several complexes (especially relevant in the case of trivalent ions). However, AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) [13, 14] was specifically designed to measure free metal ion concentrations for amalgamating ions with negative standard redox potentials. AGNES has dealt with Zn, Cd and Pb, in a range of systems including seawater [15], river water [16-18], estuarine water [19], soil extracts [16], wine [20], hydroponic media [21] as well as solutions containing dissolved organic matter [22, 23], and nanoparticles [24-32]. Very recently, AGNES has been applied to indium solutions with either the hanging mercury drop electrode [33] or the thin film rotating disc electrode [34]. Free indium concentration at $\text{pH}=3$ determined with AGNES also allowed an insight into the speciation of In-nitrilotriacetic acid and In-Oxalate mixtures.

Yet, at higher pH values, the free concentration of indium decreases so dramatically that the deposition times needed in AGNES may be long and/or difficult to assess.

Deposition times shorten when labile and mobile complexes contribute to the supply of indium towards the electrode [35]. To quantify this contribution, the concept of lability degree was developed [36]. Previous work measured lability degrees of complexes of Cd with nitrilotriacetic acid or citrate with the technique SCP (Stripping Chronopotentiometry) [37] by comparing limiting transition times in presence and absence of ligands. However, this approach did not take into account the formation of metal-nitrate complexes nor the possibility of sequential complexation (i.e. complexes with different number of ligands bound to the metal ion). This extension is tackled here with a new technique that can be called Accumulation under Diffusion Limited Conditions (ADLC). The knowledge of the lability degrees will provide useful estimates of optimum deposition times for AGNES in solutions where the free indium concentration is extremely low, as in natural non-acidic solutions.

This work aims at developing new methodologies to: i) measure lability degrees for complexes, ii) use lability degrees in the estimation of optimal deposition times for AGNES, iii) dramatically reduce the deposition times in precipitated systems with the addition of ligands forming labile complexes. These methodologies are illustrated for the case of indium, so that they will allow the checking of the robustness of the accepted solubility product of $\text{In}(\text{OH})_3$.

The outline is as follows. Section 2 provides experimental information, such as the principles of AGNES and ADLC. Section 3 derives the mathematical expressions that allow to compute the lability degree from ADLC measurements and those that estimate AGNES deposition times when complexes contribute to the accumulation. Section 4 discusses the experimentally obtained lability degrees of indium-oxalate complexes.

Section 5 applies previous information (together with a new strategy of adding oxalate) to the measuring, at pH values up to 6, of the free indium concentration in equilibrium with precipitated $\text{In}(\text{OH})_3$, whose K_{sp} is confirmed.

2. Experimental

2.1 Reagents

Indium solutions were prepared by dilution from a 1000 mg L^{-1} stock solution (indium standard for ICP, Fluka, St Louis, USA). Potassium nitrate was used as the inert supporting electrolyte at 0.1 mol L^{-1} (for all experiments) and prepared from solid KNO_3 (TraceSelect, Fluka, St Louis, USA).

Potassium oxalate monohydrate (analytical grade, Fluka, Buchs, Switzerland) was used as a ligand. KOH 0.1 mol L^{-1} (Fluka, St Louis, USA) and HNO_3 0.1 mol L^{-1} (Fluka, St Louis, USA) were used to adjust the pH of the solutions. 2-(*N*-morpholino)ethanesulfonic acid (MES) buffer (> 99%, Sigma, St Louis, USA) 0.1 mol L^{-1} was prepared and used to fix the pH of the solutions at 5.5, 5.6 and 6.0.

2.2 Instrumentation

Voltammetric measurements were carried out with Autolab PGSTAT10 and PGSTAT101 potentiostats attached to Metrohm 663 VA Stands. All experiments were performed using GPES 4.9.007 (Eco Chemie) or NOVA 1.11 (Metrohm Autolab) software. The working electrode was a Metrohm Hanging Mercury Drop Electrode. Glassy carbon was used in the auxiliary electrode and the reference electrode was double-junction $\text{Ag}/\text{AgCl}/3 \text{ mol L}^{-1} \text{ KCl}$ with KNO_3 0.1 mol L^{-1} in the salt bridge. A glass jacketed cell was used in all the experiments and thermostated at 25.0°C . A glass

combined electrode (Crison, 5209) was attached to an Orion Dual Star ion analyzer (Thermo) and introduced in the cell to control the pH. Purging with N₂ (purity ≥ 99.999%) avoids a large signal from oxygen reduction and pH increases close to the electrode surface [38].

2.3 Procedures

2.3.1 AGNES

AGNES is used to determine free concentration of indium. This technique consists of two stages with specific goals. See existing literature [13, 14, 25] and the Supporting Information of this work for details about the principles and application of this technique, but a brief description follows. The first stage seeks equilibrium at the electrode surface and uniform concentration profiles in the electrode-solution system (see Fig SI-8 in the Supporting Information). Nernst equilibrium can be written as:

$$Y = \frac{[\text{In}^0]}{[\text{In}^{3+}]} = \exp\left[-\frac{3F}{RT}(E_1 - E^{0'})\right] \quad (2)$$

where $[\text{In}^0]$ is the concentration of reduced indium in the amalgam, $[\text{In}^{3+}]$ the concentration of free indium in solution, F is the Faraday constant, R the gas constant and $E^{0'}$ is the standard formal potential of the indium redox couple. Due to the reached Nernstian equilibrium, the preconcentration factor or gain, Y , can be tuned via the deposition potential E_1 . For a list of symbols, see the Supporting Information (SI). In the variant 1P (for “one pulse”), E_1 is applied during a time (t_1) of which t_1-t_w with stirring and t_w without stirring. In the variant 2P, an extra sub-stage for a duration $t_{1,a}$ (at an extremely negative potential $E_{1,a}$) precedes the equilibration sub-stage during which E_1 is applied (for a time $t_{1,b}$). See SI for schematic representations and further explanations.

The aim of the second stage (or stripping phase) is the quantification of the amount of In^0 accumulated in the first stage. From the various available stripping variants [13], one based on the deposited charge, AGNES-Q, was selected here with a stripping potential of -0.450 V to avoid any possible Pb interference [33]. A sufficiently long stripping time ($t_2=50\text{ s}$) was used to achieve full depletion of the amalgamated In^0 . The (faradaic) stripped charge Q (obtained from integration of the stripping intensity current) is proportional to the free metal ion concentration in solution, with η_Q being a proportionality factor depending on the volume of the mercury electrode:

$$Q = Y\eta_Q [\text{In}^{3+}] \quad (3)$$

In the case of indium [33], a calibration Q vs. $[\text{In}^{3+}]$ allows the determination of the gain (corresponding to the applied deposition potential) from a known $\eta_Q=0.0034\text{ C L mol}^{-1}$.

One example calibration is shown in Fig SI-14.

Blanks were conducted in the supporting electrolyte (the so-called synthetic blank [13]) at the same gain or interpolated from a large set of blanks at various gains.

Equilibrium is recognized from the stabilization of the stripped charge at long enough deposition times (i.e. sufficiently long t_1 or $t_{1,b}$). The attainment of equilibrium can be diagnosed from a plateau in the trajectory, which is a plot of charge versus deposition time, also called time course or time profile, i.e. a set of experiments with a given gain and successively longer deposition times.

2.3.2 ADLC

ADLC (Accumulation under Diffusion Limited Conditions) was used to estimate the lability degree of indium complexes. In this technique, presented here, we apply an extremely negative potential $E_{1,a}$ (so that deposition proceeds under diffusion limited

conditions) during a time $t_{1,a}$ and, then, we measure the charge in the stripping stage. This charge is equal to the charge accumulated in the deposition stage and (if we reasonably neglect the short initial transient) is proportional to the steady-state flux J (of In atoms arriving from the solution to the drop surface, where they are converted into In^0) and $t_{1,a}$:

$$Q = 3FAJ_{t_{1,a}} = \text{slope}_\alpha t_{1,a} \quad (4)$$

where A is the area of the electrode and the subscript α is a reminder that the parameter is dependent on some conditions (e.g. pH or solution composition). The negative potential that is used in ADLC corresponds to a huge gain, similar to the one prescribed during the first sub-stage of the variant 2P of AGNES. Fig 1 provides a schematic representation of the potential program of ADLC. Fig 2 shows an example of ADLC experiment at pH=3.0 with only indium, where we measured the total charge accumulated under diffusion limited conditions at different $t_{1,a}$. The linearity of the plot lends support to the hypothesis that the ADLC measurements are done under steady state. As detailed in the next section, the lability degree can be determined from ADLC experiments and, then, their values can be used to optimize the deposition time in AGNES-2P experiments (as implemented in section 5).

3. Theoretical background

3.1 The concept of lability degree

Let us consider the reaction of one generic metal (M) with just one ligand (L) to form one complex (ML) in solution:



The total steady-state supply of this metal from the medium towards an M consuming surface of a sensor or organism can be split as the contribution of its free form plus the contribution of the complexed form:

$$J = J_{\text{free}} + J_{\text{complex}} \quad (6)$$

The lability degree, ξ , is a quantification of the contribution of the complex to the total flux. ξ is defined as the ratio of the current complex contribution to the flux over the maximum possible contribution [36, 39]:

$$\xi = \frac{J_{\text{complex}}}{J_{\text{complex,max}}} = \frac{J - J_{\text{free}}}{J_{\text{labile}} - J_{\text{free}}} \quad (7)$$

where J is the current flux, J_{labile} is the hypothetical flux if the complexes were fully labile and J_{free} is the hypothetical flux if the complexes were totally inert (equivalent to the flux in a system with just the free ion at the same concentration, but no complex). The value of ξ ranges from zero (totally inert) to 1 (fully labile).

From the previous definition, it follows that the total flux can be computed as the summation of the contribution of the free metal ion plus the maximum possible contribution of the complex multiplied by the lability degree. If we further assume a steady state where the species diffuse through a diffusion layer of thickness δ ,

$$J = D_{\text{M}} \frac{[\text{M}]}{\delta} + D_{\text{ML}} \frac{[\text{ML}]}{\delta} \xi \quad (8)$$

where D_{M} and D_{ML} stand for the diffusion coefficients of free metal and complex, respectively. The normalized diffusion coefficient, ε , is defined as

$$\varepsilon = \frac{D_{\text{ML}}}{D_{\text{M}}} \quad (9)$$

The conditional ligand-excess stability constant, K' , associated to reaction (5), can be defined as the ratio between the concentration of the complex and the free concentration of the metal, both in the bulk solution:

$$K' \equiv \frac{[\text{ML}]}{[\text{M}]} = K [\text{L}] \quad (10)$$

where K is the conditional stability constant (for concentrations) of reaction (5).

The expression of the total flux can be condensed into

$$J = \frac{D_M [\text{M}]}{\delta} + \xi \frac{D_{\text{ML}} [\text{ML}]}{\delta} = D_M \frac{[\text{M}](1 + \varepsilon K' \xi)}{\delta} \quad (11)$$

For a collection of complexes, each one labelled with a subscript i , [40, 41]

$$J = D_M \frac{[\text{M}] \left(1 + \sum_{i=1}^{\text{num complexes}} \varepsilon_i K'_i \xi_i \right)}{\delta} \quad (12)$$

3.2 Formulas to compute lability degrees from ADLC experiments

Combining eqns. (4) and (12) for the specific case of indium, one obtains:

$$Q_\alpha = 3FAJ_{t_{1,a}} = 3FAD_{\text{In}^{3+}} \frac{[\text{In}^{3+}]_\alpha (1 + \sum \varepsilon_i K'_{i,\alpha} \xi_{i,\alpha})}{\delta} t_{1,a} = \text{slope}_\alpha t_{1,a} \quad (13)$$

where slope_α indicates the slope of the plot of charge versus deposition time at the conditions denoted by α and can be identified with

$$\text{slope}_\alpha = 3FAD_{\text{In}^{3+}} \frac{[\text{In}^{3+}]_\alpha (1 + \sum \varepsilon_i K'_{i,\alpha} \xi_{i,\alpha})}{\delta} \quad (14)$$

Since all here considered complexes are of a similar size to that of the free indium cation, we will assume

$$\varepsilon_{\text{InNO}_3} = \varepsilon_{\text{In}(\text{Ox})_n} = 1 \quad (15)$$

where the charges of the oxalate complexes are omitted.

The lability degree of indium-nitrate can be taken as equal to one because one expects a weak and labile binding in this ion pair:

$$\xi_{\text{InNO}_3} = 1 \quad (16)$$

For the sake of simplicity in the notation, we specify now the treatment assuming oxalate and nitrate complexes as the only ones relevant in solution (e.g. neglecting concomitant hydroxides, whose concentrations are negligible when compared to oxalate complexes in the experimental conditions performed here for determining the lability degrees, see e.g. Table SI-2) and ligand excess conditions.

In this case, there is a mixture of sequential complexes, each one with its own conditional ligand-excess stability constant

$$K'_{\text{In}(\text{Ox})_n, \alpha} = \frac{[\text{In}(\text{Ox})_n]_{\alpha}}{[\text{In}^{3+}]_{\alpha}} = K_{\text{In}(\text{Ox})_n} \left([\text{Ox}^{2-}]_{\alpha} \right)^n \quad (17)$$

where n is the number of oxalate ligands bound to the indium ion. We can define a collective conditional ligand-excess stability constant as:

$$K'_{\text{oxalates}, \alpha} \equiv \frac{\sum_{n=1}^{n_{\text{max}}} [\text{In}(\text{Ox})_n]_{\alpha}}{[\text{In}^{3+}]_{\alpha}} = \sum_{n=1}^{n_{\text{max}}} K'_{\text{In}(\text{Ox})_n, \alpha} = \sum_{n=1}^{n_{\text{max}}} K_{\text{In}(\text{Ox})_n} \left([\text{Ox}^{2-}]_{\alpha} \right)^n \quad (18)$$

where n_{max} is the maximum number of oxalate ligands that form a complex with indium. Charges of the complexes are omitted for simplicity. Notice that this average conditional ligand-excess stability constant depends on the conditions of the experiments (indicated by the subscript α) and is a function of the free ligand concentration.

We can also define a collective lability degree for oxalates

$$\xi_{\text{oxalates},\alpha} \equiv \frac{\sum_{n=1}^{n_{\text{max}}} \xi_{\text{In}(\text{Ox})_n} K'_{\text{In}(\text{Ox})_n,\alpha}}{K'_{\text{oxalates},\alpha}} = \frac{\sum_{n=1}^{n_{\text{max}}} \xi_{\text{In}(\text{Ox})_n} [\text{In}(\text{Ox})_n]_{\alpha}}{\sum_{n=1}^{n_{\text{max}}} [\text{In}(\text{Ox})_n]_{\alpha}} \quad (19)$$

as a kind of weighted average of the labilities of all sequential complexes with a weighting factor given by the relative abundance of each complex.

It can be easily seen that the contribution of all complexes of In with oxalates can be written as:

$$\text{slope}_{\text{oxal}} = 3FAD_{\text{In}^{3+}} \frac{[\text{In}^{3+}]_{\alpha} (1 + \xi_{\text{oxalates},\alpha} K'_{\text{oxalates},\alpha})}{\delta} \quad (20)$$

For determining the collective lability degree of oxalates, we compare the ADLC slopes from two experiments with different composition, using eqn. (14). One solution, which could be called the “reference solution”, contains just In and KNO₃ at pH 3.0 (indicated by subscript “R”, which replaces α), while the other solution has added oxalate (indicated by subscript “oxal” which will be omitted for variables that already bear the subscript “oxalates”).

By dividing eqn (14) applied to both solutions,

$$\frac{\text{slope}_{\text{oxal}}}{\text{slope}_{\text{R}}} = \frac{[\text{In}^{3+}]_{\text{oxal}} (1 + K'_{\text{InNO}_3^{2+}} + \xi_{\text{oxalates}} K'_{\text{oxalates}})}{[\text{In}^{3+}]_{\text{R}} (1 + K'_{\text{InNO}_3^{2+}})} \quad (21)$$

where $K'_{\text{InNO}_3^{2+}}$ is the same in both solutions as we are working with a fixed large concentration of KNO₃ (0.1 mol L⁻¹) in both solutions.

Previous equation relies on the values of the stability constants of oxalates, because of the presence of K'_{oxalates} . Following previous work [33], we have replaced the existing stability constants in the speciation code VMINTEQ [42] (from NIST 46.7) with those

of Vasca *et al.* [43], although it is not yet clear which set of constants is optimum for all concentrations [34]. So, we will label as “Vasca” (ξ^{Vasca}) the lability degrees computed with eqn. (22) together with Vasca *et al.*'s values of the stability constants for oxalate complexes.

Solving (from eqn (21)) for the desired lability degree of the mixture of In-oxalate complexes, one obtains:

$$\xi_{\text{oxalates}}^{\text{Vasca}} = \frac{\frac{\text{slope}_{\text{oxal}} [\text{In}^{3+}]_{\text{R}} (1 + K'_{\text{InNO}_3^{2+}}) - (1 + K'_{\text{InNO}_3^{2+}})}{\text{slope}_{\text{R}} [\text{In}^{3+}]_{\text{oxal}}} - (1 + K'_{\text{InNO}_3^{2+}})}{K'_{\text{oxalates}}^{\text{Vasca}}} = \left(\frac{\text{slope}_{\text{oxal}} [\text{In}^{3+}]_{\text{R}}}{\text{slope}_{\text{R}} [\text{In}^{3+}]_{\text{oxal}}} - 1 \right) \frac{(1 + K'_{\text{InNO}_3^{2+}})}{K'_{\text{oxalates}}^{\text{Vasca}}} \quad (22)$$

In order not to depend on the accuracy of a given set of constants (such as those of Vasca *et al.*), we derive now an alternative expression where the knowledge of these constants is not needed. As the result will depend on AGNES measurements of the free concentration, we will label the lability degree computed in this manner with the superscript “AGNES”. We start by replacing the summation in eqn (18) by a balance of indium (in non-precipitated solutions): the amount in oxalate complexes is the total indium in solution minus what is bound to nitrate (the principal complex after the ones with oxalate) and minus what is free:

$$K'_{\text{oxalates}} \equiv \frac{\sum_{n=1}^{n_{\text{max}}} [\text{In}(\text{Ox})_n]_{\text{oxal}}}{[\text{In}^{3+}]_{\text{oxal}}} = \frac{c_{\text{T,In,oxal}} - [\text{In}^{3+}]_{\text{oxal}} - [\text{InNO}_3^{2+}]_{\text{oxal}}}{[\text{In}^{3+}]_{\text{oxal}}} \quad (23)$$

Substitution in eqn. (21) and simple algebra, leads to

$$\xi_{\text{oxalates}}^{\text{AGNES}} = \left(\frac{\text{slope}_{\text{oxal}} [\text{In}^{3+}]_{\text{R}}}{\text{slope}_{\text{R}} [\text{In}^{3+}]_{\text{oxal}}} - 1 \right) \frac{(1 + K'_{\text{InNO}_3^{2+}}) [\text{In}^{3+}]_{\text{oxal}}}{c_{\text{T,In,oxal}} - [\text{In}^{3+}]_{\text{oxal}} - [\text{InNO}_3^{2+}]_{\text{oxal}}} \quad (24)$$

So, we have the possibility of computing lability degrees (either with Vasca's constants, eqn. (22) or without any specific assumption, eqn (24)) from the comparison of the measured ADLC slopes.

3.3 Reduction of the deposition time in AGNES due to the contribution of the complexes

The presence of labile complexes reduces the deposition time because they contribute to the flux [35]. In this section, we derive guidelines for the deposition times $t_{1,a}$ required in the 2 Pulse strategy of AGNES if we take into account the support of the complexes. This support of the complexes can be estimated with values of the lability degrees found with the technique ADLC (because the first sub-stage of AGNES-2P is equivalent to the first stage of ADLC). As in reference [44], one can equate the number of moles of In^0 desired inside the amalgam by the end of the first substage of AGNES-2P computed from:

- i) Multiplication of the area of the drop ($4\pi r_0^2$) by the steady-state flux under diffusion-limited conditions (see equation (11)) and by the time of accumulation ($t_{1,a}$).
- ii) Multiplication of the volume of the drop ($4\pi r_0^3 / 3$) by $[\text{In}^0]$, which is $Y [\text{In}^{3+}]$.

So,

$$4\pi r_0^2 \frac{D_{\text{In}^{3+}} \left(1 + \sum \varepsilon_i K'_i \xi_i \right) [\text{In}^{3+}]}{\delta} t_{1,a} = \frac{4}{3} \pi r_0^3 Y [\text{In}^{3+}] \quad (25)$$

Then, we can solve for $t_{1,a}$

$$t_{1,a} \approx \frac{\delta r_0 Y}{3D_{\text{In}^{3+}} \left(1 + K'_{\text{oxalates}} \xi_{\text{oxalates}} + K'_{\text{hydroxides}} \xi_{\text{hydroxides}} + K'_{\text{InNO}_3} \xi_{\text{InNO}_3} + K'_{\text{buffer}} \xi_{\text{buffer}} + \dots \right)} \quad (26)$$

We will refer to the product $K'_{\text{oxalates}} \xi_{\text{oxalates}}$ as “helping factor of oxalates”. Analogous helping factors can be identified for each complex or group of complexes. The time needed for the particular case without help of any complex is included in previous equations by just taking all $K'=0$.

When using the smallest Hg drop of the Metrohm Stand, the numerical factors can be gathered in

$$\frac{\delta r_0}{3D_{\text{In}^{3+}}} \approx \frac{2.0 \times 10^{-5} \text{ m} \times 141 \times 10^{-6} \text{ m}}{3 \times 4.363 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}} \approx 2 \text{ s} \quad (27)$$

if one takes a value of 20 μm for δ [14]. So, it turns out that a theoretical simple rule, when having no help from any complex, would be

$$t_{\text{l,a}}^{\text{theoretical}} = \frac{\delta r_0 Y}{3D_{\text{In}^{3+}}} \approx 2Y \quad (\text{s}) \quad (28)$$

However, we prefer to rely on the experimental result found in our previous work for $K'=0$ (only metal), where we needed a time $10 \times Y$ seconds for the AGNES-1P variant (see eqn. 11 in [33])

$$t_1 - t_w = 10 \times Y \quad (\text{s}) \quad (29)$$

combined with the fact that the rules for 2P with other analytes had been found to be 10 times shorter than for 1P [25, 35, 45]. So, the practical rule, for a case without ligands, is:

$$t_{\text{l,a}}^{\text{practical}} \approx Y \quad (\text{s}) \quad (30)$$

This result can also be reached if a value of 10 μm is taken for δ in eqn. (27).

So, from eqn. (26), we can use the practical general rule :

$$t_{1,a} \approx \frac{Y}{1 + K'_{\text{oxalates}} \xi_{\text{oxalates}} + K'_{\text{hydroxides}} \xi_{\text{hydroxides}} + K'_{\text{InNO}_3} \xi_{\text{InNO}_3} + K'_{\text{buffer}} \xi_{\text{buffer}} + \dots} \quad (s) \quad (31)$$

Hence, this means that the more complexes contribute to the flux, the sooner the equilibrium situation will be reached. Quantitatively, we have a formula, eqn. (31), that can be adapted to account for whatever complexes might be contributing and, thus, to obtain an estimation of the needed deposition time for the first sub-stage of AGNES. The formula needs inputs such as: i) the lability degrees of the relevant complexes, that can come from ADLC experiments or from theoretical considerations, and ii) values of the stability constants (from AGNES experiments or from the literature). In the following sections, we will measure the lability degree of indium oxalate complexes and demonstrate that these complexes play a crucial role in reducing the deposition time.

4. Lability degree of indium oxalate complexes

Table 1 presents the lability degrees of indium-oxalate mixtures at pH=3.0 and pH=4.0 computed from ADLC experiments either relying on AGNES concentrations or on the set of constants of Vasca *et al* (see last two columns in the table). As it can be shown that the lability degree is -among others- a function of the free ligand concentration [46], the obtained lability degrees are plotted against the free oxalate concentration in Fig 3. Given the dispersion of results, the lability degree of indium-oxalate complexes can be considered practically constant (despite some decrease could be predicted for increasing ligand concentration [47]). In principle, ξ_{oxalates} is expected to be a function of all conditions, pH included, because -for instance- the relative composition of the mixture of sequential complexes changes with pH (see eqn. (19)). No relevant difference in the calculated lability degree of indium-oxalate complexes is seen for pH 3.0 and pH 4.0, especially if we take into account the limited reproducibility for very similar conditions. The average of all these values of $\xi_{\text{oxalates}}^{\text{AGNES}}$ and $\xi_{\text{oxalates}}^{\text{Vasca}}$ is 0.86 and 0.97, respectively, so

the mean of all measurements yields 0.91, which will be the value used for further computations (even at higher pH values). The average value $\xi_{\text{oxalates}}=0.91$ indicates that indium oxalate complexes are very labile and this confirms the results discussed in our previous work [33], where the needed deposition time to reach equilibrium for a gain as high as $Y=3.1\times 10^5$ under large oxalate excess conditions was very short (just 25 s).

5. Determining free concentrations of indium in precipitated indium hydroxide solutions

5.1 Evolution of the free indium concentration with pH

To assess the validity of the accepted value of K_{sp} for $\text{In}(\text{OH})_3$ and illustrate the exploitation of the obtained lability degrees, the free indium concentration in precipitated solutions at various pH values was determined using AGNES technique. A large amount of total indium was added to the voltammetric cell and the pH was set to selected values in the range 4 to 6. AGNES experiments were only started when the precipitate was evident from visual inspection. The precipitation process was completed very slowly (sometimes it took longer than one week). To induce the precipitation, solid $\text{In}(\text{OH})_3$ from other precipitated solutions at the same pH was added in some cases. Adding solid $\text{In}(\text{OH})_3$ to the new solution did not change the free concentration of indium inside the solution. Details on the probed systems and applied strategies are given in Table **SI-1** of the Supporting information.

The regression line for a large collection of blanks (i.e. with just background electrolyte) at various gains yields the blank charge (Q_b):

$$Q_b = 2.25 \times 10^{-10} \log(Y) \quad (32)$$

which is reasonable for the main component of the blank being the capacitive one which is proportional to the potential jump [48]. Even for the largest used gains (say $Y=5.7\times 10^7$), Q_b was less than 3 nC and the estimated limit of quantification was of the order of 4 nC, so desired faradaic charges above 30 nC were aimed as safe values sufficiently above the blank value (which was, in any case, subtracted from the total recorded charge).

As the free concentration of indium at each pH could be initially estimated with NIST database, a guideline for Y was found from eqn. (3), an η_Q value of 3.4×10^{-3} C mol L⁻¹ [33] and the desired faradaic charge.

Deposition times for the first trials at each pH followed from the application of the rules (29) for 1P and (30) for 2P (for cases without added ligands). In general, the strategy 2P was used when 1P was considered to require too long deposition times. If needed, new times (and gains) were assayed in accordance with the previously obtained results, until the equilibrium plateau (above a minimum charge of 30 nC) was clearly identified in the trajectory. For instance, if $t_{1,a}$ in a 2P experiment is too long, then too much In⁰ accumulates in the amalgam, producing an “overshoot” (more accumulation than the one aimed at, i.e. obtaining a concentration above the product $Y\times[\text{In}^{3+}]$)[35]. In this case, if one wants to keep a modest $t_{1,b}$ to reach equilibrium, one can either increase Y (if the already used deposition times are not too long) or decrease $t_{1,a}$ (if the already retrieved charge is not too low). The other option is to increase $t_{1,b}$, as much as needed, because the stripped charges progressively “relax” towards the equilibrium corresponding to the applied E_1 and will eventually attain equilibrium. Examples of overshoots can be seen in trajectories plotted in figs 4, 6, SI-2 to SI-4 and SI-6.

For pH 4.0, 4.4 and 5.0, the gains and deposition times were acceptable (see Table SI-1). However, at pH 5.5, the predicted free concentration of indium is around 3.7×10^{-11} mol L⁻¹ which leads, via eqn. (3), to a gain which we round off to 5.0×10^5 . This large gain, implies –in the strategy 2P, by applying eqn. (30) when there is absence of complexes contribution - a deposition time of 5×10^5 s, which is almost 6 days. As discussed in section 3.3 above and it is well known in AGNES literature [33-35], for a fixed free metal concentration, the complexes contribute to shorten the deposition time, but they do not alter the equilibrium value.

Thus, the proposed strategy here is to add a moderate amount of ligand to the precipitated solution. Indeed, eqn. (1) can be re-arranged as

$$[\text{In}^{3+}] = \frac{K_{\text{sp}}}{\gamma_{\text{In}^{3+}} \{\text{OH}^-\}^3} \quad (33)$$

where $\gamma_{\text{In}^{3+}}$ is the activity coefficient of the cation In^{3+} . This equation will hold for any solution in equilibrium with precipitated $\text{In}(\text{OH})_3$ (thus, the need of the addition of ligand being moderate as not to dissolve all the precipitated $\text{In}(\text{OH})_3$). K_{sp} , $\gamma_{\text{In}^{3+}}$ and $\{\text{OH}^-\}$ are fixed, if we work at constant temperature, ionic strength and pH. So, $[\text{In}^{3+}]$ will be fixed, even if there are added complexes (and a different speciation).

This non-impact on the free concentration can be seen, for instance, from the comparison between AGNES measurements around pH 5 with MES (Fig SI-2) and without MES (Figures SI-3 and SI-4): in precipitated solution the free ion concentration is fixed regardless of the amount of ligands (such as MES in this case). Notice that the stability constant of In-MES is neither known nor needed.

As indium-oxalate complexes have been shown to be extremely labile (section 4) and mobile [33], the addition of oxalate to the precipitated solution can help in reducing the needed deposition time without affecting the free concentration of indium.

For instance at pH close to 5.5, a total concentration of oxalate $1.35 \times 10^{-4} \text{ mol L}^{-1}$ was added (see Fig 4). According to VMINTEQ with NIST database, this leads to

$$K'_{\text{oxalates}} = \frac{[\text{In}(\text{Ox})_2^-] + [\text{In}(\text{Ox})_3^{3-}] + [\text{InOx}^+]}{[\text{In}^{3+}]} = \frac{3.56 \times 10^{-7} + 8.43 \times 10^{-9} + 2.03 \times 10^{-8}}{3.56 \times 10^{-11}} = 10815 \quad (34)$$

so that the helping factor $K'_{\text{oxalates}} \xi_{\text{oxalates}} = 10815 \times 0.91 = 9841$ indicates a reduction of time of the order of 10000-fold. Thus, eqn.(31) for a gain of half a million yields:

$$t_{1,a} \approx \frac{Y}{K'_{\text{oxalates}} \xi_{\text{oxalates}}} = \frac{5 \times 10^5}{9841} = 51 \text{ s} \quad (35)$$

The trajectory (or series) for $t_{1,a}=50 \text{ s}$ (squares in Fig 4) shows a complete stabilization even for very short relaxation times such as $t_{1,b}=50 \text{ s}$, confirming the suitability of the guideline provided by the rule (31). The trajectories for $t_{1,a}=75 \text{ s}$, for $t_{1,a}=30 \text{ s}$ or for 1P (i.e. $t_{1,a}=0$) are also stabilized at $t_{1,b}=250 \text{ s}$, which indicates that the rule does not preclude other values (close to the one yielded by the equation) to be also suitable, especially when the high contribution of the complexes also renders the relaxation process very efficient. In Fig 4, we notice that $t_{1,a}=250$ and 500 s produce huge overshoots, so that they illustrate another property of the 2P strategy: if $t_{1,a}$ is too long, the relaxation towards equilibrium can be even slower than just using 1P.

As a confirmation that the $[\text{In}^{3+}]$ retrieved with this new strategy of adding oxalate is correct, we also performed AGNES experiments around this pH 5.5 without the oxalate addition. The results are shown in Fig 5 which yield $[\text{In}^{3+}]=20.6 \text{ pmol L}^{-1}$, in good agreement with the one obtained with the addition of oxalate (26.6 pmol L^{-1}), taking

into account the (relatively large) impact of the unavoidable small pH variations (discussed below). In the case of Fig 5, relatively short deposition times ($t_{1,a}=1000$ s plus $t_{1,b}=100$ s) are enough to reach equilibrium, which –compared to the initially estimated $t_{1,a}=5\times 10^5$ s with no complex contribution- suggests that indium hydroxides in solution (with a computed K' of 2239) must be quite labile. So, at higher pH, a very refined calculation of $t_{1,a}$ should take into account the hydroxides contribution.

Another example of the usefulness of adding oxalate and of the rule (31), this time at pH=5.6, can be seen in Fig 6. In this case, NIST 46.7 predicts $[\text{In}^{3+}]$ around 15 pM. A suitable gain for this low concentration is $Y=5.0\times 10^6$. If no complex is taken into account, formula (29) predicts that using 1P one would need more than 578 days to measure free indium concentration. Table SI-2 details the speciation of the solution after the addition of oxalate. The helping factor of oxalate is

$K'_{\text{oxalates}} \xi_{\text{oxalates}} = 12123 \times 0.91 \approx 11032$. Using eqn. (31), a recommended initial time is

$$t_{1,a} \approx \frac{Y}{K'_{\text{oxalates}} \xi_{\text{oxalates}}} \approx \frac{5 \times 10^6}{11032} = 453 \text{ s} \quad (36)$$

Trajectories for $Y=5.0\times 10^6$ in Fig SI-6 indicate undershoot for $t_{1,a}=300$ s and a clear overshoot for $t_{1,a}=800$ s. This suggests an experimentally optimum $t_{1,a}$ value around 500 s (blue squares in Fig SI-6) quite close to the theoretically predicted one of 453 s.

At pH 6, if we take into account the helping factor due to the oxalate addition ($K'_{\text{oxalate}} = 13930$ and $\xi_{\text{oxalate}} = 0.91$), the required $t_{1,a}$ would be 4496 s. Fig SI-7 shows that, at pH=6.0, adding oxalate helped to determine free concentration of indium very fast, just with using $t_{1,a}=800$ s. So, our results suggest that reaching equilibrium in 800 s is due to the help of the contributions of complexes with oxalate, hydroxide, nitrate and MES.

Fig 7 gathers (with markers) all measurements at different pH values (also reported in Table 2). The predictions of NIST 46.7 using VMINTEQ follow (see black line) the expected linear behaviour derived from taking logarithms in the equation of the solubility product, eqn. (1),

$$\log \{ \text{In}^{3+} \} = \log (K_{\text{sp}}) + 3 \text{pOH} \quad (37)$$

Splitting the activity as a product of concentration times activity coefficient, and recalling that $\text{pH} + \text{pOH} = 14$ at 25°C ,

$$\log [\text{In}^{3+}] = -\log (\gamma_{\text{In}^{3+}}) + \log (K_{\text{sp}}) + 3 (14 - \text{pH}) = \text{constant} - 3 \text{pH} \quad (38)$$

Fig 7 indicates that the free concentration of indium measured by AGNES reasonably agrees with NIST predictions (see proximity of blue markers to the black line). The separations of the experimental values from the theoretical ones are not systematic, so that these differences can be attributed to experimental inaccuracies such as uncertainties in the pH measurement. Indeed, small variations in pH have a dramatic impact on the free concentration. In precipitated solutions, it follows from eqn. (38) that the free concentration of indium decreases by a factor of 2, when the pH of a solution increases by just 0.1 pH units.

5.2 Evolution of free indium concentration with time

We considered whether aging of the precipitates (at a fixed pH) might have an effect on the free indium concentration in equilibrium with the solid phase. As can be seen in Fig 8, once the precipitation process is completed, the free concentration is essentially the same (and so K_{sp}) within the probed elapsed time (up to 6 days). Moreover our results reveal that probably the difference between the K_{sp} of indium for the fresh and aged

precipitated solutions which was reported in the work of Orlov *et al.* [6], could be due to not enough elapsed time for the precipitation process to be completed.

6. Conclusions

Performing ADLC experiments provided an adequate way to calculate the lability degrees of indium-oxalate complexes (see eqns. (22) or (24)) and, thus, find proper guidelines for $t_{1,a}$ in AGNES measurements (see eqn.(31)). The high lability and mobility of these complexes justify their capability in shortening the predicted deposition times remarkably (e.g. by a factor 10^4). Aging seems negligible in a scale of days, once precipitation is clear (see section 5.2 and Fig 8). Additionally, the results demonstrated that AGNES measurements of precipitated solutions were very close to the predictions of the NIST 46.7, thus lending support to the value of K_{sp} adopted there ($\log K_{sp}=-39.9$). Finally, pmol L^{-1} concentrations of free indium in precipitated solutions were successfully determined.

ADLC can be used in the future to find lability degrees of complexes of ligands with metals such as Zn, Cd, Pb, etc. and of complexes of In with ligands other than oxalate. Lability degrees determined with ADLC should be compared with those obtained with other techniques (having similar space-time scale) or those derived from theoretical considerations. The strategy of forming very labile complexes to dramatically shorten the required deposition times can be extended to other systems with solid phases (e.g. precipitates or nanoparticles) where the relevant free ion concentrations can be measured by AGNES.

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7. References

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8. Tables

Table 1: Lability degree of indium-oxalate complexes from ADLC experiments using the measurements of AGNES or the predictions of Vasca. $\xi_{\text{oxalates}}^{\text{AGNES}}$ refers to the lability degree calculated using eqn.(24), while $\xi_{\text{oxalates}}^{\text{Vasca}}$ is calculated using eqn. (22). Number within parentheses indicates standard deviation and refers to the last significant digit.

pH	$c_{\text{T,In}}$ ($\mu\text{mol L}^{-1}$)	$c_{\text{T,oxalate}}$ ($\mu\text{mol L}^{-1}$)	$\log [\text{Ox}^{2-}]$ (mol L^{-1})	Slope ADLC (nA)	$[\text{In}^{3+}]^{\text{AGNES}}$ ($\mu\text{mol L}^{-1}$)	$[\text{In}^{3+}]^{\text{Vasca}}$ ($\mu\text{mol L}^{-1}$)	$\xi_{\text{oxalates}}^{\text{AGNES}}$	$\xi_{\text{oxalates}}^{\text{Vasca}}$
Ref pH=3.0	0.595	0	-	1.03	0.470(8)	0.49	-	-
4.0	0.545	1.94	-6.144	0.924	0.08(9)	0.092	1.07	1.0
4.0	0.543	18.8	-5.068	0.923	$5.74(3)\times 10^{-3}$	5.2×10^{-3}	0.80	1.0
4.0	0.542	103	-4.314	0.943	$2.68(2)\times 10^{-4}$	2.4×10^{-4}	0.92	0.96
Ref pH=3.0	0.597	0	-	0.977	0.396(6)	4.9×10^{-7}	-	-
4.0	0.542	101	-4.325	0.836	$2.43(4)\times 10^{-4}$	2.6×10^{-4}	0.73	0.90
4.0	0.536	201	-4.021	0.838	$5.91(1)\times 10^{-5}$	6.6×10^{-5}	0.73	0.91
Ref pH=3.0	0.586	0	-	0.988	0.480(8)	0.48	-	-
4.0	0.548	10.1	-5.350	0.880	0.0192(7)	0.013	0.93	1.0
4.0	0.533	10.04	-5.354	0.775	0.016(1)	0.012	0.84	0.83
4.0	0.533	20.4	-5.033	0.880	$6.30(2)\times 10^{-3}$	4.3×10^{-3}	0.94	0.95
4.0	0.523	200	-4.021	0.794	$6.2(2)\times 10^{-5}$	6.4×10^{-5}	0.86	0.87
Ref pH=3.0	0.592	0	-	0.913	0.440(9)	0.49	-	-
4.0	0.548	20.1	-5.043	0.880	$7.09(4)\times 10^{-3}$	4.7×10^{-3}	0.91	1.0
4.0	0.547	100	-4.325	0.799	$2.35(6)\times 10^{-4}$	2.6×10^{-4}	0.82	0.91
4.0	0.545	100	-4.325	0.767	$2.8(3)\times 10^{-4}$	2.6×10^{-4}	0.79	0.88
4.0	0.544	203	-4.021	0.766	$5.3(1)\times 10^{-5}$	6.7×10^{-5}	0.79	0.88
Ref pH=3.0	0.598	0	-	1.03	0.415(6)	0.49	-	-
3.0	0.600	10.9	-5.990	1.08	0.100(1)	0.085	1.0	1.0
3.0	0.590	20.1	-5.715	1.13	0.0479(9)	0.043	0.99	1.0
3.0	0.588	102	-5.001	0.973	$3.71(5)\times 10^{-3}$	4.7×10^{-3}	0.78	0.91
3.0	0.585	203	-4.711	0.940	$1.16(6)\times 10^{-3}$	1.5×10^{-3}	0.76	0.89
3.0	0.578	200	-4.714	0.998	$9.8(2)\times 10^{-4}$	1.5×10^{-3}	0.81	0.95



pH	$c_{T,In}$ ($\mu\text{mol L}^{-1}$)	$c_{T,oxalate}$ ($\mu\text{mol L}^{-1}$)	$\log [Ox^{2-}]$ (mol L^{-1})	Slope ADLC (nA)	$[In^{3+}]_{AGNES}$ ($\mu\text{mol L}^{-1}$)	$[In^{3+}]_{Vasca}$ ($\mu\text{mol L}^{-1}$)	 AGNES oxalates	 Vasca oxalates
Ref pH=3.0	0.600	0.00	-	1.075	0.420(6)	0.49	-	-
3.0	0.600	14.9	-5.860	1.09	0.063 (2)	0.064	0.94	1.0
3.0	0.595	24.0	-5.641	1.04	0.037(8)	0.037	0.85	0.95
3.0	0.593	50.8	-5.310	1.01	0.011(2)	0.014	0.79	0.92
3.0	0.592	106	-4.983	1.11	$3.41(8)\times 10^{-3}$	4.5×10^{-3}	0.86	1.0
3.0	0.591	208	-4.685	1.16	$9.9(4)\times 10^{-4}$	1.4×10^{-3}	0.90	1.1
3.0	0.585	475	-4.332	1.062	$2.3(1)\times 10^{-4}$	3.1×10^{-4}	0.83	0.98
3.0	0.571	986	-4.022	1.00	$4.8(3)\times 10^{-5}$	7.5×10^{-5}	0.80	0.94
3.0	0.569	981	-4.003	1.05	$5.8(1)\times 10^{-5}$	6.8×10^{-5}	0.85	1.0

Table 2: Free indium concentrations from AGNES results and predictions of VMINTEQ in precipitated solutions. Number within parentheses indicates standard deviation and refers to the last significant digit.

pH	nominal $c_{T,In}$ ($\mu\text{mol L}^{-1}$)	$[\text{In}^{3+}]^{\text{AGNES}}$ (nmol L^{-1})	$[\text{In}^{3+}]^{\text{NIST 46.7}}$ (nmol L^{-1})	$c_{T,MES}$ (mol L^{-1})	$\log [\text{In}^{3+}]^{\text{AGNES}}$ (mol L^{-1})	$\text{Log} [\text{In}^{3+}]^{\text{NIST 46.7}}$ (mol L^{-1})
4.0	5.02	$1.10(2) \times 10^3$	1000	-	-5.95	-5.97
4.0	5.02	$1.1(2) \times 10^3$	980	-	-5.95	-6.00
4.4	158	88.8 (3)	60.0	-	-7.05	-7.22
4.4	158	111 (3)	68.2	-	-6.95	-7.16
5.0	20.6	1.65 (8)	0.77	0.0108	-8.80	-9.11
5.0	100	1.95 (2)	1.00	-	-8.709	-9.00
5.0	100	1.9 (2)	1.10	-	-8.73	-8.96
5.5	960	0.015 (2)	0.0375	-	-10.83	-10.43
5.5	960	0.0327(3)	0.0327	-	-10.48	-10.49
5.5	960	2.06×10^{-2} (1)	0.0251	-	-10.69	-10.60
5.6	37.1	6.94×10^{-3} (2)	0.0147	-	-11.15	-10.83
6.0	140	1.37×10^{-3} (2)	1.06×10^{-3}	-	-11.86	-11.97

9. Figures

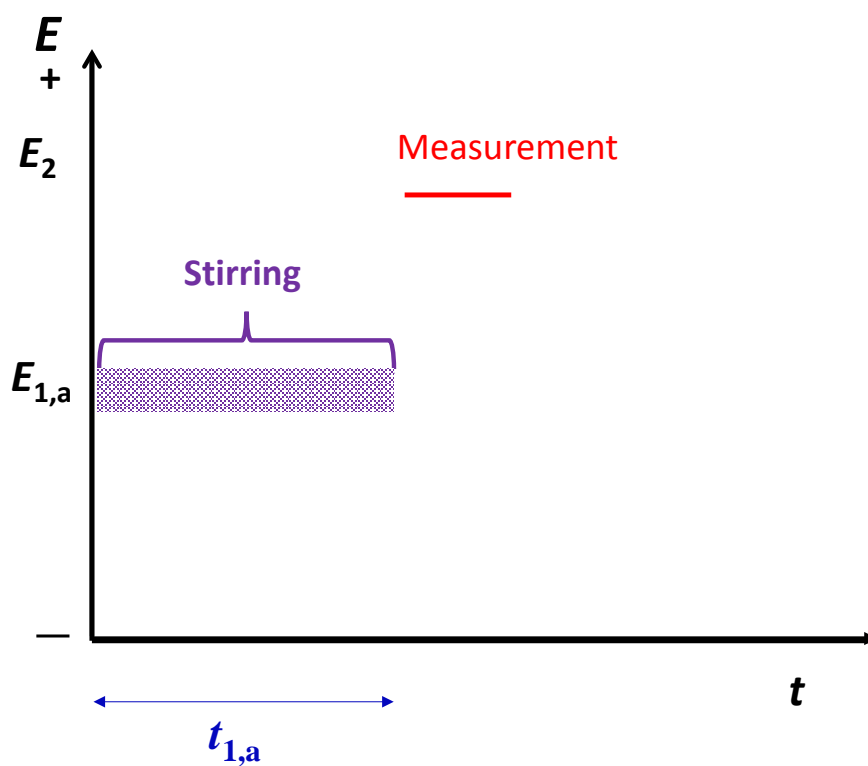


Fig 1: Schematic representation of the ADLC potential program. $t_{1,a}$ represents the accumulation time with stirring and deposition potential $E_{1,a}$ (under diffusion limited conditions), in parallel to the first sub-stage of the variant AGNES-2P. The measurement in ADLC is performed by quantifying the accumulated charge in the stripping stage.

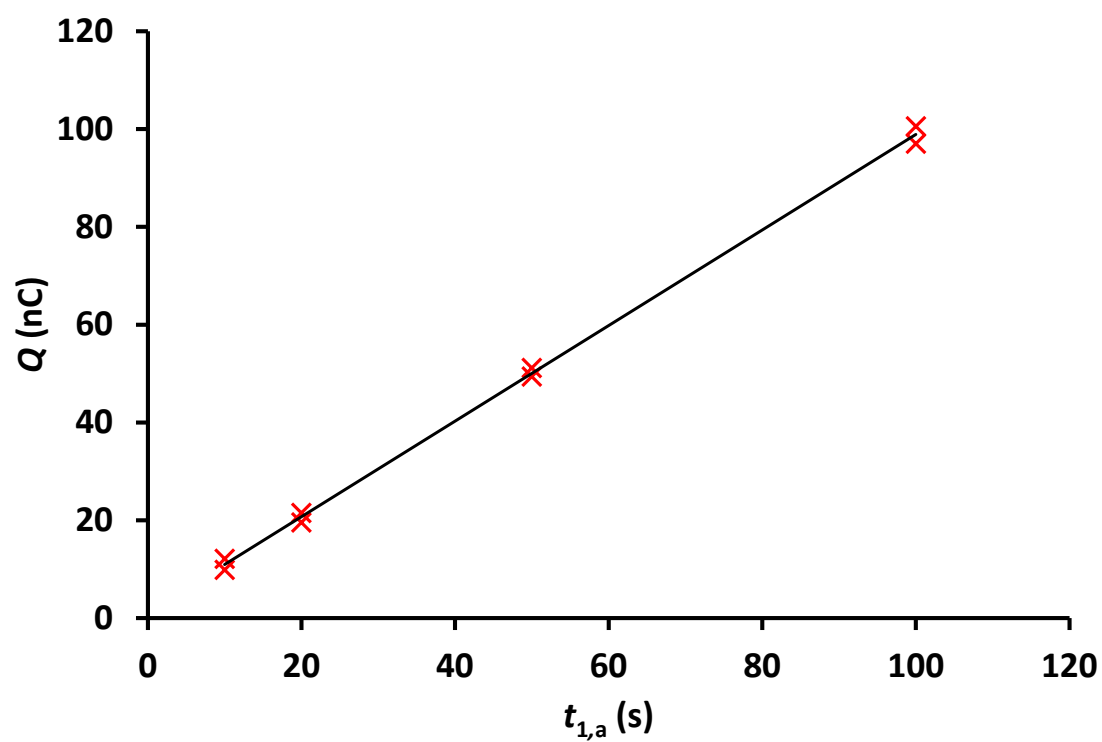


Fig 2: ADLC experiments at pH = 3.0 with $c_{T,In} = 0.600 \mu\text{mol L}^{-1}$ indicating the predominance of the steady-state regime along the deposition stage. $E_{1,a} = -0.692 \text{ V}$; $E_2 = 0.450 \text{ V}$. The resulting regression equation was $y = 0.98x + 1.18$.

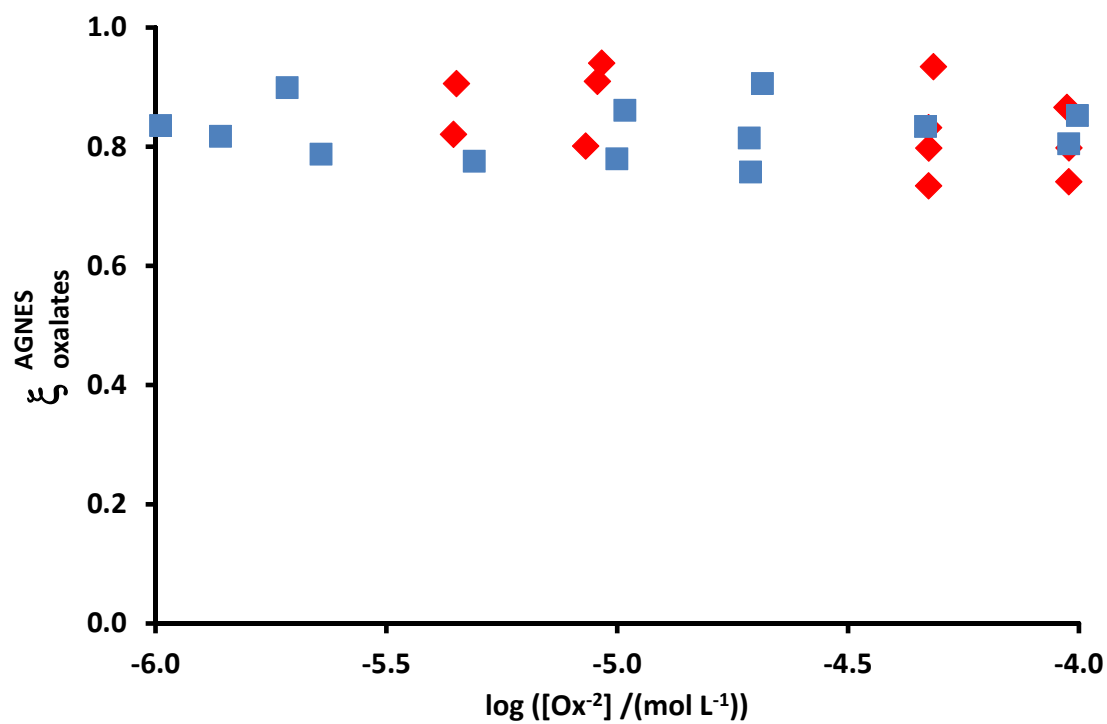


Fig 3: Lability degree of indium-oxalate complexes computed from the ADLC experiments specified in table 1 based on AGNES measurements and eqn. (24). Blue squares stand for determinations of ξ at pH=3.0, while the red diamonds stand for measurements at pH=4.0.

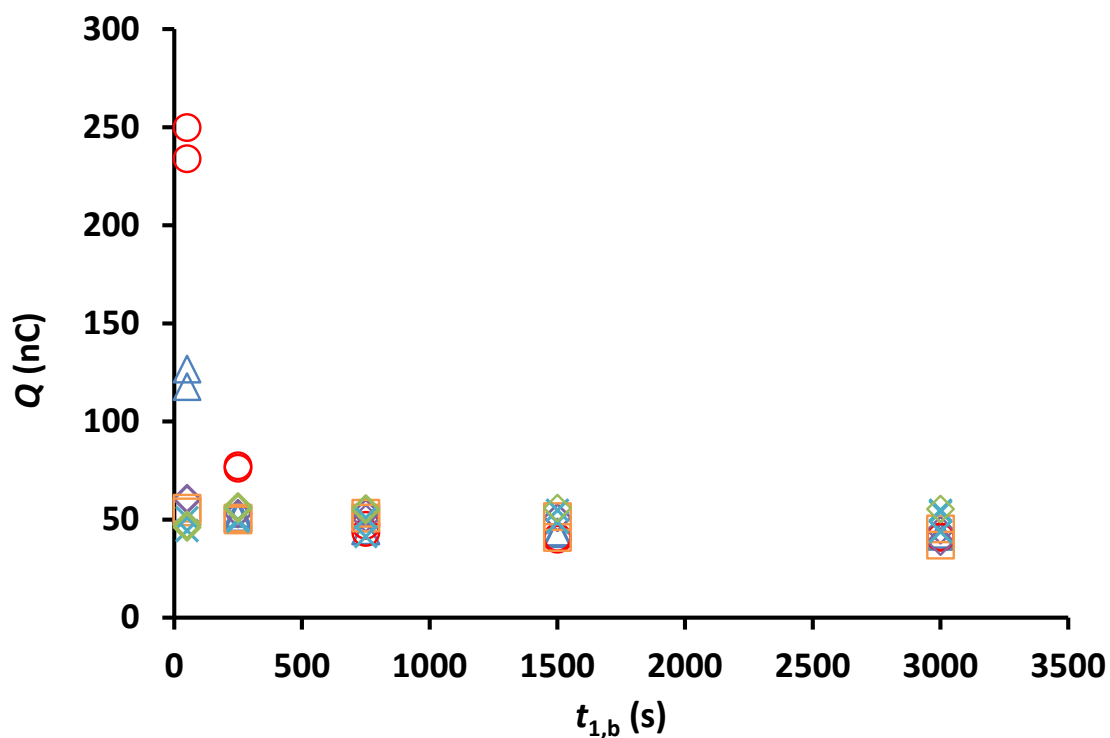


Fig 4: Trajectories showing the dramatic reduction in needed deposition times (due to the contribution of oxalate complexes) and the achievement of equilibrium situation when using optimized $t_{1,a}$ -values (close to the guideline obtained using the lability degree determined with ADLC). Blue crosses, orange squares, purple diamonds, blue triangles and red circles correspond to $t_{1,a}$ = 30 s, 50 s, 75 s, 250 s and 500 s, respectively. Green diamonds stand for 1 P measurements. Experiments were done in presence of large excess of precipitated $\text{In}(\text{OH})_3$. Nominal total concentration of indium: $5.00 \times 10^{-5} \text{ mol L}^{-1}$, total oxalate concentration: $1.35 \times 10^{-4} \text{ mol L}^{-1}$. $c_{\text{T,MES}}=0.01 \text{ mol L}^{-1}$. $\text{pH}= 5.5$. $Y=5.0 \times 10^5$.

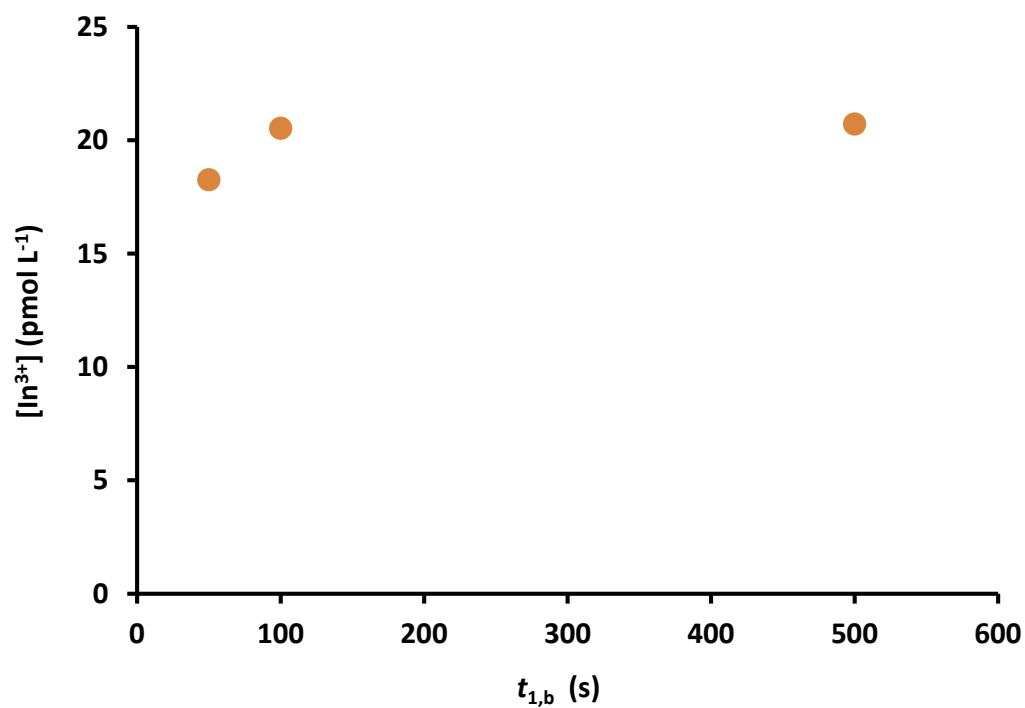


Fig 5: 2P trajectory showing the achievement of equilibrium from $t_{1,b}=100$ s onwards in a case without oxalate. pH=5.55 with nominal total indium concentration in the dispersion of $960 \mu\text{mol L}^{-1}$, $Y = 5.0 \times 10^5$, $t_{1,a}=1000$ s.

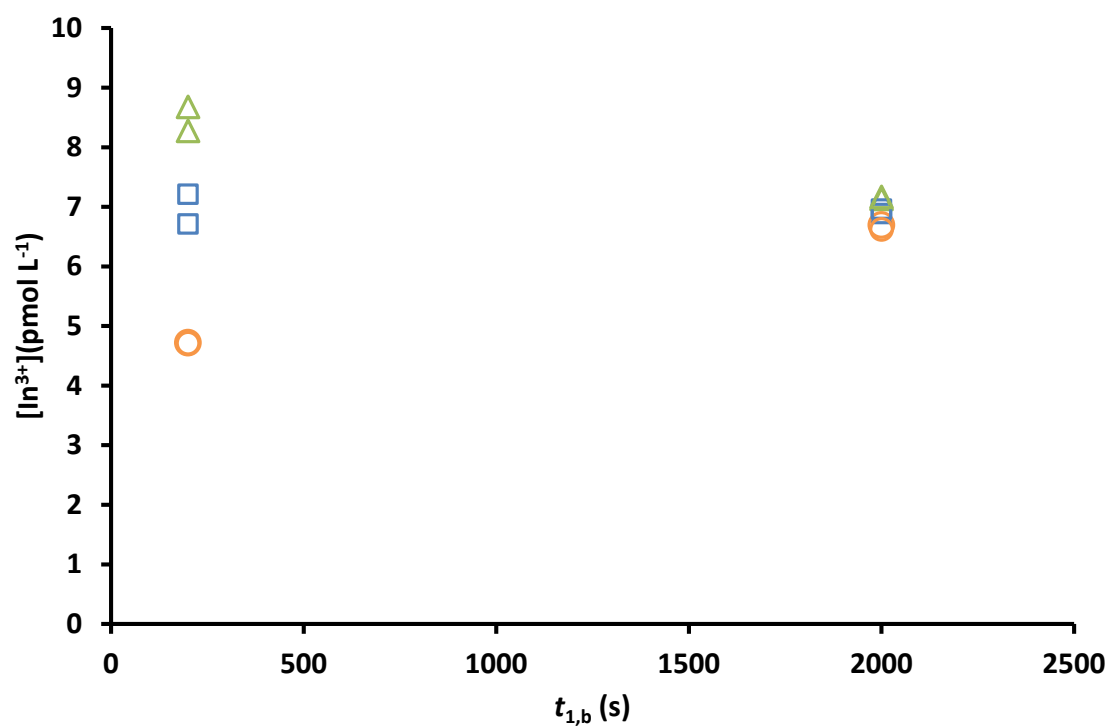


Fig 6: 2P trajectories showing the achievement of equilibrium situations when using optimized $t_{1,a}$ -values close to the guideline obtained using the lability degree determined with ADLC. Orange circles, blue squares and green triangles stand for $t_{1,a}=300$ s, 500 s and 800 s, respectively. $Y= 5.0 \times 10^6$, $pH= 5.6$, nominal total indium in the dispersion $37.1 \mu mol L^{-1}$, $c_{T,Ox}=142 \mu mol L^{-1}$ and $c_{T,MES}=0.0100 mol L^{-1}$.

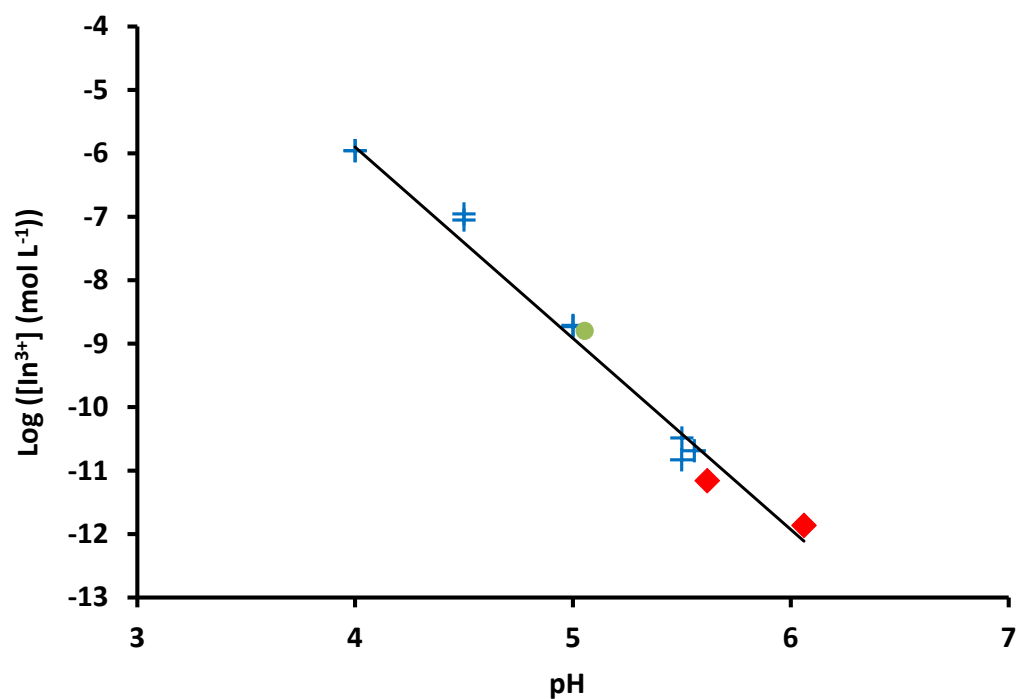


Fig 7: Free indium concentrations in precipitated solutions at different pH values. Markers stand for experimental determinations, while the black line indicates the prediction of VMINTEQ using the database NIST 46.7. Blue cross shows the results of AGNES without added oxalate, while the red diamond markers show the results with oxalate and MES, and green circle stands for AGNES measurement only with added MES.

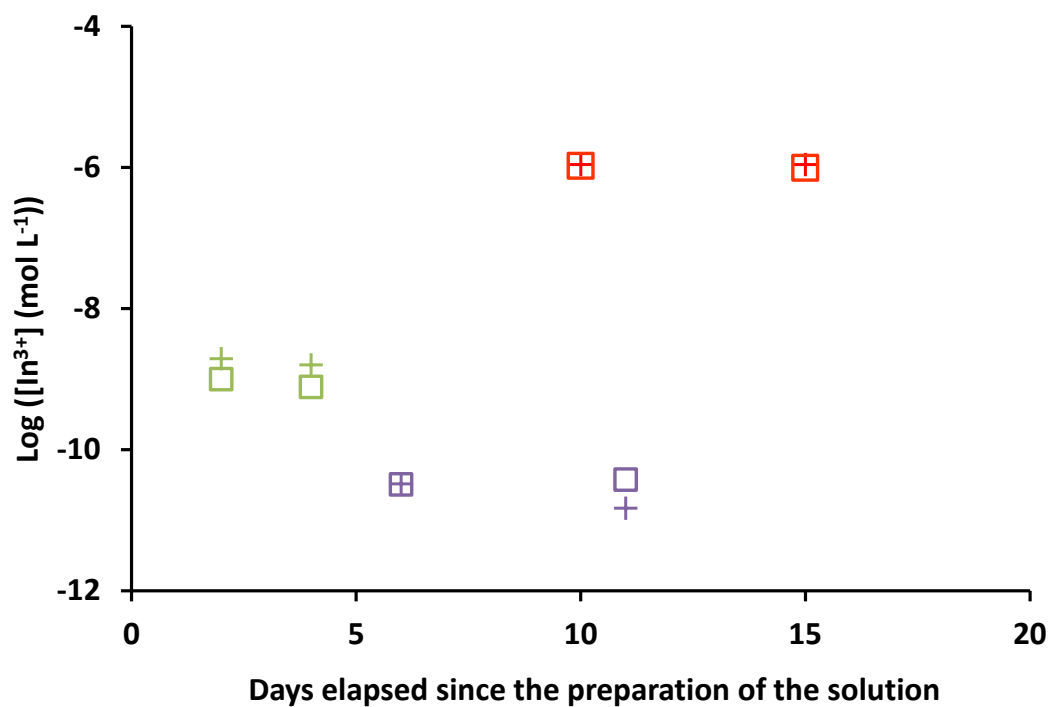


Fig 8: Free indium concentration measured in aging precipitated solutions, showing a negligible evolution with time (at each fixed pH). Square symbols stand for VMINTEQ predictions and cross symbols indicate AGNES measurements. Red, green and purple square symbols stand for the measurements at pH=4.0 (see fig. SI-1), at pH=5.0 (see figures SI-2, SI-3 and SI-4) and at pH=5.5 respectively (see figs. 5 and SI-5).