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Electrochemical activity of various types of aqueous In(III) species at a mercury electrode

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Electrochemical activity of various types of aqueous In(III) species at a mercury electrode

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Abstract

An interpretation framework is presented which provides a straightforward means to characterise the electrochemical reactivity of aqueous ions together with their various hydrolysed counterparts. Our novel approach bypasses the more laborious strategy of solving rigorously, for all relevant species, the complete set of Butler Volmer equations coupled to diffusion differential equations. Specifically we consider the spatial variable via a Koutecky-Koryta type of differentiation between nonlabile and labile zones adjacent to the electrode. The theory is illustrated by an assessment of the electrochemical reactivity of aqueous In(III) species based upon proper comparison between relevant time scales of the involved interfacial processes, i.e. diffusion, (de)protonation of inner-sphere water, dissociation/release of H₂O and OH⁻, and electron transfer. The analysis reveals that whilst all In(III) species are labile on the experimental timescale with respect to (de)protonation and (de)hydration, there are large differences in the rates of electron transfer between In(H₂O)₆³⁺ and the various hydroxy species. Specifically, in the case of In(H₂O)₆³⁺ the rate of electron transfer is so slow that it replaces the traditional Eigen rate-limiting water release step in the overall passage from hydrated In³⁺ to its reduced metallic form; in contrast the In(III) hydroxy species display electrochemically reversible behaviour.

Keywords electrochemical irreversibility, indium, SSCP, reaction layer, lability

Declarations

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36 Introduction

37 The electrochemical features of In(III) in aqueous solution are strongly pH-dependent. In(III) readily
38 hydrolyses at low pH: see ref [1] for a critical review of the literature on the hydrolysis constants. Literature
39 from the 1960s evidences that voltammetric waves recorded for free $\text{In}(\text{H}_2\text{O})_6^{3+}$ with a dropping mercury
40 electrode at a pH sufficiently low to suppress hydrolysis, show a drawn-out electrochemically irreversible
41 wave for the $\text{In}(\text{H}_2\text{O})_6^{3+}$ species with halfwave potential, $E_{1/2}$, of -0.95 V (vs. saturated calomel electrode
42 (SCE)); as the pH is increased an electrochemically reversible diffusion-controlled wave with $E_{1/2}$ of -0.55 V
43 (vs. SCE) is observed [2-4]. These observations suggest that In(III) hydroxy species are the predominant
44 electroactive contributors to the electrodic reduction current [5-7].

45
46 In recent years, the widespread use of so-called technology relevant elements such as indium will potentially
47 lead to increasing concentrations of such elements in the environment [8]. This situation has motivated efforts
48 to apply electroanalytical techniques to the determination of In(III) species in aqueous media. Some of these
49 have made the assumption that $\text{In}(\text{H}_2\text{O})_6^{3+}$ is the exclusively measured species [9-11], which at first sight
50 seems questionable in light of its established electrochemical irreversibility.

51
52 The potential for increasing amounts of In(III) to be released into the environment also calls for evaluation
53 of its bioavailability and potential ecotoxicological effects [12-15]. In the case of algae, the concentration of
54 the $\text{In}(\text{H}_2\text{O})_6^{3+}$ species was shown to be a poor predictor of biouptake [16]. A proper understanding of the
55 (electro)chemical reactivity of In(III) is fundamental to characterising and predicting its bioavailability and
56 potential toxicity [17].

57
58 A rigorous analysis of the overall In(III) reduction process in aqueous media requires consideration of the
59 electrochemical activity of the various trivalent In species. The overall electrochemical activity derives from
60 the rates of electron transfer of each species (electrochemical reversibility), the rates of dehydration or even
61 mere deprotonation of H_2O in the inner-hydration sphere of each ion, as well as the lability of each species
62 on the effective timescale of the measuring methodology. For example, the reported greater electrochemical
63 reactivity of In(III) hydroxy species goes in hand with their enhanced dehydration rates as compared to that
64 of the aqueous ion $\text{In}(\text{H}_2\text{O})_6^{3+}$ [18]. Similarly, the ability of coordinated halides to facilitate In(III)
65 electroreduction is ascribed to their labilizing effect on the remaining inner-sphere water molecules [4, 19-
66 21]. The pH dependent features of the voltammetric waves for In(III) further suggest that the irreversibility
67 of $\text{In}(\text{H}_2\text{O})_6^{3+}$ reduction by a mercury electrode is so strong that its rate of dehydration is fast compared to
68 that for electron transfer. Herein we develop a conceptual framework to describe the electrochemical
69 reactivity and chemodynamic features of aqueous In(III) species. The treatment includes accounting for their
70 rates of electron transfer together with their rates of formation and dissociation. The theoretical concepts are

71 successfully illustrated by experimental data obtained by stripping chronopotentiometry at scanned
72 deposition potential (SSCP) [22-24].

73

74 Theory

75 In the bulk aqueous medium, the very fast exchange rate of protons warrants true equilibrium to be established
76 between the various types of In(III) species (see Table 1 and elaboration below). Thus, maintenance of
77 equilibrium over a steady-state diffusion layer adjacent to the interface between a macroelectrode and the
78 aqueous medium is also expected (see below). Differences in reactivity of the In(III) species, according to
79 their pertaining relative rates of electron transfer, dehydration and/or (de)protonation, will show up in the
80 reaction layer, i.e. the zone adjacent to the electrode/medium interface within which equilibrium is no longer
81 maintained between the electroactive and electroinactive forms of the various In(III) species. In *all* these
82 types of elementary processes, any In(III) species with a significant reactivity in *all* of them is inherently
83 electroactive.

84

85 Reaction layer and lability considerations for the aqueous In(III) system

86 Computation of the reaction layer thickness during electroodic reduction of In(III) and ensuing analysis of the
87 lability characteristics of the various In(III) species requires knowledge of the thermodynamic and kinetic
88 features of their complexes with H₂O. In aqueous solution, In(III) has 6 water molecules in its inner-hydration
89 sphere [25, 26]. To our knowledge, there are no reliable published data on the dehydration rate constants, k_w ,
90 for In(III) species [27]; for $\text{In}(\text{H}_2\text{O})_6^{3+}$ a tentative value for k_w of the order of 100 s^{-1} has been indicated [28].
91 As a proxy, we proceed using the k_w values reported for Fe(III) species as a kind of guide, i.e.: $k_w(\text{Fe}(\text{H}_2\text{O})_6^{3+}) = 200 \text{ s}^{-1}$;
92 $k_w(\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}) = 10^5 \text{ s}^{-1}$; $k_w(\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^+) = 10^7 \text{ s}^{-1}$; $k_w(\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3^0) = 10^9 \text{ s}^{-1}$ [18]. In
93 support of this approximation, we note that the k_w for Fe^{3+} is of the same order of magnitude as that reported
94 for Ga^{3+} which is in the same periodic group as In [18]. These k_w values correspond to the dissociation rate
95 constant, k_d , for the dehydration reaction, i.e. the release of one H₂O (or OH⁻).

96

97 For the thermodynamic stability constant of the hydrated/hydroxy entities we use the values for the outer-
98 sphere association, K^{os} ($\text{m}^3 \text{ mol}^{-1}$) computed on the basis of point charges [29], while accounting for the multi-
99 site nature of the di- and tri-hydroxy entities [30-32]. Computations were performed for an ionic strength of
100 100 mol m^{-3} (with a corresponding Debye layer thickness $\kappa^{-1} = 9 \times 10^{-10} \text{ m}$), a charge separation distance of
101 0.5 nm within the ion pair, and $T = 293 \text{ K}$. Values are given in Table 1.

102

103

104 **Table 1: k_w , k_a and K^{os} values for aqueous In(III) species, $I = 100 \text{ mol m}^{-3}$**

In(III) species	$k_w = k_d / \text{s}^{-1}$ ^(a)	$K^{os} / \text{m}^3 \text{mol}^{-1}$	$k_a = k_w K^{os} / \text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
$\text{In}(\text{H}_2\text{O})_6^{3+}$	200	3.15×10^{-4}	0.063
$\text{In}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	10^5	5.18×10^{-3}	518
$\text{In}(\text{H}_2\text{O})_4(\text{OH})_2^+$	10^7	0.11	1.1×10^6
$\text{In}(\text{H}_2\text{O})_3(\text{OH})_3^0$	10^9	2.07	2.07×10^9

105 ^(a) the k_w values are those reported for Fe(III); see text for details

106

107 *(De)protonation kinetics*

108 The dynamic complexation features of the aqueous In(III) species are concerned with the
 109 protonation/deprotonation rates of water in the inner hydration sphere, together with the
 110 association/dissociation rate of the ions with protonated/deprotonated water. In *bulk* aqueous solution, the
 111 association/dissociation reaction for H_2O can be written as:



113 The values of the rate constants at 298 K have been reported as $k_{a,\text{H}_2\text{O}} = 1.4 \times 10^8 \text{ m}^3 \text{mol}^{-1} \text{s}^{-1}$ and $k_{d,\text{H}_2\text{O}} =$
 114 $2.5 \times 10^{-5} \text{ s}^{-1}$ [33-35]. The magnitude of $k_{a,\text{H}_2\text{O}}$ implies that the association reaction of H^+ and OH^- in bulk
 115 solution is diffusion limited. In such case, the rate constant can be calculated via [34]:

$$116 \quad k_a = \frac{4\pi N_{\text{Av}} z^+ z^- e^2 (D_{\text{H}^+} + D_{\text{OH}^-})}{\varepsilon \varepsilon_0 k T [\exp(z^+ z^- e^2 / \varepsilon \varepsilon_0 a k T) - 1]} \quad [\text{m}^3 \text{mol}^{-1} \text{s}^{-1}] \quad (2)$$

117 where N_{Av} is the Avogadro number ($6.022 \times 10^{23} \text{ mol}^{-1}$), z is the charge on the respective ions, e is the
 118 elementary charge ($1.6 \times 10^{-19} \text{ C}$), $\varepsilon \varepsilon_0$ is the dielectric permittivity of the aqueous solution ($= 7 \times 10^{-10} \text{ F m}^{-1}$ at
 119 293 K), k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), T is the temperature (K), a is the distance of closest
 120 approach (m), $D_{\text{H}^+} = 9.3 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ and $D_{\text{OH}^-} = 5.3 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ [36]. The k_a computed using Eq. 2 is
 121 approximately equal to the measured $k_{a,\text{H}_2\text{O}}$ for $a = 0.75 \text{ nm}$ [34]. In present context, the various In(III) species
 122 comprise hydrated In^{3+} ions which differ in the extent to which H_2O is deprotonated in the inner hydration
 123 sphere. On a simple electrostatic basis, one might expect the release rate of water to be greater than that of
 124 OH^- . In practice the detailed picture may be more involved. Notably, the dissociation equilibrium of H_2O is
 125 strongly perturbed in the inner-hydration sphere of charged ions, and water speciation in the inner hydration
 126 sphere is highly dynamic with an OH^- being turned into an H_2O on a timescale much shorter than that for
 127 reorganization of the complex structure of the In(III) species. The rate of recombination of an OH^- in the
 128 inner-hydration sphere with a proton is essentially diffusion controlled and largely unaffected by the charge
 129 of the hydroxy complex [37,38]; the rate constant for this process for a trivalent ion is estimated to be *ca.*
 130 $5 \times 10^6 \text{ m}^3 \text{mol}^{-1} \text{s}^{-1}$ [38]. This value, together with the stepwise hydrolysis constants, K^* , of *ca.* $10^{-1} \text{ m}^3 \text{mol}^{-1}$
 131 for each of the In(III) species [39], enables the rate constant for loss of a proton from a given In(III) species

132 to be estimated as *ca.* $5 \times 10^5 \text{ s}^{-1}$ [6]. This value confirms that there will be rapid interchange between H_2O and
133 OH^- in the inner-hydration sphere, whilst the equilibrium concentrations of the various In(III) species derive
134 from the hydrolysis constants.

135

136 During an electrodic reduction process at a mercury electrode, the “free” In(III) ions are reduced to elemental
137 In^0 and accumulate in the electrode volume. In the present case, electron transfer can occur with *all* the In(III)
138 species, i.e. the overall electrodic reduction does not rely on interconversion with a singular electroactive
139 species, and the “free” In(III) comprises *all* species that have lost one H_2O or OH^- . Whilst release of H_2O
140 and/or OH^- is not a prerequisite for electron transfer, we proceed with the assumption that the electroactive
141 form of *each* of the In(III) species is that which has lost (at least) one H_2O (protonated or deprotonated) from
142 its inner hydration sphere. Support for this strategy is provided by the qualitative correlation observed
143 between k_w and electron transfer reversibility (see Introduction and Table 1) which evidences the connection
144 between lability and reversibility, in contrast to the option of a direct complex reduction of the pertaining
145 complex species. In this context we highlight that an n electron process takes place via n distinct, albeit
146 practically indistinguishable, electron transfer steps [40]. Each electron transfer step reduces the charge on
147 the In ion, thereby facilitating the release of H_2O and OH^- , all of which are lost over the course of the reduction
148 to metallic In^0 . As documented above (Table 1), k_w increases as the metal ion becomes increasingly
149 hydrolysed, and loss of the first water molecule from the inner-hydration sphere is generally the slowest step
150 in the context of metal complexation kinetics [41].

151

152 The concept of *lability* describes the extent to which the various In(III) species can maintain equilibrium with
153 each other in the context of the ongoing interfacial reduction process [17]. A given species is denoted as labile
154 if it undergoes frequent interconversions with the electroactive form during its transport through the diffusion
155 layer. In the present case, the consideration of lability refers to *both* (1) interconversions between the various
156 fully hydrated species, i.e. protonation/deprotonation rate of inner-sphere water molecules, and (2)
157 interconversion between the fully hydrated and partially dehydrated forms of a given species. Considering
158 case (1), as discussed above, the rate constant for loss of a proton from each of the In(III) species is *ca.* 5×10^5
159 s^{-1} . The lifetime of the various species, $1/(5 \times 10^5 \text{ s}^{-1}) = 2 \times 10^{-6} \text{ s}$, is much shorter than the diffusion timescale
160 of *ca.* 3 s given by δ^2/D_{In} , where δ is the thickness of the diffusion layer in solution ($\approx 5 \times 10^{-5} \text{ m}$ for the
161 hanging mercury drop electrode used herein with constant stirring of the solution during deposition [42]) and
162 D_{In} is the diffusion coefficient ($= 8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ [2] for all In(III) species considered, i.e. since the diffusion
163 layer thickness is much greater than the Debye screening length, κ^{-1} , we can neglect any effect of
164 electrostatics on the diffusion of the various In(III) species towards the electrode surface [43]). Thus the
165 various protonated/deprotonated species will maintain full equilibrium with each other in the steady-state
166 diffusion layer throughout the electrodic reduction step.

167

168 *(De)hydration kinetics*

169 Considering interconversions between the fully hydrated and partially dehydrated forms of a given species –
 170 case (2) above – the pertaining k_w values are involved (Table 1), and the lability features of the various In(III)
 171 species are conveniently analysed by invoking the approximative reaction layer concept developed by
 172 Koutecký-Koryta (KK) [44-46]. The KK approximation has proven useful in describing the lability features
 173 of a wide range of metal complex systems [47-50]. The KK approach describes the transition from
 174 complexation equilibrium control (with coupled diffusion of all species) to kinetic control (with dissociation
 175 rate limitation) at the reaction layer boundary in the vicinity of a metal-consuming interface such as an
 176 electrode or an organism. The reaction layer concept derives from the relative mobilities and lifetimes of the
 177 various metal species in the medium. Conventionally, the reaction layer thickness, μ_i , for each species, i ,
 178 derives from the mobility of the free ion in the medium (i.e. that which has lost one H_2O or OH^-) and its mean
 179 free lifetime, $1/k_{a,i}c_L$ (in present context, governed by the rate of re-association with a water molecule or an
 180 OH^- , see above) [51]:

$$181 \quad \mu_i = \left(\frac{D_{\text{In}}}{k_{a,i}c_L} \right)^{1/2} \quad [\text{m}] \quad (3)$$

182 where c_L , is the concentration of the ligand, L, where L may be H_2O or OH^- , and refers to that of their free
 183 forms, i.e. not associated with In(III). For the case of $\text{In}(\text{H}_2\text{O})_6^{3+}$, $c_L = c_{\text{H}_2\text{O}} = 5.55 \times 10^4 \text{ mol m}^{-3}$, whilst for the
 184 various hydroxy species, c_L is c_{OH^-} according to the pH of the medium. For the case of $\text{In}(\text{H}_2\text{O})_6^{3+}$, the lifetime
 185 of the free form $\text{In}(\text{H}_2\text{O})_6^{3+}$ ($1/k_{a,i}c_L$) is $2.86 \times 10^{-4} \text{ s}$, and the corresponding μ_i is $4.8 \times 10^{-7} \text{ m}$ (Eq. 3). When
 186 several In(III) species are simultaneously present, a combined μ can be formulated according to:

$$187 \quad \mu = \left(\frac{D_{\text{In}}}{\left[\sum_i (1/k_{a,i}c_L) \right]^{-1}} \right)^{1/2} \quad [\text{m}] \quad (4)$$

188 More rigorously, the formulation of the reaction layer thickness should also take into account the mobility of
 189 the fully hydrated form and its mean free lifetime, $1/k_{d,i}$, (governed by the rate of release of water). The
 190 expression for such a generalised reaction layer thickness, λ_i , defined by both the associative and dissociative
 191 terms for a given species i , is given by [52, 53]:

$$192 \quad \lambda_i = \left(\frac{k_{a,i}c_L}{D_{\text{In}}} + \frac{k_{d,i}}{D_{\text{In}}} \right)^{-1/2} \quad [\text{m}] \quad (5)$$

193 For the case of $\text{In}(\text{H}_2\text{O})_6^{3+}$, its mean free lifetime, $1/k_{d,i}$, is $5 \times 10^{-3} \text{ s}$, whilst that of the hydroxy species
 194 decreases with increasing degree of hydrolysis, i.e. increasing k_w values (Table 1). Eq. 5 can also be written
 195 in combined form to include the cumulative contributions to the free lifetime from the various species i :

$$196 \quad \lambda = \left(\frac{\left[\sum_i (1/k_{a,i}c_L) \right]^{-1}}{D_{\text{In}}} + \frac{\left[\sum_i (1/k_{d,i}) \right]^{-1}}{D_{\text{In}}} \right)^{-1/2} \quad [\text{m}] \quad (6)$$

197 The conventional and generalised reaction layer thicknesses are given in Table 2 as a function of pH for each
 198 individual In(III) species. Note also that for $\text{In}(\text{H}_2\text{O})_6^{3+}$, the $k_{a,i}$ term governs the thickness of its individual

199 reaction layer λ_i (Eq. 5), i.e. the lifetime of the free form, given by $1/k_{a,i}c_L$ (2.86×10^{-4} s), is less than that of
 200 the fully hydrated form, given by $1/k_{d,i}$ (5×10^{-3} s). The opposite holds for the various hydroxy species, i.e. the
 201 respective $k_{d,i}$ terms in Eq. 5 determine the reaction layer thickness. At each pH, the magnitude of the
 202 *combined* μ (Eq. 4) and the *combined* λ (Eq. 6) is approximately equal to the respective individual values for
 203 $\text{In}(\text{H}_2\text{O})_6^{3+}$, which is a consequence of the low k_w for this species (Table 1). Due to the large differences in
 204 magnitude of the individual reaction layer thicknesses across the various $\text{In}(\text{III})$ species (Table 2), we proceed
 205 by considering the kinetic behaviour of each species to be governed by its *individual* reaction layer thickness.
 206 This approach is analogous to the situation of separate diffusion layers being operable for free and complexed
 207 metal species when their diffusion coefficients are very different, even if they are labile [54], and is supported
 208 by the experimental data reported herein (see Results and Discussion).

209

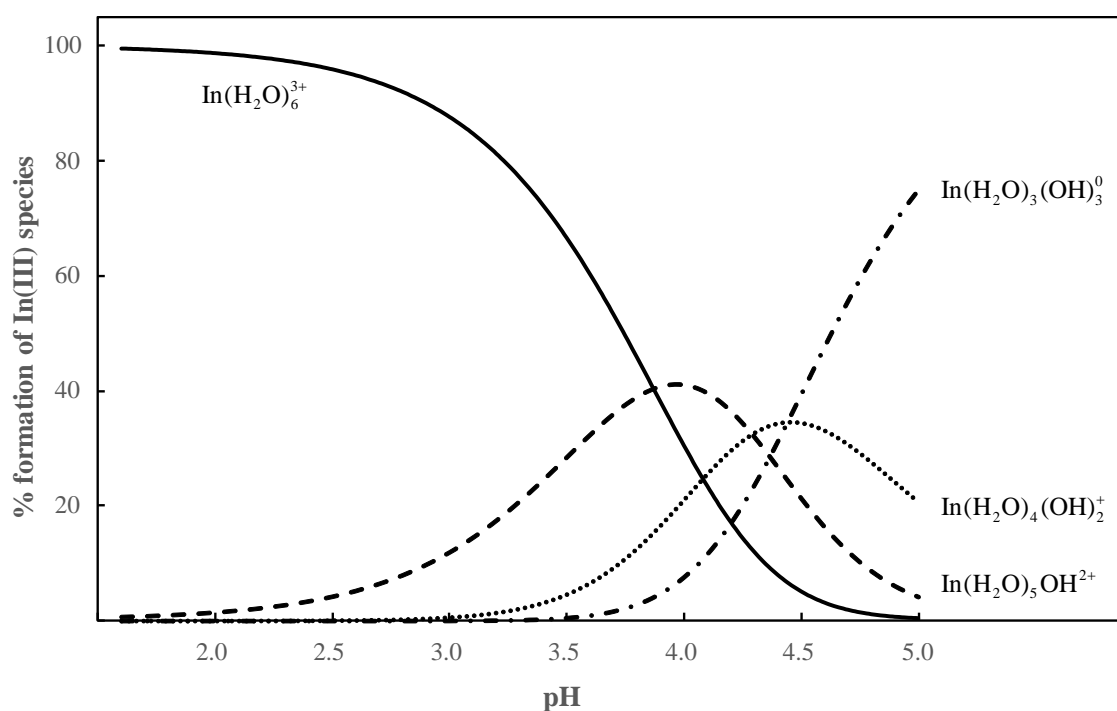
210 **Table 2. Conventional, μ_i , and generalised, λ_i , reaction layer thicknesses for individual aqueous $\text{In}(\text{III})$**
 211 **species, $I = 100 \text{ mol m}^{-3}$**

In(III) species	μ for individual species / m				λ for individual species / m			
	pH 1.8	pH 2.5	pH 3.0	pH 3.5	pH 1.8	pH 2.5	pH 3.0	pH 3.5
$\text{In}(\text{H}_2\text{O})_6^{3+}$	4.8×10^{-7}	4.8×10^{-7}	4.8×10^{-7}	4.8×10^{-7}	4.65×10^{-7}	4.65×10^{-7}	4.65×10^{-7}	4.65×10^{-7}
$\text{In}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	0.050	0.022	0.012	7.0×10^{-3}	8.9×10^{-8}	8.9×10^{-8}	8.9×10^{-8}	8.9×10^{-8}
$\text{In}(\text{H}_2\text{O})_4(\text{OH})_2^+$	1.07×10^{-3}	4.8×10^{-4}	2.7×10^{-4}	1.5×10^{-4}	8.9×10^{-9}	8.9×10^{-9}	8.9×10^{-9}	8.9×10^{-9}
$\text{In}(\text{H}_2\text{O})_3(\text{OH})_3^0$	2.5×10^{-5}	1.1×10^{-5}	6.2×10^{-6}	3.5×10^{-6}	8.9×10^{-10}	8.9×10^{-10}	8.9×10^{-10}	8.9×10^{-10}

212

213 The species distribution of $\text{In}(\text{III})$ in the bulk aqueous medium is computed using the literature cumulative
 214 hydrolysis constants, β^* ($\text{dm}^3 \text{ mol}^{-1}$; average of 4 independent publications at ionic strength *ca.* 100 mM) [39,
 215 55-57]: i.e. $\log \beta_1^* = -3.87$, $\log \beta_2^* = -8.16$, and $\log \beta_3^* = -12.6$ (the formulation of these constants is given in
 216 the Supporting Information). The resulting speciation of $\text{In}(\text{III})$ as function of pH is shown in Fig. 1.

217



218

219 **Fig. 1** Percent formation of aqueous In(III) species as a function of pH. Values were computed using hydrolysis
 220 constants from the literature: $\log \beta_1^* = -3.87$, $\log \beta_2^* = -8.16$, and $\log \beta_3^* = -12.6$ (average values from 4
 221 publications measured at ionic strength *ca.* 100 mM; see list of symbols for elaborated definitions of the β^*
 222 values) [39, 55-57]. As indicated on the figure, the various curves correspond to $\text{In}(\text{H}_2\text{O})_6^{3+}$ (solid line),
 223 $\text{In}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ (dashed line), $\text{In}(\text{H}_2\text{O})_4(\text{OH})_2^+$ (dotted line), and $\text{In}(\text{H}_2\text{O})_3(\text{OH})_3^0$ (dot-dashed line)

224

225 The kinetic flux for each In(III) species, $J_{\text{kin},i}$, is given by :

$$226 \quad J_{\text{kin},i} = k_{w,i} c_i \lambda_i \quad [\text{mol m}^{-2} \text{s}^{-1}] \quad (7)$$

227 where λ_i is the *individual* value in Table 2, and c_i is obtained from the hydrolysis constants (Fig. 1). The
 228 ensuing $J_{\text{kin},i}$ values for each species as a function of pH are given in Table 3.

229

230 **Table 3: Kinetic flux, $J_{\text{kin},i}$, (Eq. 7) for individual In(III) species as a function of pH**

In(III) species	$J_{\text{kin},i}$ for each species, $\text{mol m}^{-2} \text{s}^{-1}$			
	pH 1.8	pH 2.5	pH 3.0	pH 3.5
$\text{In}(\text{H}_2\text{O})_6^{3+}$	9.2×10^{-5}	8.9×10^{-5}	8.2×10^{-5}	6.1×10^{-5}
$\text{In}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	7.4×10^{-5}	3.6×10^{-4}	1.04×10^{-3}	2.5×10^{-3}
$\text{In}(\text{H}_2\text{O})_4(\text{OH})_2^+$	0	8.9×10^{-5}	5.3×10^{-4}	4.1×10^{-3}
$\text{In}(\text{H}_2\text{O})_3(\text{OH})_3^0$	0	0	0	1.3×10^{-2}

231

232 *Lability*

233 As detailed above (see (De)protonation kinetics section), interconversions between the various
 234 protonated/deprotonated species are labile on the timescale of diffusion in the steady-state diffusion layer. Here

235 we assess the situation with respect to interconversions between the fully hydrated and partially dehydrated
 236 forms of each individual In(III) species. In this case, the lability parameter for each species, \mathcal{L}_i , is conveniently
 237 expressed as the ratio of the individual kinetic flux and the diffusive flux, $J_{\text{kin},i}$ and J_{dif} respectively [17]:

$$238 \quad \mathcal{L}_i = J_{\text{kin},i}/J_{\text{dif}} \quad (8)$$

239 where $J_{\text{kin},i}$ (Eq. 7) corresponds to the rate of dissociation of the complexed form (i.e. that which is fully
 240 hydrated) into the free form (i.e. that which has lost one H₂O or OH⁻), and J_{dif} is the diffusion-limited flux of
 241 all the In(III) species from bulk solution to the electrode, given by:

$$242 \quad J_{\text{dif}} = D_{\text{In}} c_{\text{In,t}}^* / \delta \quad [\text{mol m}^{-2} \text{s}^{-1}] \quad (9)$$

243 where $c_{\text{In,t}}^*$ (mol m⁻³) is the total concentration of In(III) in the bulk aqueous medium.

244

245 A given species is labile if $\mathcal{L}_i \gg 1$ [17]. The lability parameter (Eq. 8) for each In(III) species with respect to
 246 interconversions between its fully and partially dehydrated forms in the pH range 1.8 to 3.5 follow as:

247 $\text{In}(\text{H}_2\text{O})_6^{3+} : \mathcal{L}_i = 6 \text{ to } 4$; $\text{In}(\text{H}_2\text{O})_5(\text{OH})^{2+} : \mathcal{L}_i = 5 \text{ to } 156$; $\text{In}(\text{H}_2\text{O})_4(\text{OH})_2^+ : \mathcal{L}_i = 6 \text{ to } 256$; and $\text{In}(\text{H}_2\text{O})_3(\text{OH})_3^0$
 248 $: \mathcal{L}_i = 812$. Thus full equilibrium will be maintained between the various (partially) hydrated forms of each
 249 individual In(III) species in the steady-state diffusion layer throughout the electrodic reduction step.

250

251 **Electrochemical reactivity**

252 All In(III) species will contribute to the overall electrodic reduction to an extent determined by the relative
 253 magnitudes of their diffusive flux towards the electrode, their rate of release of H₂O and/or OH⁻, and their rate
 254 of electron transfer. Thus, for present purposes of describing the electrochemical reactivity, it is necessary to
 255 compare the rate of supply of each individual species, i , in its individual reaction layer, λ_i (Table 2) versus its
 256 rate of electron transfer, i.e. $\min(D_{\text{In}}c_i / \lambda_i, k_{\text{d},i}c_i\lambda_i)$ versus $k_i^0c_i$, where k_i^0 is the rate constant for electron
 257 transfer (m s⁻¹), c_i (mol m⁻³) is obtained from the hydrolysis constants (see above and Fig. 1), and as before,
 258 D_{In} is the same for all species ($8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$). The rate of supply of each species to the electrode surface will
 259 be rate limiting when $k_i^0 \gg \min(D_i / \lambda_i, k_{\text{d},i}\lambda_i)$. Meeting this criterion requires $k^0(\text{In}(\text{H}_2\text{O})_6^{3+}) \gg 9 \times 10^{-5} \text{ m}$
 260 s^{-1} , $k^0(\text{In}(\text{H}_2\text{O})_5(\text{OH})^{2+}) \gg 9 \times 10^{-3} \text{ m s}^{-1}$, $k^0(\text{In}(\text{H}_2\text{O})_4(\text{OH})_2^+) \gg 0.09 \text{ m s}^{-1}$, and $k^0(\text{In}(\text{H}_2\text{O})_3(\text{OH})_3^0) \gg 0.9$
 261 m s^{-1} .

262

263 Values of k_i^0 in the range 10^{-11} to $10^{-14} \text{ m s}^{-1}$ have been derived for $\text{In}(\text{H}_2\text{O})_6^{3+}$ from measurements with a
 264 dropping mercury electrode in acidic media [2, 58]. Thus the rate of electron transfer is the rate limiting step
 265 in the reduction of $\text{In}(\text{H}_2\text{O})_6^{3+}$, and its contribution to the overall electrodic reduction will be limited by its
 266 slow rate of electron transfer in agreement with experimental data [2-4]. As the pH is increased to values at
 267 which hydroxy species are present in non-negligible concentrations, a reversible reduction process is detected
 268 at potentials much more positive than those at which the irreversible reduction of $\text{In}(\text{H}_2\text{O})_6^{3+}$ occurs. The
 269 reversible wave reported at $E_{1/2}$ of -0.55 V (vs. SCE) [2-4] indicates that the contribution of the various In(III)

270 hydroxy species to the overall electrodic reduction is governed by their rate of diffusion towards the electrode
 271 surface (also see Results and Discussion). The differences between the various In(III) species in terms of the
 272 relative rates of the elementary processes governing electrochemical reactivity, determine their relative
 273 contributions to the overall electrodic reduction. As an illustrative example, at pH 1.8, for a total In(III)
 274 concentration of $10^{-3} \text{ mol m}^{-3}$, the concentration of $\text{In}(\text{H}_2\text{O})_6^{3+}$ is $9.92 \times 10^{-4} \text{ mol m}^{-3}$ and of InOH^{2+} is 8×10^{-6}
 275 mol m^{-3} (Fig. 1), thus the contribution of the irreversible reduction of $\text{In}(\text{H}_2\text{O})_6^{3+}$ to the overall electrodic
 276 reduction will be *ca.* 7 orders of magnitude lower than that of the reversible reduction of $\text{In}(\text{H}_2\text{O})_5(\text{OH})^{2+}$,
 277 even using the highest reported value of k_i^0 for $\text{In}(\text{H}_2\text{O})_6^{3+}$ of $10^{-11} \text{ m s}^{-1}$. Specifically, $J_{\text{In}(\text{H}_2\text{O})_6^{3+}}$ (electron
 278 transfer limited rate in the reaction layer) = $10^{-11} \text{ m s}^{-1} \times 9.92 \times 10^{-4} \text{ mol m}^{-3} = 9.92 \times 10^{-15} \text{ mol m}^{-2} \text{ s}^{-1}$, *cf.*
 279 $J_{\text{In}(\text{H}_2\text{O})_5\text{OH}^{2+}}$ (diffusive flux in the reaction layer) = $8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \times 8 \times 10^{-6} \text{ mol m}^{-3} / 8.9 \times 10^{-8} \text{ m} = 7.2 \times 10^{-8} \text{ mol}$
 280 $\text{m}^{-2} \text{ s}^{-1}$.

281

282 Experimental

283 Reagents

284 All solutions were prepared in distilled, deionised water from a Milli-Q system (resistivity > 18 MΩ cm). Test
 285 solutions containing $5.6 \times 10^{-4} \text{ mol m}^{-3}$ In(III) were prepared by dilution of a standard (TraceCERT, Sigma-
 286 Aldrich). Ionic strength was maintained at 100 mM with NaClO_4 , prepared from the solid (puriss p.a.).
 287 Perchlorate ions do not form inner-sphere complexes with In(III) [59], and do not specifically adsorb on Hg in
 288 the potential range used herein [60]. The pH of the test solutions was adjusted to the target value by addition
 289 of HClO_4 and NaOH , and remained constant over the duration of the experiments.

290 Electrochemical measurements

291 The electrochemical measurements were performed with an Ecochemie μ Autolab potentiostat (input
 292 impedance > 100 GΩ) coupled with a Metrohm VA stand. The working electrode was a multimode hanging
 293 mercury drop electrode (HMDE) with radius *ca.* $2 \times 10^{-4} \text{ m}$, the auxiliary electrode was glassy carbon, and the
 294 reference electrode was $\text{Ag}|\text{AgCl}|\text{KCl}(\text{sat})$ encased in a 100 mM NaClO_4 jacket. Solutions were initially purged
 295 with oxygen-free N_2 and a nitrogen blanket was maintained during measurements. Stripping
 296 chronopotentiometric measurements were performed over a range of deposition potentials, E_d , i.e. the solution
 297 is stirred and the electrode potential is held at the chosen E_d for a fixed deposition time, t_d , during which In^0
 298 accumulates in the Hg electrode; at the end of the t_d , a stripping (oxidising) current, I_s , is applied in quiescent
 299 solution until the potential reaches a value well past the transition plateau. The area under the recorded dt/dE
 300 *vs.* E curve corresponds to the stripping time, τ . A stripping current of 2 nA was used which corresponds to
 301 complete depletion conditions for the HMDE used herein [61]. Stripping chronopotentiometry at scanned
 302 deposition potential (SSCP) comprises plots of τ as a function of E_d . Such SSCP waves, analogous to
 303 conventional voltammograms, scan the relevant parts of the stability distribution and the rate constant
 304 distributions. An overview of the fundamental principles of SSCP is given in the Supporting Information and

305 the reader is referred to our previous work for further details of the SSCP methodology and the advantages of
306 the complete depletion regime for metal speciation analysis [62-65].

307

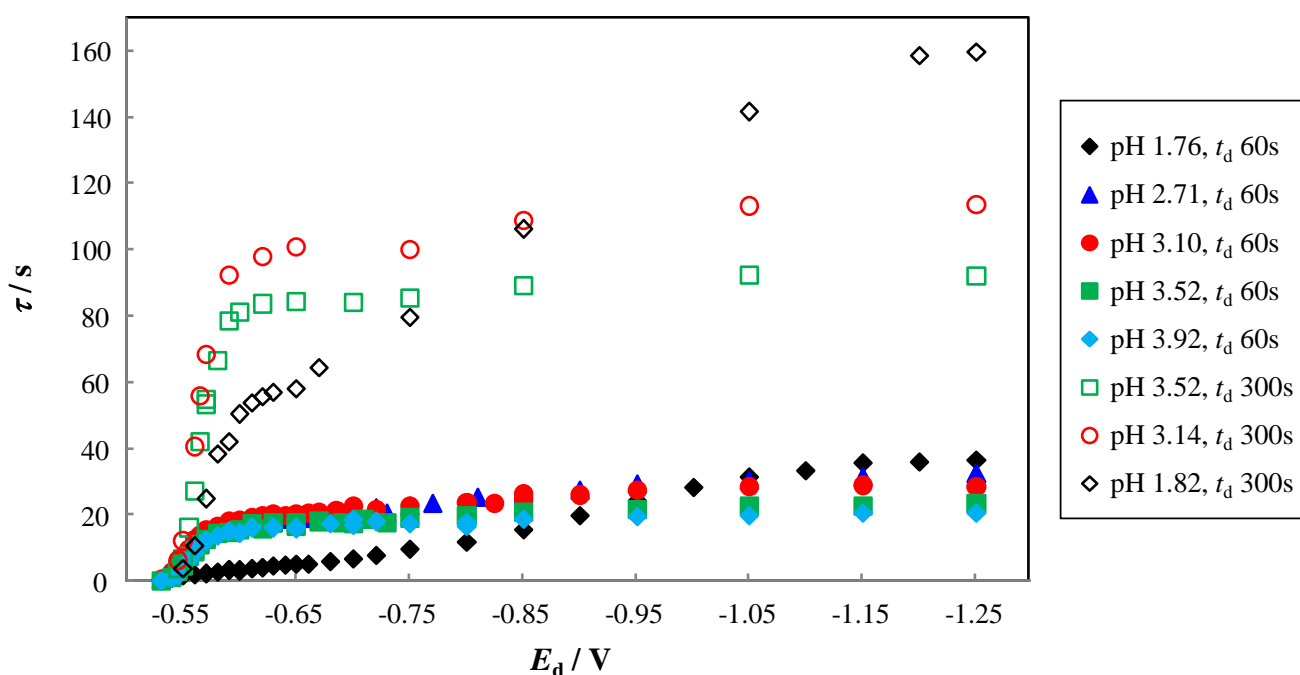
308 **Results and Discussion**

309 **Reversibility of the electrodic reduction**

310 Voltammetric waves recorded for In(III) show an irreversible wave for $\text{In}(\text{H}_2\text{O})_6^{3+}$ ($E_{1/2} = -0.95\text{V vs. SCE}$)
311 when the pH is sufficiently low to suppress hydrolysis; as the pH is increased to values at which hydroxy
312 species are present in solution a reversible diffusion-controlled wave appears ($E_{1/2} = -0.55\text{ V vs. SCE}$) [2-4].
313 This behaviour was also observed in the present work (Fig. S1). The transition from reversible to irreversible
314 electrochemical behaviour depends on the timing characteristics of the technique, which for SSCP corresponds
315 to k^0 values in the range from *ca.* 10^{-4} to 10^{-6} m s^{-1} [47]. That is, once k^0 is of $\text{O}(10^{-6})\text{ m s}^{-1}$ or less, the slope of
316 a $\log[\tau^* - \tau]/\tau$ vs. E_d plot (where τ^* is the limiting value of τ obtained when the concentration of the
317 electroactive species at the electrode surface essentially equals zero) is independent of t_d , and lower than that
318 for the reversible case [47]. SSCP curves recorded for In(III) as a function of pH feature two distinct waves
319 with half-wave deposition potentials $E_{d,1/2}$ of *ca.* -0.56 V and *ca.* -0.95 V ; Fig. 2. The wave with $E_{d,1/2} \approx -0.56$
320 V is ascribed to reversible reduction of In(III) hydroxy species (see further discussion below), whilst the drawn-
321 out wave with $E_{d,1/2} \approx -0.95\text{ V}$ corresponds to irreversible reduction of $\text{In}(\text{H}_2\text{O})_6^{3+}$.

322 As the pH is increased from 1.8 to 3.1, the height of the first plateau increases, and that of the second decreases.
323 At higher pH, the slight decrease in the height of the first wave may reflect the formation of multi-nuclear
324 hydroxy species with a somewhat lower diffusion coefficient than the mononuclear ones and/or low solubility:
325 precipitation of In(III) hydroxy species begins at pH *ca.* 3.4 [66]. The decrease in the height of the plateau at
326 $E_d -1.25\text{ V}$ with increasing pH reflects the decreasing concentration as well as the increasing irreversibility of
327 the $\text{In}(\text{H}_2\text{O})_6^{3+}$ species. At pH 1.8, the magnitude of τ at an E_d of -1.25 V corresponds to the value predicted
328 on the basis of the diffusive flux of the total In(III), in line with the conventional overcoming of irreversibility
329 at extreme overpotentials [40].

330



331

332 **Fig. 2** SSCP waves for In(III) as a function of pH for a deposition time, t_d , of 60 s (solid symbols) and 300 s
 333 (open symbols). Total concentration of In(III) = $5.6 \times 10^{-4} \text{ mol m}^{-3}$, $I = 100 \text{ mol m}^{-3} \text{ NaClO}_4$

334

335 Estimation of k^0 for In(III) hydroxy species

336 The full SSCP curve of τ versus E_d is given by [22]:

$$337 \quad \tau = \frac{I_d^* \tau_d}{I_s} [1 - \exp(-t_d / \tau_d)] \quad [\text{s}] \quad (10)$$

338 where I_d^* (A) is the limiting value of the deposition current obtained when the concentration of the
 339 electroactive species at the electrode surface essentially equals zero, and τ_d (s) is the potential-dependent time
 340 constant of the deposition process. With appropriate elaborations of the I_d^* and τ_d terms, Eq. 10 has been
 341 demonstrated to describe the SSCP waves measured for a wide range of metal complex systems, including
 342 those involving kinetic currents [47, 49], heterogeneity in the chemical speciation [48, 62], and electrochemical
 343 irreversibility [23, 67]. In the case of nonreversible electron transfer processes, the expressions for the general
 344 quasi-reversible case are [23, 67]:

$$345 \quad I_d^* = \frac{nFAk^0}{1 + nFAk^0 m_{in} \theta_\alpha} c_{in,t}^* \theta_\alpha \quad [\text{A}] \quad (11)$$

346 and

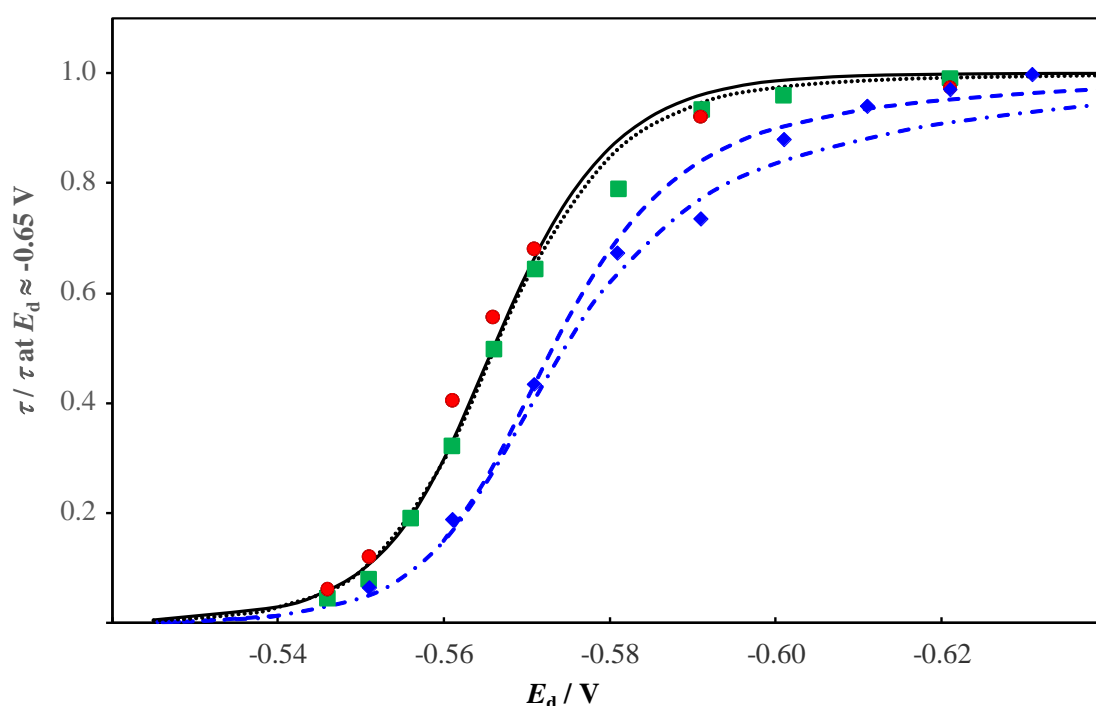
$$347 \quad \tau_d = \frac{nFVm_{in}}{\theta} + \frac{nFV}{nFAk^0 \theta_\beta} \quad [\text{s}] \quad (12)$$

348 where A and V are the surface area and volume of the electrode, respectively, $m_{in} = \delta / nFAD_{in}$,
 349 $\theta = \exp[nF(E_d - E^0) / RT]$ where E^0 is the formal potential, $\theta_\alpha = \exp(-\alpha y)$ and $\theta_\beta = \exp(\beta y)$ where α is
 350 the charge transfer coefficient, $\beta = 1 - \alpha$, and $y = nF(E_d - E^0) / RT$. Eq. 11 has sound limits: for very fast

351 mass transport, $m_{\text{in}} \rightarrow \text{zero}$ and $I_{\text{d}}^* \rightarrow nFAk^0c_{\text{in,t}}^* \exp(-\alpha y)$, i.e. the totally irreversible current, whilst for
 352 electrochemically reversible systems with $nFAk^0c_{\text{in,t}}^* \exp(-\alpha y) \gg 1$, $I_{\text{d}}^* \rightarrow c_{\text{in,t}}^* / m_{\text{in}}$, i.e. the diffusive limiting
 353 current. Eqs. 10, 11, and 12 evidence that the shape of the SSCP wave for a quasi-reversible electrodic
 354 reduction is sensitive to the magnitude of k^0 , and a steepening of the wave with increasing t_{d} is a characteristic
 355 feature of such systems [23, 67].

356

357 For the case of In(III) at pH values greater than *ca.* 2.5, the shape of the SSCP wave with $E_{\text{d},1/2}$ *ca.* -0.56 V is
 358 practically independent of t_{d} . Comparison with computed curves (Eqs. 10, 11, and 12; Fig. 3) establishes that
 359 at pH values above *ca.* 2.5 the electrodic reduction of the In(III) hydroxy species is practically reversible (k^0
 360 $\rightarrow \infty$), whilst at pH 1.8 the effective rate constant for electron transfer, k_{eff}^0 , is of the order of 10^{-5} m s^{-1} .



361

362 **Fig. 3** SSCP curves normalised with respect to τ measured at an E_{d} of *ca.* -0.65 V. Deposition time, $t_{\text{d}} = 300\text{s}$.
 363 Symbols correspond to experimental data at pH 1.82 (blue diamonds), 3.14 (red dots), and 3.52 (green squares).
 364 The lines correspond to computed curves for the reversible case with $E^{0'} = -0.534 \text{ V}$ (solid black line), the
 365 quasi-reversible case with $k^0 = 2 \times 10^{-4} \text{ m s}^{-1}$ and $E^{0'} = -0.534 \text{ V}$ (black dotted line), $k^0 = 4 \times 10^{-5} \text{ m s}^{-1}$ and $E^{0'}$
 366 $= -0.540 \text{ V}$ (blue dashed line), and $k^0 = 2 \times 10^{-5} \text{ m s}^{-1}$ and $E^{0'} = -0.540 \text{ V}$ (blue dot-dashed line). Computations
 367 were performed for $n = 3$, $\alpha = 0.22$ [2, 58]

368

369 Estimation of k^0 for $\text{In}(\text{H}_2\text{O})_6^{3+}$

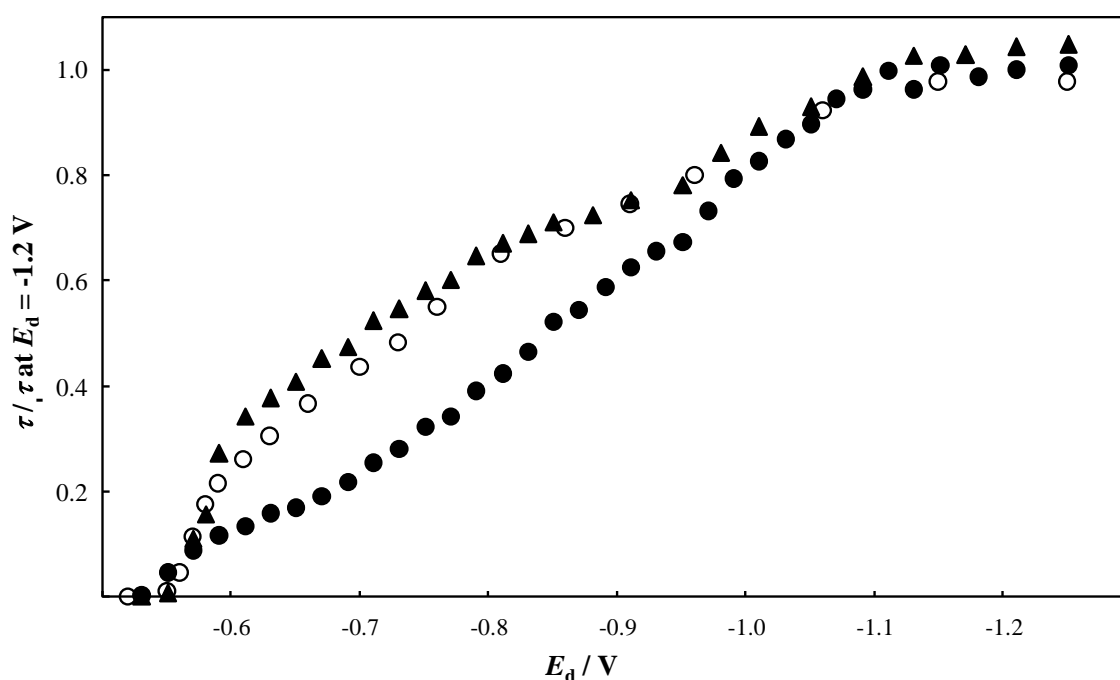
370 The observed irreversibility of the $\text{In}(\text{H}_2\text{O})_6^{3+}$ wave ($E_{\text{d},1/2} \approx -0.95 \text{ V}$) is in agreement with the predicted
 371 behaviour of this species (see Introduction and Theory sections). In this context it is relevant to note that the
 372 reported k^0 values for $\text{In}(\text{H}_2\text{O})_6^{3+}$ of 10^{-11} to $10^{-14} \text{ m s}^{-1}$ [2, 58] are so-called ‘true’ values. Since reduction of

373 In(III) species takes place at potentials that are negative of the pzc of the mercury electrode (*ca.* -0.5 V [60]),
 374 the magnitude of the Frumkin correction must also be considered in assessment of the reversibility of the
 375 electrodic reduction process. The effective rate constant for electron transfer, k_{eff}^0 , can be computed from the
 376 true value, k^0 , via [40]:

$$377 \quad k_{\text{eff}}^0 = k^0 \exp[(\alpha n - z)F\psi_{\text{OHP}} / RT] \quad (13)$$

378 where α is the charge transfer coefficient, n is the number of electrons transferred, z is the charge on the ionic
 379 species, F is the Faraday constant (96485 C mol⁻¹), ψ_{OHP} is the potential at the outer Helmholtz plane (V), R
 380 is the gas constant (8.314 J K⁻¹ mol⁻¹), and T is the temperature (K). In this context we highlight that there is
 381 no specific adsorption of electrolyte perchlorate anions, OH⁻ or H⁺ ions on the Hg electrode over the potential
 382 range considered [60], and perchlorate ions do not form inner-sphere complexes with In(III) [59]. For the case
 383 of In(III) in acidic perchlorate media, αn is 0.66 [2,58], and for a mercury electrode at an applied potential of
 384 -0.60 V in acidic perchlorate media, ψ_{OHP} is *ca.* -0.03 V [68]. Using Eq. 13, these values yield a k_{eff}^0 for
 385 $\text{In}(\text{H}_2\text{O})_6^{3+}$ at $E_d = -0.60\text{V}$ that is *ca.* 16 times greater than the true value, and still many orders of magnitude
 386 below that of a reversible electrodic reduction process. This finding confirms that the wave with $E_{d,1/2} \approx -0.56$
 387 V can be ascribed to reduction of hydroxy In(III) species.

388 The SSCP waves recorded at pH 1.8 (Fig. 2) show that the height of the first plateau – corresponding to quasi-
 389 reversible reduction of In(III) hydroxy species (Fig. 3) – increases to a greater extent than expected on the
 390 basis of the increased t_d (for a reversible electrochemical reaction the SCP τ in the plateau region is directly
 391 proportional to t_d [22]), and the slope of the first wave becomes somewhat steeper. In the case of (quasi)-
 392 reversible systems, a longer t_d serves to shift the location of the SSCP wave on the potential axis to more
 393 negative values, thus the observed features are analogous to the conventional overcoming of irreversibility by
 394 going to more extreme potentials. The reader is referred to our previous work for more detailed explanation of
 395 this feature of SSCP [23, 69]. This aspect is highlighted in Fig. 4, which shows the SSCP waves recorded at
 396 pH 1.8 for several t_d , normalised relative to τ at -1.2 V. Once k^0 becomes less than O(10⁻⁶) m s⁻¹, the electrodic
 397 process is irreversible on the SSCP timescale. The shape of an irreversible SSCP wave and its position on the
 398 E_d axis are invariant with t_d [23]. The data shown in Fig. 4 show that the slope and position on the potential
 399 axis of the electrodic reduction process occurring at the most negative deposition potentials is approximately
 400 invariant with t_d , thereby confirming the irreversibility of the pertaining process, i.e. reduction of $\text{In}(\text{H}_2\text{O})_6^{3+}$.
 401 The SSCP wave for an irreversible process shifts to increasingly more negative E_d as k^0 decreases, by a factor
 402 of *ca.* 50 mV per 10-fold decrease in k^0 [23, 67]. These features enable us to estimate the k_{eff}^0 for $\text{In}(\text{H}_2\text{O})_6^{3+}$:
 403 at pH 1.8, the wave for the In(III) hydroxy species at $E_{d,1/2}$ *ca.* -0.56 V corresponds to k_{eff}^0 *ca.* 2×10^{-5} m s⁻¹ (Fig.
 404 3), and the $E_{d,1/2}$ for the irreversible wave for $\text{In}(\text{H}_2\text{O})_6^{3+}$ is located *ca.* 0.4 V more negative, and thus the
 405 corresponding k_{eff}^0 will be *ca.* 8 orders of magnitude lower, i.e. *ca.* 10⁻¹³ m s⁻¹, in agreement with literature
 406 values [2, 58].



407

408 **Fig. 4** SSCP waves for In(III) at pH 1.8 normalised relative to τ at $E_d = -1.2$ V for a deposition time, t_d , of 60
 409 s (solid circles), 180 s (open circles), and 300 s (solid triangles). Total concentration of In(III) = 5.6×10^{-4} mol
 410 m^{-3} , $I = 100$ mol m^{-3} NaClO₄

411

412 Consequences for speciation analysis of In(III)

413 The preceding discussion evidences the irreversibility of the electrodic reduction of $\text{In}(\text{H}_2\text{O})_6^{3+}$. Our results
 414 have consequences for interpretation of stripping chronopotentiometric data that purport to measure
 415 exclusively the $\text{In}(\text{H}_2\text{O})_6^{3+}$ species at a potential of -0.58 V (corresponding to the foot of the SSCP wave
 416 recorded with a mercury film electrode) [10]. It is evident from the results presented herein that at such a
 417 potential only the In(III) hydroxy species will contribute significantly to the electrodic reduction. Furthermore,
 418 the decrease in τ measured at an E_d of -0.58 V with increasing pH has been erroneously interpreted as reflecting
 419 the decrease in the concentration of $\text{In}(\text{H}_2\text{O})_6^{3+}$ [10]. Our findings show that such data rather reflect the shift
 420 in the reversible reduction wave for the In(III) *hydroxy* species towards more negative potentials as their degree
 421 of formation increases with increasing pH (i.e. increasing c_{OH^-} in the aqueous medium; Fig. 1), as described
 422 by the DeFord-Hume equation [70]. Specifically, an increase in pH from 2.8 to 3.5 would shift the reduction
 423 wave by -2.5 mV (computed using the literature hydrolysis constants given above); at a given potential
 424 corresponding to, say, 5% of the wave height at pH 2.8, the reduction current would be *ca.* 25 % lower at the
 425 same potential at pH 3.5. This value is in remarkable agreement with the reported *ca.* 23 % decrease in the
 426 “concentration of $\text{In}(\text{H}_2\text{O})_6^{3+}$ ” derived from the decrease in magnitude of the SCP τ value over this pH range
 427 [10]; our results underscore that the published data [10] simply reflect the contribution from the In(III) hydroxy
 428 species. Evidently, our findings call for reinterpretation of the recent literature [9-11].

429

430

431 **Conclusions and Outlook**

432 The interpretation framework presented herein provides a straightforward means to characterise the
 433 electrochemical reactivity of aqueous ions together with their various hydrolysed counterparts. The theory is
 434 illustrated with experimental data for In(III). Specifically, invoking a Koutecky-Koryta type approximation
 435 for the reaction layer adjacent to the electrode/medium interface enables differences in reactivity of the aqueous
 436 In(III) species to be described according to their relative rates of electron transfer, dehydration, and/or
 437 (de)protonation. All In(III) species are found to be labile on the experimental timescale with respect to
 438 (de)protonation and (de)hydration, but large differences show up in to the rates of electron transfer. In the case
 439 of $\text{In}(\text{H}_2\text{O})_6^{3+}$, the rate of electron transfer is found to be so slow that it replaces the traditional Eigen rate-
 440 limiting water release step in the overall passage from $\text{In}(\text{H}_2\text{O})_6^{3+}$ to In^0 . In contrast, the In(III) hydroxy species
 441 display reversible electrochemical behaviour. SSCP waves, which record the electrochemical reactivity as a
 442 function of reduction potential, are shown to be a useful tool for exploring the features of such systems. The
 443 results are of great consequence for electrochemical speciation analysis of In(III) and other hydrolysable ions,
 444 i.e. characterisation of all elementary processes which contribute to the electrochemical reactivity of all species
 445 is fundamental for robust data interpretation.

446

447 **List of Symbols and Abbreviations**

448 Latin

449	a	distance of closest approach of ions (m)
450	A	electrode surface area (m^2)
451	c_i	concentration of species i (mol m^{-3})
452	$c_{\text{In,t}}^*$	total concentration of In(III) in the bulk aqueous medium (mol m^{-3})
453	D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
454	e	elementary charge ($1.6 \times 10^{-19} \text{ C}$)
455	E_d	deposition potential (V)
456	$E_{d,1/2}$	half-wave deposition potential (V)
457	$E_{1/2}$	half-wave potential (V)
458	$E^{0'}$	formal potential (V)
459	F	Faraday's constant (96485 C mol^{-1})
460	HMDE	hanging mercury drop electrode
461	I	ionic strength (mol m^{-3})
462	I_d^*	limiting value of the deposition current (A)
463	I_s	stripping current (A)
464	J_{dif}	diffusion controlled flux from the bulk medium to the electrode surface ($\text{mol m}^{-2} \text{s}^{-1}$)
465	J_{kin}	kinetically controlled flux in the reaction layer ($\text{mol m}^{-2} \text{s}^{-1}$)
466	k	Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$)
467	k_a	association rate constant ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)

468	k_d	dissociation rate constant (s^{-1})
469	k^0	electron transfer rate constant ($m s^{-1}$)
470	k_{eff}^0	effective electron transfer rate constant ($m s^{-1}$)
471	KK	Koutecký-Koryta
472	K^{os}	stability constant for an outer-sphere reactant pair ($m^3 \text{ mol}^{-1}$)
473	k_w	inner-sphere dehydration rate constant of hydrated metal ions (s^{-1})
474	L	ligand
475	\mathcal{L}	lability parameter (dimensionless)
476	m_{In}	charge transport coefficient for In in aqueous solution
477	n	number of electrons transferred in the electrochemical reaction
478	N_{Av}	Avogadro number ($6.022 \times 10^{23} \text{ mol}^{-1}$)
479	OHP	outer Helmholtz plane
480	R	gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
481	SCE	saturated calomel electrode
482	SSCP	stripping chronopotentiometry at scanned deposition potential
483	t_d	deposition time (s)
484	T	temperature (K)
485	V	electrode volume (m^3)
486	y	$nF(E_d - E^0) / RT$
487	z	charge on an ion
488		
489	Greek	
490	α	charge transfer coefficient
491	β	$1 - \alpha$
492	β_1^*	stability constant for the reaction $\text{In}(\text{H}_2\text{O})_6^{3+} \rightleftharpoons \text{In}(\text{H}_2\text{O})_5(\text{OH})^{2+} + \text{H}^+$
493	β_2^*	stability constant for the reaction $\text{In}(\text{H}_2\text{O})_6^{3+} \rightleftharpoons \text{In}(\text{H}_2\text{O})_4(\text{OH})_2^+ + 2\text{H}^+$
494	β_3^*	stability constant for the reaction $\text{In}(\text{H}_2\text{O})_6^{3+} \rightleftharpoons \text{In}(\text{H}_2\text{O})_3(\text{OH})_3^0 + 3\text{H}^+$
495	δ	thickness of the diffusion layer in solution at the electrode/medium interface (m)
496	$\varepsilon\varepsilon_0$	dielectric permittivity of the aqueous solution ($7 \times 10^{-10} \text{ F m}^{-1}$ at 293 K)
497	θ	$\exp(y)$
498	θ_α	$\exp(-\alpha y)$
499	θ_β	$\exp(\beta y)$
500	κ^{-1}	Debye layer thickness (screening length) in the bulk electrolyte medium (m)
501	λ	thickness of the generalised reaction layer at the electrode/medium interface (m)
502	μ	thickness of the conventional association reaction layer at the electrode/medium interface (m)
503	τ	SCP transition (stripping) time (s)

504 τ_d characteristic time constant of the SCP deposition process (s)

505 ψ_{OHP} potential at the outer Helmholtz plane (V)

506

507 **References**

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