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Variable temperature complexation studies of Cd(II)-dipicolinic acid revealing an endothermically formed species at $T = 313$ K

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ABSTRACT

The Cd(II)-dipicolinic acid (pyridine-2,6-dicarboxylic acid) system was studied by polarography in the temperature range (298 to 313) K and ionic strength of (0.25 to 0.5) mol · dm^{-3} (H,K)NO_3. Apart from detecting the already reported ML and ML_2 complexes and reporting the log β values at T = (298, 305 and 313) K, an ML_3 complex was also found to form at 40 °C giving a log β value of 13.5 ± 0.1. ML_3 was not present to a significant extent at lower temperatures indicating an endothermic formation process. This finding is supported by the ML_3 structure being reported for crystals grown at $T = 313$ K. The system was also studied from pH 1 using protocols developed employing Tl(I) as an internal reference. The MLH species was found in the low pH range with log β values of 8.4 ± 0.2, 8.2 ± 0.2 and 8.0 ± 0.1 found at T = (298, 305 and 313) K, respectively.

1. Introduction

Formation constants can be determined using a wide range of techniques, however, the underlying procedures are similar with the need to strictly adhere to a number of criteria in order to produce values that are comparable, meaningful and as accurate as possible. These criteria are clearly outlined by Martell and Hancock [1] and involve aspects such as temperature (T), ionic strength (μ), supporting electrolytes, calibration procedures and so on. This appears to have led to certain protocols being adopted, even though it is strictly not a requirement. One of those is the temperature at which these constants are determined. Formation constants are temperature dependent and most work has justifiably been done at room temperature (either 293 or 298 K) which allows the stability of complexes to be directly compared (provided the solvent, supporting electrolyte and ionic strengths are similar). Occasionally measurements are made at $T = 310$ K for physiological applications.

For the cadmium(II)-dipicolinic acid (DPA) system, which was studied in this work, formation constants have been reported at either T = (293 or 298) K (and a range of ionic strengths). The critically assessed log β values for the ML and ML_2 species in table 1 were given in the NIST database [2]. Values found by Suzuki and Yamasaki [3] appeared to be too low (log β(ML) = 5.7 and log β(ML_2) = 10 species at $T = 298$ K and $\mu = 0.1$ mol · dm^{-3}) and Norkus *et al.* [4] determined log β(ML_2) = 11.0 at $T = 293$ K (μ = 0.4 mol · dm^{-3}) but did not consider the ML species.

Due to our interest in investigating the relationship between solution complexes and those formed in the solid state, it was noted that for the Cd(II)-DPA system no structures were published for the ML species, but several were reported for the ML_2 complex in the Cambridge Structural Database (REFCODES: CONXEJ, DAZNAU, IWIREL, MELYOS, NOJDOG, RIVHIO) [7]. Interestingly, two structures for a ML_3 complex were also found [8,9], yet this complex has not been reported in any solution studies before. The ML_3 crystals were grown from aqueous solutions, using either ammonia or ethylenediamine to possibly aid dissolution or crystallization, but it did not coordinate to Cd(II). Additionally, due to the relatively poor solubility of DPA (5.0 g · dm^{-3} [10] = 0.30 mol · dm^{-3} at $T = 293$ K), solutions were heated to $T = 333$ K when preparing the liquors from which the crystals were grown. The question as to why this species was never detected in solution arose. Did the amine stabilise the ML_3 complex or could heating the solution have played a role? In this work solutions were studied at T = (305 and 313) K in order to investigate the latter.

Furthermore, since protocols had been developed to study complex formation below pH 2 using polarography, these were applied here to gain insight into the very acidic region [11,12]. This involves incorporating thallium(I) as a reference ion in solution to monitor the diffusion junction potential (E_j) and also assist in the accurate determination of the reduction potential of the

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TABLE 1
Formation constants for the Cd(II)-DPA system at the given temperatures and ionic strengths.

Log β(ML)	Log β(ML_2)	T/K	μ/mol · dm^{-3}	Ref.
6.75	11.15	293	0.1	[2,5]
6.36	10.90	298	0.1	[2]
6.51	10.77	298	1.0	[2,6]

uncomplexed metal ion (E(M)). Tl(I) was selected as it does not readily form complexes, especially under very acidic conditions, thus any changes in its reduction potential for pH < ~2 could be ascribed to E_j. Previously, when considering the Cd(II)-picolinic acid system in studies from pH 0.3 [11], the MLH species was predicted to exist in the low pH range but was only a minor species under the conditions used. The structure of the MLH species was determined from crystals grown in solutions adjusted to the pH predicted by the solution studies, thus supporting the finding in solution [13]. It was found that the pyridyl nitrogen was protonated and the cadmium was bound via the two carboxylate oxygens. Forming a protonated DPA species is certainly structurally conceivable and a MLH species has been reported for the Cu(II) complex [2].

2. Experimental

2.1. Reagents

Deionized water from a Milli-Q water purification unit (resistivity = 18 MΩ cm) and analytical grade reagents were used throughout. Stock solutions containing 0.100 mol · dm^{-3} Cd(II) nitrate tetrahydrate (⩾99%, Fluka) and 0.100 mol · dm^{-3} Tl(I) nitrate (⩾99%, Merck), both in 0.5 mol · dm^{-3} HNO_3 were made up. Dipicolinic acid was ⩾99% pure (Sigma–Aldrich). Solutions for polarographic analysis were purged with ultra-high purity (99.999%) nitrogen.

2.2. Instrumentation

The polarographic cell incorporated a dropping mercury electrode (DME), a Ag/AgCl (3 mol · dm^{-3} KCl) reference electrode in a salt bridge containing 0.5 mol · dm^{-3} KNO_3 and a platinum counter electrode (all supplied by Metrohm). The temperature of the cell was maintained by using a jacketed-cell connected to a Labcon CPE 100 thermostat and monitored using Metrohm Pt 1000 thermocouple. Polarographic experiments were conducted at T = (298.2, 305.2 and 313.2) ± 0.1 K. The pH was measured using a combined glass electrode (GE) which was calibrated at the required temperature by titration of 0.5 mol · dm^{-3} HNO_3 by 0.5 mol·dm^{-3} KOH (both standardized) thus giving pH = $-\log[H^+]$. For the accurate determination of pH especially in the very acidic region, any slight deviation from linearity on the calibration plot was accounted for as previously described [14]. An automated system comprising a BAS CV-27 potentiostat and various Metrohm components (713 pH meter, 765 Dosimat, 663 VA stand and 728 magnetic stirrer) were linked to a computer running LabVIEW software (version 7) via a homemade interface as previously described [15]. Sampled direct current polarography (DC_{TAST}) was used in the potential range –(200 to 850) mV, with a step time of 1 s, a step potential of 4 mV and a current integration time of 60 ms.

2.3. Procedure

Initial polarographic-pH titration experiments were conducted in the absence of ligand in order to derive models for determining E_j and E(Cd) as previously described [11,12]. Solutions containing 9.98 · 10^{-5} mol · dm^{-3} Cd(II) and 1.99 · 10^{-4} mol · dm^{-3} Tl(I) in 0.5 mol·dm^{-3} HNO_3 were titrated with 0.5 mol · dm^{-3} KOH using a pH step of about 0.1, where the GE potential and a polarogram were recorded at each step, between pH 0.3 and 7. This was done at each temperature (five experiments at 298 K and three each at 305 and 313 K). Unfortunately, during these titrations the ionic strength decreases from (0.5 to 0.25) mol · dm^{-3} as no inert electrolyte was added because it was aimed at working at ionic strengths not too different from that used in work already reported.

Complexation experiments were run as above, but DPA was added together with the Cd(II) and Tl(I) to the 0.5 mol · dm^{-3} HNO_3 solution before titration with 0.5 mol · dm^{-3} KOH commenced. Experiments were performed at three different DPA-to-Cd(II) concentration ratios (approximately equal to 20, 40 and 50) at each temperature and 40 to 60 polarograms were collected for each experiment.

A ligand titration was conducted at T = 313 K and pH 8. A solution containing 0.5 mol dm^{-3} KNO_3 and 1.00 · 10^{-4} mol · dm^{-3} Cd (II) adjusted to pH 8 was titrated by a solution of 0.01018 mol · dm^{-3} DPA in 0.5 mol · dm^{-3} KNO_3 also adjusted to pH 8, such that [L]:[M] was varied between 10 and 140.

Experimental half-wave potentials ($E_{1/2}$) and diffusion-limited currents (I_d) were obtained from polarograms recorded at each pH for both metal ions using fitting procedures described elsewhere [11]. Formation constants were calculated using the relationship proposed by Cukrowski [16].

$$\{E(\mathrm{M}) - E(\mathrm{M_{comp}})_i\} - \frac{\mathrm{RT}}{\mathrm{nF}}\ln\frac{I(\mathrm{M_{comp}})_i}{I(\mathrm{M})_i} = \frac{\mathrm{RT}}{\mathrm{nF}}\ln\frac{[\mathrm{M}_T]_i}{[\mathrm{M}]_i} \tag{1}$$

where E(M) and $E(M_{comp})$ are the half-wave potentials of the free (uncomplexed) and complexed metal ion, I(M) and I(M_{comp}) are the diffusion-limited currents for the free and complexed metal ion, [M] and [M_T] are the free and total metal ion concentrations, respectively. The subscript i indicates the value obtained at each pH step or ligand concentration, depending on the type of titration experiment. The left side of the equation (called the corrected potential shift) plotted *vs.* pH represents the experimental complex formation curve (ECFC) which was calculated from experimental data. The right side of the equation is computed using mass-balance equations and stability constants incorporating all possible solution species to yield the calculated complex formation curve (CCFC) when plotted *vs.* pH.

Protonation constants for DPA, Cd(II)-hydroxide formation constants and the dissociation constant for water, all at T = 298 K, are given in table 2. Only formation constants for the Cd(II)-DPA species were refined when determining the CCFC, all others were kept unchanged. Constants for experiments at T = (305 and 313) K were determined using the van't Hoff equation and enthalpies of formation (ΔH) as will be discussed in Section 3.3.

TABLE 2
Constants for the given equilibria at T = 298 K and the given ionic strengths.

Equilibrium	Log β	μ/mol · dm^{-3}	Ref.
$H_2O \rightleftharpoons H^+ + OH^-$	−13.74	0.5	[2]
$L^{2-} + H^+ \rightleftharpoons HL^-$	4.51	0.5	[2]
$HL^- + H^+ \rightleftharpoons H_2L$	2.05	0.5	[2]
$Cd^{2+} + OH^- \rightleftharpoons CdOH^+$	3.32	0.5	[17]
$Cd^{2+} + 2OH^- \rightleftharpoons Cd(OH)_2$	6.75	0.5	[17]
$Cd^{2+} + 3OH^- \rightleftharpoons Cd(OH)_3^-$	10.3	3	[2]
$Cd^{2+} + 4OH^- \rightleftharpoons Cd(OH)_4^{2-}$	12.0	3	[2]
$2Cd^{2+} + OH^- \rightleftharpoons Cd_2(OH)^{3+}$	5.06	3	[2]
$4Cd^{2+} + 4OH^- \rightleftharpoons Cd_4(OH)_4^{4+}$	23.7	3	[2]