

# A novel approach to monitoring of the diffusion junction potential in speciation studies by polarography under very acidic conditions. Part I: The reversible Cd(II)-picolinic acid system

Caren Billing,<sup>a,\*</sup> Ignacy Cukrowski,<sup>b</sup> Blake Jordan<sup>a</sup>

<sup>a</sup> Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, P.O. Wits, Johannesburg, 2050, South Africa

<sup>b</sup> Department of Chemistry, University of Pretoria, Pretoria, 0002, South Africa

\* e-mail: [caren.billing@wits.ac.za](mailto:caren.billing@wits.ac.za)

## Abstract

A new polarographic procedure has been developed for the study of metal-ligand equilibria at  $\text{pH} < 2$  by applying an in-situ monitoring of the diffusion junction potential by introducing a non-complexing witness metal ion, Tl(I). As a case study, this procedure was applied to the Cd(II)-picolinic acid (pyridine-2-carboxylic acid) system;  $\text{DC}_{\text{TAST}}$  polarography was employed at 25 °C and ionic strength of 0.25–0.5 M  $(\text{H}_2\text{Na})\text{NO}_3$ .  $\log \beta$  values of  $4.26 \pm 0.03$ ,  $7.86 \pm 0.11$  and  $10.47 \pm 0.12$  were obtained for the  $\text{ML}$ ,  $\text{ML}_2$  and  $\text{ML}_3$  complexes, respectively, and compare well to literature values. The first  $\log \beta$  ( $6.27 \pm 0.07$ ) value for the MLH species was successfully determined, for which a crystal structure has been reported recently.

**Keywords:** Cadmium, diffusion junction potential, formation constants, picolinic acid, voltammetry

## 1. Introduction

As a technique for studying metal-ligand speciation, glass electrode potentiometry (GEP) is the most versatile (in principle any metal ion and protonatable ligand can be studied), powerful (it provides a direct measure of proton concentration/activity which can vary over 10 orders of magnitude and extremely complex equilibria can be investigated), reliable (electrode potential readings are assumed to be free of interferences) and precise (electrode potential readings, in mV, to the third decimal place allow for computing of formation or protonation constants with uncertainties in refined  $\log \beta$  values typically on the second decimal place). Because of the overall phenomenal performance of GEP, it has been the most frequently used technique in the field of metal-ligand equilibria studies and most reported formation constants were generated by use of GEP [1,2].

However, the chemistry of metal ions at extreme acidic conditions is almost unknown and can be regarded as largely unexplored territory. This is because GEP has two major limitations when  $\text{pH} < 2$  is considered: (i) the linear response (mV-readings vs. pH) is restricted to the 2–12 pH range due to a significant and varying diffusion junction potentials at  $\text{pH} < 2$  and (ii) in the mass-balance equations (MBEs) the free hydrogen ion concentration must come predominantly from the deprotonation of the ligand caused by the complexation reaction and not from

the excess of mineral acid which is needed to work at extremely low pH. Even though relatively high ligand concentrations of  $10^{-3} - 10^{-2}$  M are typically used in GEP for high precision and accuracy, yet still ensuring negligible contribution from the ligand to the ionic strength of a sample solution, below pH 2 the proton concentration from the mineral acid dominates.

Most of the above GEP-related limitations do not apply to polarography which, as an analytical tool, performs very well under highly acidic conditions. In metal-ligand equilibria studies by polarography, both the position along the potential scale and the intensity of the signal are utilised as they depend on the kind of species in which a metal ion is involved. The reduction potentials of either the complexed metal species,  $E(\text{M}_{\text{comp}})$ , or the uncomplexed (or free) metal ion,  $E(\text{M})$ , as well as a decrease in the reduction current can be monitored as a function of either pH or free ligand concentration,  $[\text{L}]$ . Note that  $E(\text{M}_{\text{comp}})$  usually shifts towards more negative potentials relative to  $E(\text{M})$  which, in principle, should not depend on pH.

In a pH titration it is preferred (or it may only be possible) to start at a low pH where there is only a small degree of complexation and move to higher pH where complex formation is promoted. Regardless of the electroanalytical technique used, a major hurdle to overcome when working under very acidic conditions is the large and pH-dependent diffusion junction potential,

$E_j$ , formed between the sample solution and the salt bridge solution in which the reference electrode (RE) is placed. Variation in  $E_j$  at pH < 2 is due to the extremely high mobility of the hydrogen ion [3] and change in the total proton concentration when a sample solution is titrated with a base solution to increase pH. As a result, the experimentally measured potential,  $E_{\text{exp}}$ , is unavoidably composed of two major components: the reduction potential is either  $E_{\text{exp}}(\text{M}) = E(\text{M}) + E_j$  for a free metal ion or  $E_{\text{exp}}(\text{M}_{\text{comp}}) = E(\text{M}_{\text{comp}}) + E_j$  for a complexed ion.

Various methods for the calculation of diffusion junction potentials for simple electrolytes have been suggested [3-9], each making different assumptions in their derivations which are not necessarily met by the experimental conditions used here; clearly, an experimental determination of  $E_j$  would be favoured. Previously [10,11],  $E_j$  was evaluated in polarographic studies by a separate pH titration of the metal ion solution just prior to the pH titration of a sample containing M and L. This procedure, however, cannot be applied to metal ions which undergo hydrolysis under acidic conditions. Additionally, since there are variations in  $E_j$  and  $E_{\text{exp}}$  between titrations often due to irreproducible performance of the RE system, this procedure could be improved upon.

In this paper the concept of using a witness metal ion for *in-situ* monitoring of the junction potential and performance of a RE system is introduced. Ideally, the witness metal ion should not form complexes with the ligand and its polarographic signal should not interfere with that of the metal-ligand system being studied. Thallium(I) is known to generally form extremely weak complexes [12,13] and was used in this work. No complex formation takes place with picolinic acid in the pH region studied, so any variation in  $E_{\text{exp}}(\text{Tl})$  during a pH titration experiment could be attributed to the variation in  $E_j$  (as well as the performance of the RE system). This *in-situ* determination of the junction potential could then be used to correct  $E_{\text{exp}}(\text{M})$  of the metal ion of interest. This postulate was tested by investigating the Cd(II)-picolinic acid system.

## 2. Experimental

### 2.1. Materials

All reagents used were of analytical grade. Water was deionised using a Milli-Q water purification unit. Stock solutions of 0.100 M Tl(I) nitrate and 0.100 M Cd(II) nitrate, both in 0.5 M HNO<sub>3</sub>, were made up. NaOH solutions were standardised against potassium hydrogen phthalate and HNO<sub>3</sub> solutions were standardised against these NaOH solutions, using phenolphthalein as indicator. NaOH solutions were protected from

atmospheric CO<sub>2</sub> by filling the drying tubes with ascarite<sup>®</sup>.

### 2.2. Instrumentation

Polarographic experiments were carried out using an automated setup described previously [14]. A jacketed titration vessel was used and the temperature maintained at 25.0 ± 0.1 °C using a water bath with a Labcon CPE100 temperature controller and the temperature of the sample solutions were monitored using a Metrohm thermocouple. Solutions were deoxygenated by purging with UHP (99.999%) nitrogen. A glass electrode (Cat. no. 6.0234.100), multimode mercury electrode (Cat. no. 6.1246.020), platinum counter electrode (Cat. no. 6.0343.000) and a Ag/AgCl (3 M KCl) RE (Cat. no. 6.0728.020) were from Metrohm. A salt bridge (Cat. no. 6.1245.010) contained 0.5 M NaNO<sub>3</sub>. Sampled direct current polarography was used with a step time of 1 s, current integration time of 60 ms and step potential of 4 mV.

### 2.3. Experimental procedure

The glass electrode (GE) was calibrated as described previously [15] using 0.5 M HNO<sub>3</sub> and NaOH solutions. After each addition of titrant, the free proton concentration, [H<sup>+</sup>], was calculated and used to determine pH, thus pH implies -log[H<sup>+</sup>] in this work.

Preliminary polarographic pH titration experiments, without added ligand, were carried out to investigate the variation in  $E_j$  with pH. Solutions initially contained 0.5 M HNO<sub>3</sub> and the two metals ions, 9.98 × 10<sup>-5</sup> M Cd(II) and 1.99 × 10<sup>-4</sup> M Tl(I). After recording a polarogram, the solutions were titrated with 0.5 M NaOH ensuring a pH step of about 0.07 pH units, and at each step the potential at the GE and a polarogram were recorded.

The study of metal-ligand equilibria also started from 0.5 M HNO<sub>3</sub> solution with Cd(II) and Tl(I) present. After recording a polarogram on that solution, solid picolinic acid was added, such that the ligand-to-Cd(II) concentration ratios ([L]<sub>T</sub>: [M]<sub>T</sub>) were between 100 and 200, and titration with NaOH was executed as described for the metal ions above. Examples of polarograms in the absence and presence of picolinic acid at various pHs are given in Figures S1 and S2, respectively, in the Supplementary Information.

Experimental half-wave potentials ( $E_{1/2}$ ) and diffusion limited currents ( $I_d$ ) were obtained simultaneously for both metal ions from polarograms recorded at a particular pH by fitting Eq. 1 to the experimental data:

$$f(x) = \left( \frac{I_d}{\exp(\delta F / RT)(x - E_{1/2}) + 1} \right)_{\text{Tl}} + \left( \frac{I_d}{\exp(2\delta F / RT)(x - E_{1/2}) + 1} \right)_{\text{Cd}} + I_b \quad (1)$$

where  $x$  is the applied potential,  $I_b$  is the background current and  $\delta$  measures the steepness of the reduction wave and should be unity for reversible electron transfer processes. All polarograms indicated fully reversible electrochemical processes, so  $\delta$  was set to one to reduce the number of parameters to be fitted. In solutions with high proton concentrations,  $I_b = a + bx + c \exp(dx)$ , where the linear part describes the capacitance current and the exponential term accounts for the current due to hydrogen evolution. In less acidic solutions  $I_b = a + bx$  was used. All potentials further analysed in this work are half-wave potentials, so for example, where the symbol  $E(M)$  is given it implies  $E_{1/2}(M)$ .

During a ligand titration the pH was kept constant while the ligand concentration was increased, thus  $E_j$  remained essentially unchanged throughout the titration and was negated when calculating the shift in potential,  $\Delta E = E(M) - E(M_{\text{comp}})$ . Ligand titrations were performed by adding 0.5 M picolinic acid solution to the sample solutions containing Cd(II). Both the titrant and sample solutions were adjusted to the same pH using 0.5 M HNO<sub>3</sub> and 0.5 M NaOH. The [L]<sub>T</sub>: [M]<sub>T</sub> concentration ratio was varied stepwise between 10 and 200; a polarogram and the GE potential were recorded at each titration step.

Polarographic data, corrected for  $E_j$  where necessary, were used to evaluate formation constants employing the procedure previously described [16,17]. The following relationship, which is applicable to electrochemically reversible processes as was found to be the case here, was used:

$$\left\{ E(M) - E(M_{\text{comp}})_{(i)} \right\} - \frac{RT}{nF} \ln \frac{I(M_{\text{comp}})_{(i)}}{I(M)_{(i)}} = \frac{RT}{nF} \ln \frac{[M_T]_{(i)}}{[M]_{(i)}} \quad (2)$$

where (i) indicates the value at each pH step or after each addition of a ligand solution, depending on the type of titration performed. The left side of the equation is calculated from experimental data and when plotted vs. pH or log [L], it gives the experimental complex formation curve (ECFC). For a fully labile system, the main component of the ECFC is the shift in potential. The right side of the equation is calculated using mass-balance equations containing formation constants (those that are known and the unknown values being refined), and when plotted vs. pH or log [L], it generates the calculated complex formation curve (CCFC). The formation constants are refined such that the difference between the ECFC and the CCFC is minimised. In the refinement process, the overall formation constants for cadmium hydroxide complexes, the stepwise protonation constants for the ligand and the dissociation constant for water, as given in Table 1, were kept constant.

Table 1. The formation constant for water, the stepwise protonation constants for picolinic acid at 25°C and 0.5 M ionic

strength, and the overall stability constants for cadmium hydroxides at 25°C and 3 M ionic strength [12]. Values in brackets are uncertain.

Equilibrium	log $\beta$
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	-13.74
$\text{L}^- + \text{H}^+ \rightleftharpoons \text{HL}$	5.18
$\text{HL} + \text{H}^+ \rightleftharpoons \text{H}_2\text{L}^+$	(0.86)
$\text{Cd}^{2+} + \text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})^+$	4.0
$\text{Cd}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_2$	7.7
$\text{Cd}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_3^-$	10.3
$\text{Cd}^{2+} + 4\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_4^{2-}$	12.0
$2\text{Cd}^{2+} + \text{OH}^- \rightleftharpoons \text{Cd}_2(\text{OH})^{3+}$	5.06
$4\text{Cd}^{2+} + 4\text{OH}^- \rightleftharpoons \text{Cd}_4(\text{OH})_4^{4+}$	24.9

### 3. Results and Discussion

#### 3.1. Evaluation of $E(\text{Cd})$ using $E(\text{Tl})$

Fig. 1 shows the experimental reduction half-wave potentials of Cd(II),  $E_{\text{exp}}(\text{Cd})$  shown as (○), obtained from the pH titration performed on a solution containing the two metal ions, Cd(II) and Tl(I). The large shift in the reduction potentials clearly illustrates variation in  $E_j$  in the low pH region. Above a pH of about 2,  $E_j$  remains almost constant as indicated by the unchanging half-wave potentials of both metal ions. At pH > 2, the  $E_{\text{exp}}(\text{Cd})$  values were averaged and the parameter obtained,  $E(\text{Cd})_{\text{ave}}$ , corresponds to the free Cd(II) reduction potential ( $E(\text{Cd}) = E(\text{Cd})_{\text{ave}}$ ) and is indicated by the solid line in Fig. 1; note that  $E(M)_{\text{ave}}$  must be determined for each titration due to instability in the performance of the RE system. The value of  $E(\text{Tl})_{\text{ave}}$  was determined in the same way and the difference,  $\Delta E(M) = E(\text{Cd})_{\text{ave}} - E(\text{Tl})_{\text{ave}}$ , was calculated. To facilitate the analysis of  $E_{\text{exp}}(M)$  vs. pH relationships for both metal ions, all the  $E_{\text{exp}}(\text{Tl})$  values were adjusted (by adding  $\Delta E(M)$ ) and they are shown as (×) in Fig. 1.

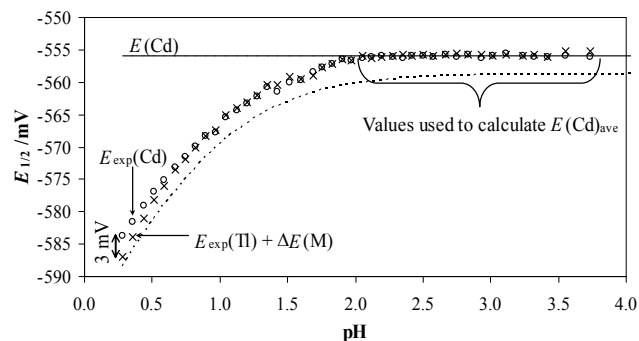


Fig. 1. Experimental (○) and adjusted (×)  $E_{1/2}$  values for reduction of Cd(II) and Tl(I), respectively. The theoretically predicted trend in the reduction potential of Cd(II) is shown as a dotted line.

It is seen that the thallium points (×) reproduced those of cadmium (○) well except at the lowest pH values. This observation, the origin of which will be explained later, is an additional factor which had to be accounted for.

Fortunately, we found  $\Delta E(M)$  to be fairly constant for various data sets when points above pH 2 were considered, irrespective of the actual potentials measured which fluctuated with any variation in the reference system; an average  $\Delta E(M)$  of  $-121.4 \pm 0.6$  mV was found for six data sets. This is an important finding because, for each individual pH titration where the ligand was included in the sample solution, the value of  $E(\text{Cd})$  could be calculated by adding  $-121.4$  mV to  $E(\text{Tl})_{\text{ave}}$  determined from the same experiment. One must remember that the value of  $E(M)$  is critical since the computed (refined) formation constants for all species included in the mass balance equations describing the investigated M-L-OH model depend on this single value (see Eq. 2).

### 3.2. Theoretically modelled $E_j$ vs. pH relationship

Two theories for calculating  $E_j$  were considered, namely using the Henderson equation [3] and the Planck equation [5]. Both of these relationships presume that solutions are ideal and that the ion mobilities remain constant across the junction. In deriving the Henderson equation the formation of a continuous mixture junction is assumed and  $E_j$  between solutions 1 and 2 is calculated by:

$$E_j = \frac{RT}{F} \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1' + V_1') - (U_2' + V_2')} \ln \left( \frac{U_1' + V_1'}{U_2' + V_2'} \right) \quad (3)$$

where  $U = \sum c_+ \lambda_+$ ,  $V = \sum c_- \lambda_-$ ,  $U' = \sum z_+ c_+ \lambda_+$ ,  $V' = \sum z_- c_- \lambda_-$ , and  $c$ ,  $\lambda$  and  $z$  are the molar concentration, conductivity and the charge for each ion, respectively. The Planck equation assumes a constrained diffusion type junction which physically represents the experimental setup used here more closely. If the concentration of solutions 1 and 2 are the same and all ions are singly charged, the Planck equation can be written as [5]:

$$E_j = \frac{RT}{F} \ln \frac{\sum (c_+ u_+)_{1} + \sum (c_- u_-)_{2}}{\sum (c_+ u_+)_{2} + \sum (c_- u_-)_{1}} \quad (4)$$

where  $u$  is the ionic mobility and  $u = \lambda / |z| F$ .

The values of  $E_j$  were calculated and considered only for the junction between the sample solution and the salt bridge solution. The junction between the salt bridge solution and the RE solution was ignored since this potential (about 2.8 mV) essentially remained constant throughout the titration. Thus, for  $E_j$  calculations, solution 1 consisted of a mixture of  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{NO}_3^-$  and  $\text{OH}^-$  ions of varying concentration as the 0.5 M  $\text{HNO}_3$  solution in the polarographic cell was titrated with the 0.5 M  $\text{NaOH}$  solution. Note that the  $\text{Cd(II)}$  and  $\text{Tl(I)}$  metal

ion concentrations were too low to affect the calculated value of  $E_j$  and were thus omitted. Solution 2, in a salt bridge, was kept constant for all pH values and contained 0.5 M of both  $\text{Na}^+$  and  $\text{NO}_3^-$  ions (concentrations of  $\text{H}^+$  and  $\text{OH}^-$  ions due to the dissociation of water were once again too low to affect the calculation). Values of  $E_j$  were determined using limiting conductivities, as well as conductivities at 0.1 M and 0.5 M ionic strength where interionic forces play a larger role. The latter values were calculated using the Onsager limiting law in the form used by Zusková *et al.* [18], even though it is known that the Onsager limiting law is valid for ionic strengths of at most 0.1 M and at higher concentrations the predicted mobilities are too low [3]. We noted that the  $E_j$  values calculated were (i) essentially the same using the two equations for this junction, (ii) larger than those observed experimentally when using conductivities calculated at 0.1 M and 0.5 M ionic strength, and surprisingly (iii) comparable to experimental data when limiting conductivities were used. The simulated  $E_{1/2}$  values accounting for  $E_j$  which was calculated using the Henderson equation and limiting conductivities is shown as the dotted line in Fig. 1.

Clearly, in the M-L equilibrium studies, the theoretically predicted trend in  $E_j$  can only be used as a guide to ensure that the values for  $E_{\text{exp}}(\text{Tl})$  are not problematic and hence give confidence to the calculated potential values for the metal ion being studied, here  $\text{Cd(II)}$ . Additionally, the presence of a witness ion in any polarographic experiment for equilibria studies, not only under acidic conditions, could monitor the behaviour of the reference system. Without a witness ion, any shift in potential would be attributed to the formation of metal complexes when the ligand is present hence deviation in potential of a reference system would go undetected.

### 3.3. The overall $\Delta E(M)$ vs. pH relationship across the pH range

From Fig. 1, it can be seen that the magnitude of  $E_j$  (where  $E_j = E(\text{Cd}) - E_{\text{exp}}(\text{Cd})$  and  $E(\text{Cd})$  depends only on the potential of the RE whereas  $E_{\text{exp}}(\text{Cd})$  also incorporates variation in  $E_j$ ) is about 30 mV at pH 0.3 and decreases as the pH is raised. Also, the experimentally determined  $E_j$  appears to be larger for  $\text{Tl(I)}$  than for  $\text{Cd(II)}$  at the very low pH range (by 2 – 3 mV at pH 0.3). This difference cannot be due to the actual junction (between the sample and the salt bridge solutions) as it is the same regardless of the metal ion being reduced at the working electrode. In the expression derived by Lingane [19] to describe the physical nature of  $E_{1/2}$ , it is seen that  $E_{1/2}$  depends on the standard potential of the amalgam for the cell, as well as on diffusion rates and activity coefficients. The half-wave potential is therefore dependent on the ionic strength of the solution. In these

titration experiments the ionic strength ( $\mu$ ) varied between 0.5 M and 0.25 M; an unfortunate consequence of working in very acidic solutions and at a relatively low ionic strength. As a test, solutions containing Tl(I) and Cd(II) were made up in either 0.5 M or 0.25 M  $\text{KNO}_3$  and the  $E_{1/2}$  values were measured.  $E_{1/2}$  for Cd(II) remained constant (thus the change in ionic strength did not affect the shift in potentials used to evaluate stability constants for the Cd(II)-ligand system), but  $E(\text{Tl})_{\mu=0.5} - E(\text{Tl})_{\mu=0.25} = -2$  mV which correlates well with the observation in Fig. 1.

We decided to account for the experimentally observed difference in  $E_{1/2}$  caused by the change in the ionic strength as a function of pH. Six data sets were collected for pH titrations involving only metal ions and the differences ( $\Delta E(M) = E_{\text{exp}}(\text{Cd}) - E_{\text{exp}}(\text{Tl})$ ) were calculated in the whole pH range for each set of data (i.e. for each individual titration) – see points in Fig. 2. Since  $E_j$  is negligible and constant above pH 2.1, a straight line was fitted resulting in  $\Delta E(M) = -121.4 \pm 0.6$  mV. In the region below pH 2.1, a sixth order polynomial was used to reproduce the nonlinear variation in  $\Delta E(M)$ .

An overall  $\Delta E(M)$  vs. pH relationship was thus generated across the pH range which could be used to calculate the expected experimental reduction potential for cadmium,  $E_{\text{exp}}(\text{Cd})$ , from thallium data recorded on the same solution sample. As a check, the experimental reduction potentials for the uncomplexed Cd(II) were

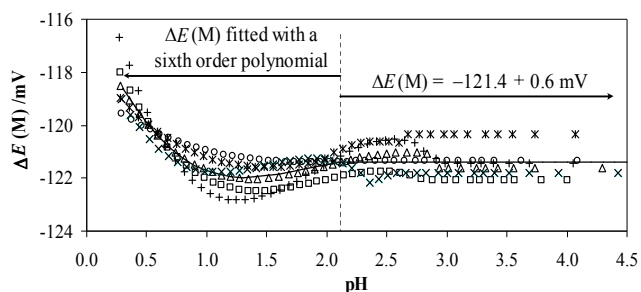


Fig. 2. Variation in  $\Delta E(M)$  with pH for Tl(I) and Cd(II) (solid line). Points represent differences between half-wave potentials of Cd(II) and Tl(I) obtained from individual experiments.

then predicted across the pH range using this model and the  $E_{\text{exp}}(\text{Tl})$  data for each data set (it was assumed that the reference system must have the same effect on the potential measurements for both metal ions). Standard deviations between the experimental and calculated values for each individual experiment varied between 0.3 and 1.8 mV. From that we have concluded that including Tl(I) in the sample solution should enable the  $E_{\text{exp}}(\text{Cd})$  potentials (which also incorporates variation in  $E_j$ ) to be predicted with acceptable accuracy when experiments start below pH 2. Once the overall  $\Delta E(M)$  vs. pH relationship has been established between Cd(II) and

Tl(I), it should, in principle, be possible to apply it in the study of any Cd(II)-ligand system provided that the experimental conditions remain the same.

#### 3.4. Modelling of the Cd(II)-picolinic acid system using the $\Delta E(M)$ function

The  $E_{\text{exp}}(\text{Tl})$  vs. pH curves for titrations in the presence and absence of picolinic acid in the polarographic cell were almost identical; this indicated that no complex formation with Tl(I) occurred in the pH region studied. Fig. 3 shows the experimentally determined Cd(II) potentials ( $\circ$ ) in the presence of picolinic acid ( $[\text{L}]_{\text{T}}:[\text{Cd}]_{\text{T}} = 100.5$ ). To perform speciation analysis (i.e. to establish an M-L model and refined formation constants) one must correct the raw experimental data for  $E_j$  and establish  $E(\text{Cd})$  which is needed to calculate shifts in the reduction potential,  $\Delta E$ , at each pH step in the titration. To achieve this, several operations were performed. Initially, hypothetical reduction potentials for uncomplexed Cd(II) (which incorporate variations in  $E_j$  with pH) were calculated using (i)  $E_{\text{exp}}(\text{Tl}) + \Delta E(M)$  for data obtained at  $\text{pH} < 2.1$ , where  $\Delta E(M)$  values were computed from the 6<sup>th</sup> order polynomial discussed above, and (ii)  $E(\text{Tl})_{\text{ave}} - 121.4$  mV for data recorded at  $\text{pH} > 2.1$ , where  $E(\text{Tl})_{\text{ave}}$  was obtained by averaging the  $E_{\text{exp}}(\text{Tl})$  data collected during this experiment at  $\text{pH} > 2.1$ . The predicted reduction potentials of uncomplexed Cd(II) are shown as ( $\times$ ) in Fig. 3; it is seen that below pH 1 the calculated ( $\times$ ) points coincide with experimental data well indicating the absence of cadmium complexes.

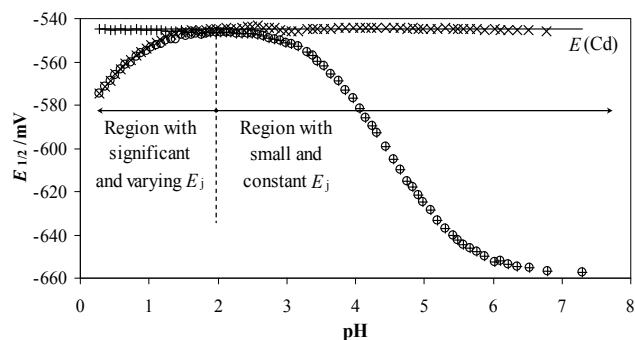


Fig. 3. Half-wave potentials for pH titration where  $[\text{L}]_{\text{T}}:[\text{Cd}]_{\text{T}} = 100.5$ . ( $\circ$ ) - experimental data,  $E_{\text{exp}}(\text{Cd})$ ; ( $\times$ ) - predicted  $E_{\text{exp}}(\text{Cd})$  values incorporating  $E_j$  for uncomplexed Cd(II) using  $E_{\text{exp}}(\text{Tl})$  values; (+) - experimental  $E_{\text{exp}}(\text{Cd})$  corrected for  $E_j$ .  $E(\text{Cd})$  predicted by adding  $-121.4$  mV to  $E(\text{Tl})_{\text{ave}}$  is shown as a solid line.

Finally, potential values suitable for modelling and refinement of formation constants data (shown as (+) in Fig. 3) were obtained by correcting  $E_{\text{exp}}(\text{Cd})$  for  $E_j$  (where  $E_j = E(\text{Cd}) - E(\text{points marked with } (\times))$ ). Two

important observations can be made: (i) above pH of about 2, the calculated (+) and experimental (○) points coincide, and (ii) the calculated  $E(M)$  values at low pH (+) and at higher pH (×) reproduced the estimated  $E(\text{Cd}) = E(\text{Ti})_{\text{ave}} - 121.4 \text{ mV}$  value very well - see solid horizontal line in Fig. 3. This provides some credibility as far as the theoretically generated relationship, (+)-points vs. pH, is concerned.

Fig. 4 depicts the ECFC (○) for  $[\text{L}]_{\text{T}}:[\text{Cd}]_{\text{T}} = 100.5$ ; note that (○)-points were generated from the data seen in Fig. 3 using Eq. 2, where  $E(M) = E(\text{Ti})_{\text{ave}} - 121.4 \text{ mV}$  and  $E(M)_{\text{comp}}$  values are the (+)-points in Fig. 3. From the analysis of the slopes of the ECFC [20], the predominant species in solution could be proposed using the relationship: slope =  $60 \times (\text{number of protons involved})/(\text{number of electrons transferred})$ . A slope of about 47 mV/pH unit in the pH region where the singly protonated form of the ligand (HL) is predominant, indicates the formation of both ML and  $\text{ML}_2$  species. This was deduced from the predicted slopes for the reduction of the ML and  $\text{ML}_2$  complexes being 30 and 60 mV/pH unit, respectively. However, the CCFC for only the two species does not reproduce the ECFC curve fully (see dashed line in Fig. 4) and it is only after the inclusion of  $\text{ML}_3$  that a reasonable fit was produced (solid line in Fig. 4).  $\text{ML}_3$  exists in solution where the ligand is fully deprotonated and hence cannot be predicted from the slope analysis.

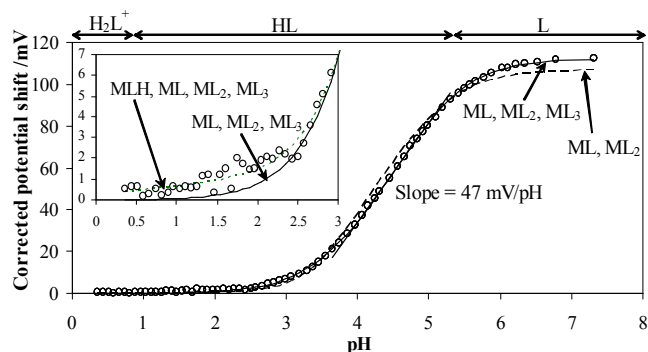


Fig. 4. The ECFC (○) for  $[\text{L}]_{\text{T}}:[\text{Cd}]_{\text{T}} = 100.5$  and two CCFCs for ML and  $\text{ML}_2$  (dashed line) and ML,  $\text{ML}_2$ ,  $\text{ML}_3$  (solid line) models. The inset highlights the very acidic region which shows the effect of incorporating MLH into the model (dotted line).

This model is in agreement with previous GEP [21] and polarographic [11] results. The titration was repeated at  $[\text{L}]_{\text{T}}:[\text{Cd}]_{\text{T}} = 200.0$  and then at  $[\text{L}]_{\text{T}}:[\text{Cd}]_{\text{T}} = 97.2$  but commencing the experiment from about pH 2 in the latter case, where  $E_j$  is negligible. For titrations started at pH 0.3, the fit of the CCFC could be further improved in the very acidic region by including the MLH species, as shown in the inset of Fig. 4. The formation of this species has not, to the authors' knowledge, been

suggested before [12]. This could be due to data not being collected at such low pH values before or, in this case, it could merely be an artefact due to insufficient compensation for  $E_j$  since it is a shift of about 1 mV that leads to the inclusion of MLH in the model. To verify the formation of this complex, crystals were grown from a solution containing 0.5 M of each  $\text{Cd}(\text{NO}_3)_2$  and picolinic acid, which was further acidified using  $\text{HNO}_3$ . The pH of the solution was adjusted to about 0.4 because the species distribution diagram calculated for these solution conditions using the log  $\beta$  values determined here, showed MLH to be the dominant species in solution around pH 0.4. The structure determined [22] clearly showed a protonated pyridine nitrogen atom and the Cd(II) bound to both the carboxylate oxygen atoms. This structure reinforces the existence of the MLH species in solution and also validates the protocol developed here.

### 3.5. Ligand titrations and overall formation constants

Ligand titration experiments were done at pH 3.0, 3.8 and 5.1 and the graph of the corrected potential shift versus log [L] for all three titrations is given in Fig. 5. From the slope analysis, the predominant species in solution could be predicted using the relationship: slope =  $60 \times (\text{number of ligands involved})/(\text{number of electrons transferred})$ . The formation constants for ML and  $\text{ML}_2$  were refined using the pH 3.0 and 3.8 titration data and that for  $\text{ML}_2$  and  $\text{ML}_3$  were refined using the pH 5.1 titration data. In the latter case, the log  $\beta$  value for ML was fixed at the average determined for the other two titrations since ML is only present to a very small extent at pH 5.1, as can be seen in the species distribution diagram (Fig. 6). A ligand titration performed at pH 2.0, to detect MLH, gave noisy data and a maximum shift of 4 mV, thus accurate stability constants could not be refined. For interest, log  $\beta$  values could be refined for either ML ( $4.46 \pm 0.04$ ) or MLH ( $6.45 \pm 0.04$ ), but not for the two species together. The fact that both these values are slightly higher than previously found may indicate that the both species are present, but in very small quantities.

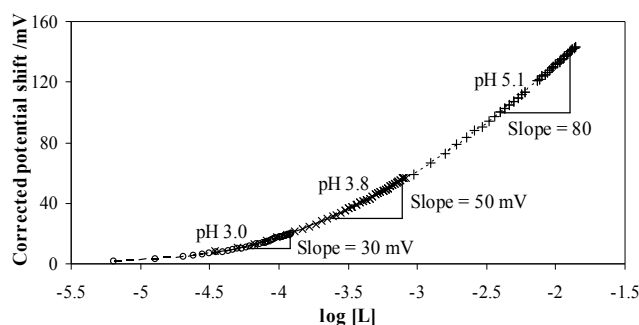


Fig. 5. The ECFCs (point markers) and CCFCs (lines) for the ligand titrations at various pHs are shown together with the slope analysis.

The formation constants determined from both the ligand and the pH titration experiments were averaged and are given in Table 2 and compared to literature data. The formation constant for MLH is only based on the average of two values as it could not be refined for the pH titration started at pH 2. It should be noted that although literature values are quoted at 0.5 M ionic strength [11], the way in which the pH titrations were performed also led to the ionic strength varying between 0.25 and 0.5 M. The species distribution diagram (Fig. 6) plotted for  $[L]_T:[M]_T = 100$  indicates that MLH is a minor species (with a maximum of a tenth of the Cd(II) in this form at pH 1.9) and that the  $ML_3$  species is predominant over a wide pH range (about pH 5 – 11.5).

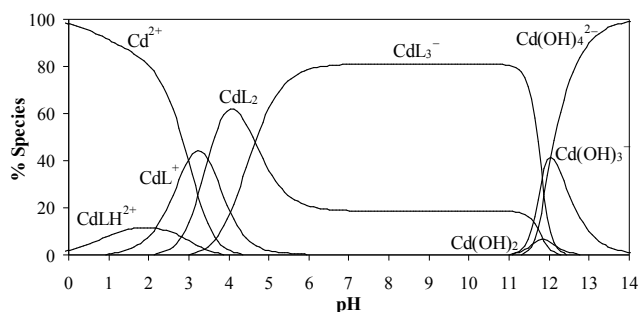


Fig. 6. Species distribution diagram for the model shown in Table 2 with  $[Cd]_T = 1 \times 10^{-4}$  M and  $[L]_T = 1 \times 10^{-2}$  M.

Table 2. Overall formation constants for cadmium-picolinic acid complexes determined in this work and elsewhere [11,12]. The  $\log \beta$  values are reported at 25°C and the given ionic strength.

Equilibrium	$\log \beta$ (This work)	$\log \beta$ [11,12]	
		0.25-0.5 M	0.5 M    0.1 M
$Cd^{2+} + H^+ + L^- \rightleftharpoons CdHL^{2+}$	$6.27 \pm 0.07$		
$Cd^{2+} + L^- \rightleftharpoons CdL^+$	$4.26 \pm 0.03$	4.29 [a]	4.35 [b]
$Cd^{2+} + 2L^- \rightleftharpoons CdL_2$	$7.86 \pm 0.11$	7.89 [a]	8.00 [b]
$Cd^{2+} + 3L^- \rightleftharpoons CdL_3^-$	$10.47 \pm 0.12$	10.49 [a]	10.76 [a]

[a] results by DPP. [b] average quoted in ref. 12 for results by DPP and GE

### 3.6. Evaluating significance of errors in computed formation constants caused by errors in junction potential correction

To evaluate the extent of errors in the computed formation constants, when applying the procedure developed to correct for  $E_j$ , a hypothetical metal-ligand system was investigated. Values selected for formation and protonation constants were loosely based on the Cd(II)-picolinic acid system, but ensuring that complexes exist under more acidic conditions (see Fig. 7) where the junction potential is most significant. Using conditions similar to those in the real experiments described above, current, potential and volume data were simulated for the hypothetical model. To calculate hypothetical  $E_{exp}(M)$  values, shifts in potential due to complex formation were calculated and subtracted from an arbitrarily chosen  $E(M)$  value to give  $E(M_{comp})$ .  $E(M_{comp})$  values were then adjusted for  $E_j$  ( $E_j$  values were calculated using the Henderson equation). The volumes used were typical for experiments run and reduction current values were adjusted by accounting for dilution. The  $\log \beta$  values were then refined for the simulated data. In the real experimental work, two parameters were evaluated using the witness ion approach, namely  $E(M)$  and  $E_j$ , and errors in these parameters were considered separately.

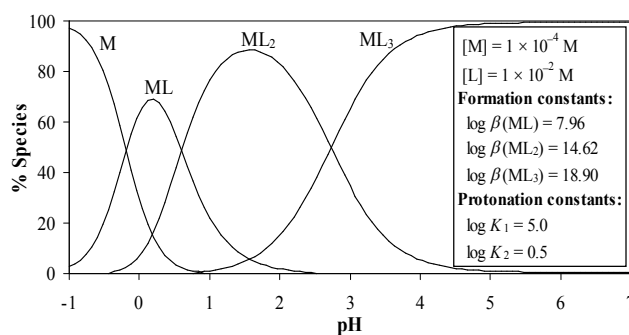


Fig. 7. Species distribution diagram for the hypothetical metal-ligand system.

Firstly, the value of  $E(M)$  was varied and the stability constants refined in each case. From experimental data, the standard deviation for the difference between the  $E(Cd)_{ave}$  and  $E(Tl)_{ave}$  for six data sets was found to be 0.60 mV. Thus the hypothetical value for  $E(M)$  was varied by  $\pm 1$  mV and the  $\log \beta$  values refined. Not surprisingly, the formation constants for all metal-ligand species were affected (this is because  $\Delta E = E(M) - E(M_{comp})$ ) but the maximum error in the refined  $\log \beta$  values was only  $\pm 0.04$  log units.

Secondly, the influence of uncertainty in  $E_j$  was evaluated. The maximum difference observed between experimental and predicted Cd(II) half-wave potentials (when applying the  $\Delta E(M)$  vs. pH relationship) for the six

data sets was 1.8 mV, so the  $E_j$  values calculated using the Henderson equation were adjusted by +2 mV or -2 mV at pH 0.3. The adjustments were then slowly reduced such that they approached zero at about pH 2.5-3. These adjusted  $E_j$  values were then added to the hypothetical  $E_{\text{exp}}(\text{M})$  values as a correction for the junction potential and the stability constants were refined. The  $E_j$  adjustment procedure was repeated using slightly different modifications, each time in line with observations of experimental data, but never adjusting the potential by more than 2 mV. The maximum error in log  $\beta$  values was  $\pm 0.10$  log units for the ML species and  $\pm 0.04$  log units for the  $\text{ML}_2$  species. The  $\text{ML}_3$  species was not really affected by the  $E_j$  correction in this case, where a maximum error of  $\pm 0.01$  log units was found. It is therefore extremely important to evaluate  $E_j$  as accurately as possible to minimise errors in the formation constants for metal-ligand species formed under very acidic conditions.

#### 4. Conclusion

It is well known that for pH values below 2 the diffusion junction potential,  $E_j$ , is (i) significant, (ii) varies with pH and (iii) cannot be directly measured when metal-ligand equilibria studies are performed, hence one must correct for this 'unwanted' and obstructing phenomenon. To correct experimental data for  $E_j$  at extreme pH conditions, an *in-situ* monitoring procedure was developed by introducing a witness ion, Tl(I), which does not undergo complexation under the experimental conditions employed. The proposed protocol, although involved and time consuming, monitors  $E_j$  vs. pH effectively and allows the experimental reduction potentials of the metal ion of interest, here Cd(II), to be corrected for  $E_j$ . We were also able to use the presence of the witness ion to accurately predict the free metal ion potential,  $E(\text{Cd})$ , using the  $E(\text{Tl})$  value. This indirect evaluation (prediction) of  $E(\text{M})$  is critical because (i) all shifts in potential used to compute the formation constants are calculated utilising this single value and (ii) the proposed protocol is also applicable to metal ions for which the free metal ion potential cannot be measured at all, such as Bi(III) which undergoes hydrolysis even in 1 M acid [12]. Furthermore, the witness ion could also be used to monitor the performance of the reference system throughout titration experiments under any conditions, not only in the very low pH region. We have established that the calculated  $E_j$  values (using the Henderson or Planck equations) gave similar trends to those obtained experimentally but they could only be used to assess whether the experimental data follows the expected trend.

The use of a witness metal ion to determine  $E_j$  and  $E(\text{Cd})$  was successfully applied to studying the Cd(II)-

picolinic acid equilibria; the log  $\beta$  values, refined from the mathematically generated rather than experimental data, compared with those found in the literature very well. Importantly, an additional MLH species was predicted in the very acidic region (even though it was only a minor species under the conditions employed) which had not been reported before. The presence of this species is fully supported by a crystal structure reported recently [22]. Successful identification of MLH and refinement of its formation constant together with the excellent agreement between the Cd-L model reported here (including log  $\beta$  values for CdL, CdL<sub>2</sub> and CdL<sub>3</sub>) fully verifies the protocol proposed in this work and opens up a new, although challenging field of speciation studies at extremely low pH values.

### 5. Appendix: List of Selected Symbols Used

#### Glossary

$E(\text{M})$	The reduction potential of the free or uncomplexed metal ion (calculated from the experimental data in this work); it is used in computing formation constants.
$E(\text{M}_{\text{comp}})$	As for $E(\text{M})$ but for the complexed metal ion.
$\Delta E$	Shift in the reduction potential ( $E(\text{M}) - E(\text{M}_{\text{comp}})$ ) used in computing formation constants.
$E_{\text{exp}}$	The experimentally measured reduction potential which also incorporates $E_j$ ; it can be either for the free ( $E_{\text{exp}}(\text{M}) = E(\text{M}) + E_j$ ) or complexed ( $E_{\text{exp}}(\text{M}_{\text{comp}}) = E(\text{M}_{\text{comp}}) + E_j$ ) metal ion.
$E_j$	Diffusion junction potential; calculated as $E_j = E(\text{M}) - E_{\text{exp}}(\text{M})$ in this work.
$E(\text{M})_{\text{ave}}$	Averaged experimental data, $E_{\text{exp}}$ , obtained at pH > 2; it is used to predict $E(\text{M})$ of metal ion under investigation.
$\Delta E(\text{M})$	The difference between $E_{\text{exp}}(\text{M})$ values of two metal ions, that one investigated and the witness metal ion, at any pH; $\Delta E(\text{M}) = E_{\text{exp}}(\text{Cd}) - E_{\text{exp}}(\text{Tl})$ in this work and is used to predict $E(\text{Cd})$ and $E_j$ .

### 6. Acknowledgements

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## Supplementary Information

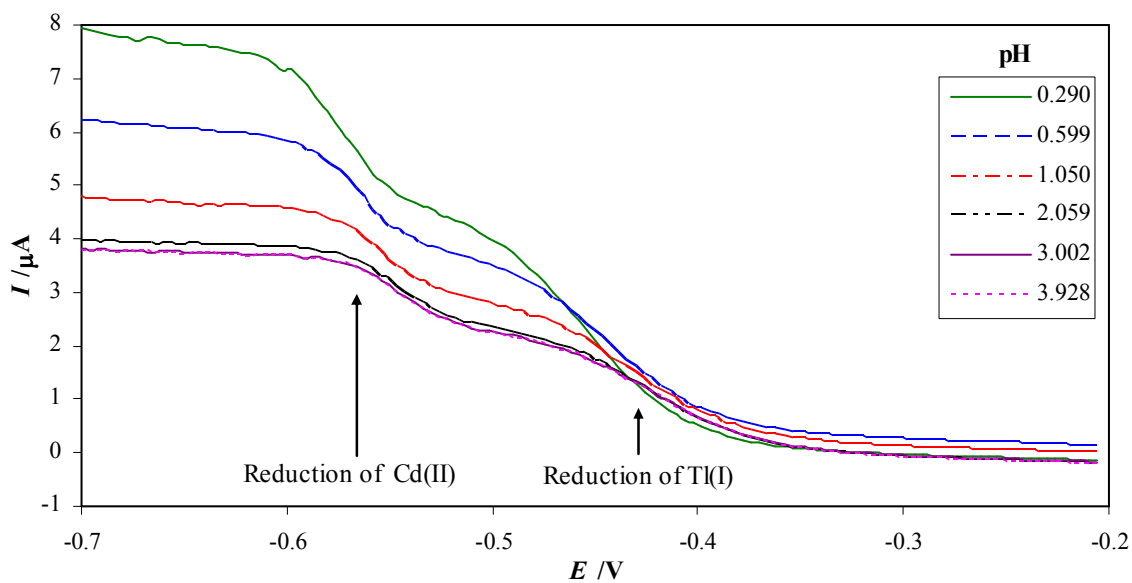


Fig. S1. Polarograms showing the reduction of Tl(I) and Cd(II) at varying pH in the absence of picolinic acid.

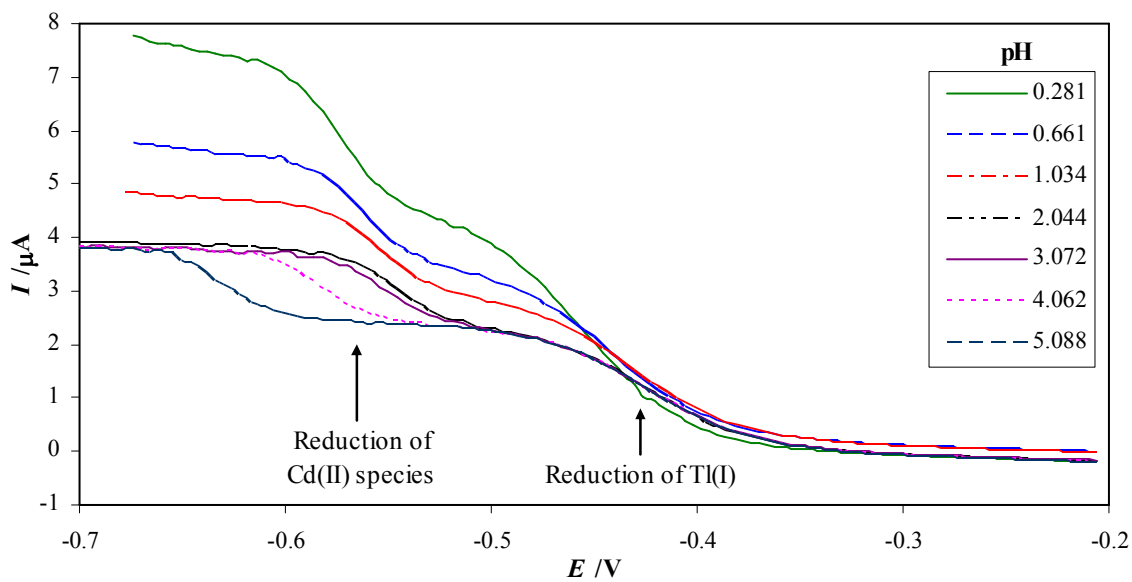


Fig. S2. Polarograms showing the reduction of Tl(I) and Cd(II) species formed with picolinic acid at varying pH for  $[L]_T:[Cd]_T = 100.5$ .