Complexation of palladium(II) with monovalent anionic ligands – a spectrophotometric investigation

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Solemn Declaration

I, Cornelius Johannes le Roux, declare herewith that the thesis entitled,

Complexation of palladium(II) with monovalent anionic ligands – a spectrophotometric investigation,

which I herewith submit to the North-West University (NWU) as completion of the requirement set for the Doctor of Philosophy in Chemistry degree, is my own work, has been text edited as required, and has not been submitted to any other tertiary institution other than the NWU.

Signature of the candidate:  University number: 12138886

Signed at **Potchefstroom** on **27 October 2018**

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Soli Deo Gloria

Preface

- This is to state that I, Cornelius Johannes le Roux, have chosen the article format for submitting my thesis as allowed by the North-West University (NWU) under the General Academic Rules (A-rules) set for post-graduate curricula.
- The thesis was written in South African English.
- The thesis consists of two published articles and one article that is currently under review:

  Article 1: Complexation of palladium(II) with thiocyanate - A spectrophotometric investigation, DOI: 10.1080/00958972.2014.918264
  Authors: C.J. le Roux, P. Gans, R.J. Kriek.

  Article 2: A detailed spectrophotometric investigation of the complexation of palladium(II) with chloride and bromide, DOI: 10.1016/j.hydromet.2017.02.023.
  Authors: C.J. le Roux, R.J. Kriek.

  Article 3: A detailed spectrophotometric investigation of the stability constants of $[PdCl_n(OH)_{4-n}]^{2-}$ and $[PdBr_n(OH)_{4-n}]^{2-}$ (n = 0 – 4). The revised manuscript was resubmitted to Hydrometallurgy and is currently under review.
  Authors: C.J. le Roux, R.J. Kriek.

- The same formatting style was used in all three articles, and the figure and table numbers were changed to match the thesis. The original published articles are attached at the end of the thesis.
- The work was done by myself, Cornelius J le Roux, with editing done and suggestions given by Prof RJ Kriek, promoter of my PhD. Dr Peter Gans (a copy of the consent email was included in the attachments) assisted with the calculation of the stability constants.
- All of the co-authors have been informed that the respective articles will form part of the candidate's PhD, submitted in article format, and have granted permission that the articles may be used for the purpose stated.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

E_h-pH	potential/pH diagram
HySS	Hyperquad Simulation and Speciation
ICP	Inductively Coupled Plasma
IUPAC	International Union of Pure and Applied Chemistry
LLE	liquid–liquid extraction
NIST	National Institute of Standards and Technology
PGM	Platinum Group Metals
tet	tetraamine
UV	Ultraviolet
UV-vis	Ultraviolet–visible
oz	Ounce

Summary

The hydrometallurgical processing of platinum group metals (PGMs) requires exact knowledge of the speciation (identity and distribution of specific metallic species/complexes in solution) of the metal complexes involved. The stability constants (also known as formation constants) convert into Gibbs free energies that, when different, result in a shift of the stability regions of different complexes that are illustrated by a Pourbaix diagram.

Information on the stability constants of palladium complexes with monovalent ligands (i.e. thiocyanate, chloride, bromide and mixed palladium(II) chloro-hydroxo and palladium(II) bromo-hydroxo complexes) in solution is not readily available and quite limited. The majority of the methods employed involved the preparation of individual solutions with varying concentrations of the base metal, ligand or both. These techniques yielded only a few useable data points. To improve on this experimental shortcoming, an improved automated titration method was developed and employed to investigate the spectrophotometry of these complexes at 25 °C and an ionic strength of 1.0 M.

This new experimental method was developed by combining two specialized analytical apparatus that made it possible to automatically vary the ligand concentration over various intervals ensuring a very accurate and consistent set of absorbance data. The ideal titration conditions were determined by employing the Hyperquad Simulation and Speciation (HySS) software, while the stability constants for all of the palladium systems were calculated with the software program HypSpec. HypSpec software is specifically developed for the determination of stability constants from spectrophotometric data.

The stability constants, log β_n, determined in this study for the palladium(II) thiocyanate complexes $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4), which are generally accepted to be square planar, are: log β_1 = 8.14, log β_2 = 15.46, log β_3 = 21.94, and log β_4 = 27.42. However, a five-coordinated species, i.e. $[Pd(SCN_5]^{3-}$, with a formation constant of log β_5 = 31.94, would seem to exist (proposed to be square pyramidal) and form part of the system. These published results represent the first complete set of communicated stability constants.

The experimental procedure was customized to determine the stability constants for the palladium(II)-chloride and -bromide complexes. For $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4), the log β

values are: log β_1 = 4.49, log β_2 = 7.80, log β_3 = 10.18 and log β_4 = 11.54, while the log β values for $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4), are: log β_1 = 5.04, log β_2 = 9.12, log β_3 = 12.38 and log β_4 = 14.55. For the chloride system our results represent a refinement of already published data, whereas our results for the bromide system represent only the second full set of published stability constants that are deemed to be much more accurate and reliable.

Similarly, the experimental procedure was again modified and applied to the mixed palladium(II) chloro-hydroxo and palladium(II) bromo-hydroxo complexes. The stability constants for the mixed chloro-hydroxo complexes $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), are: log β_1 = 18.36, log β_2 = 23.21, log β_3 = 26.91 and log β_4 = 29.68. The stepwise stability constants of the palladium(II) bromo-hydroxo system, $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), are as follows: log β_1 = 18.73, log β_2 = 22.25, log β_3 = 25.58 and log β_4 = 28.47. For the chloro-hydroxo system our results represent a refinement of already published data, whereas our results for the bromo-hydroxo system represent the first set of stability constants.

The newly developed experimental technique, linking and automating a double burette auto-titrator with a UV-vis spectrophotometer equipped with a flow-through cuvette, was applied to five different palladium(II) systems with great success. This technique can be applied to similar metal-ligand systems for the accurate determination of stepwise stability constants.

Keywords: palladium(II), bromide, chloride, thiocyanate, hydroxide, complexation, formation constants, spectrophotometry, stability constants, speciation

CHAPTER 1
INTRODUCTION & OBJECTIVES

The platinum group metals (PGMs) consists of six elements, i.e. Platinum (Pt), Palladium (Pd), Rhodium (Rh), Iridium (Ir), Ruthenium (Ru) and Osmium (Os). These elements are chemically and structurally similar and are most valued for their wide variety of industrial, medical, and electronic applications. These versatile metals play a significant role in many of the products we use every day. South Africa and Russia are the main producers of platinum, palladium, and rhodium. The world's three top PGM producers, i.e. Anglo Platinum, Impala Platinum, and Lonmin, have their mining and refining operations in South Africa [1-10].

Palladium is chemically stable, similar to platinum and has exceptional catalytic properties. Not only can it be used as a substitute for the more expensive platinum in catalytic converters, but it's unique ability to absorb hydrogen also makes it popular for a variety of chemical processes. Specific applications include the processes that require hydrogen exchange between two reactants, such as these that produce the raw materials for synthetic rubber and nylon.

Other uses include jewelry and more recent as electro catalyst in fuel cell and electrolyser technologies [9, 11-13]. The supply and demand for palladium are shown in Table 1 [14, 15].

Table 1: A summary of the supply and demand of palladium from 2014 to 2017

Palladium Supply and Demand oz (x 1000)				
Supply	**2014**	**2015**	**2016**	**2017**
South Africa	2125	2684	2574	2581
Russia	2589	2434	2773	2684
Others	1389	1336	1415	1366
Total Supply	**6103**	**6454**	**6762**	**6631**
Gross Demand				
Auto catalyst	7500	7651	7935	8217
Jewelry	272	223	189	182
Industrial	2001	2007	1938	2028
Investment	943	**-659**	**-646**	**-298**
Total Gross Demand	**10716**	**9222**	**9416**	**10129**
Recycling	**-2752**	**-2412**	**-2491**	**-2706**
Total Net Demand	**7964**	**6810**	**6925**	**7423**
Movement in Stocks	**-1861**	**-356**	**-163**	**-792**

From Table 1 it is evident that South Africa and Russia are the main suppliers of palladium, with South Africa producing more than a third of the world's platinum. The majority of palladium is used for auto catalysts and industrial applications. More than 40% of the palladium produced is recycled. It will not be possible to meet the demand without the recycled amount of palladium.

Hydrometallurgical processes play an important part in the processing, refining and recycling of the palladium. These processes are divided into three areas, i.e. leaching, solution purification and metal recovery [7, 8, 16-21]. Leaching is the process by which a precious metal like palladium is extracted by introducing it to aqueous solutions. Once the leaching process is completed, the leach liquor is processed, and by doing so, the metal ions that are to be recovered are more concentrated. Due to the leaching process, some unwanted metals may

have also been taken into solution, and the solution is often purified to eliminate these unwanted components.

Various purification techniques exist, but the two most well-known purification techniques employed are solvent extraction and ion exchange. Solvent extraction also known as liquid–liquid extraction (LLE), is a method to separate metal complexes, based on their relative solubilities in two different immiscible liquids [22]. These liquids are typically water-based solutions which are more polar and an organic-based solvent which is non-polar. Ion exchange is an exchange of ions between an electrolyte solution and a metal complex. Chelating agents, natural zeolites, activated carbon, resins, and liquid organics impregnated with chelating agents are typically used to exchange cations or anions within a solution.

A stability constant, also known as a formation constant, is an equilibrium constant that provides a measure of strength of the interaction between reagents that come together to form a complex. The speciation of a specific system, i.e. the identity and distribution of specific metallic species/complexes in solution, is essential in developing and understanding dedicated hydrometallurgical processes as the stability constants convert into Gibbs free energies that, if different, result in a shift of the stability regions of different complexes in a Pourbaix diagram.

To that regard information on the stability constants of both noble metals and base metals is imperative for the successful development of effective separation processes. Information on the stability constants of palladium complexes in solution is not readily available. The United States' NIST (National Institute of Standards and Technology) database of critically selected stability constants for metal complexes, as well as the IUPAC stability constants database, lists extremely limited data about palladium complexes.

For this study, the speciation of palladium(II) with three monovalent anionic ligands of interest, i.e. thiocyanate, chloride and bromide were investigated. All of these ligands have shown great leaching possibilities. However, as shown in Chapter 2, very little reliable speciation data exists for these metal complexes.

1.1 Aim

The aim of this study is to develop a dedicated experimental procedure to successfully determine the stability constants of various palladium(II) complexes of monovalent anionic ligands (SCN^-, Cl^- and Br^-.) and palladium(II) halide (Cl^- and Br^-) – hydroxo mixed complexes.

1.2 Objectives

The objectives of this study are:

a) A literature review of known stability constants and experimental methods used
b) The development of an extensive automated titration method specifically for accurate speciation data generation
c) The determination of stepwise formation constants for palladium(II) thiocyanate complexes
d) The determination of stepwise formation constants for palladium(II) chloride – and bromide complexes
e) The determination of stepwise formation constants for palladium(II) mixed halide (Cl^- and Br^-) hydroxo complexes
f) The validation and detailed explanation of the developed experimental method for future metal-ligand studies

1.3 Outline of the thesis

The thesis consists of seven chapters that are: the introduction and objectives, a palladium(II) speciation method review, the speciation of palladium(II) with thiocyanate, a detailed investigation into the complexation of palladium(II) with chloride and bromide, an investigation of mixed palladium(II) chloro-hydroxo and bromo-hydroxo complexes, full details of the automated speciation method and finally, a conclusion with recommendations for future work. The thesis is presented in article format, however, the original formatting of the submitted articles were changed to ensure a uniform layout and reference style. The original submitted/published articles are included in the attachments.

Experimental work, data processing and interpretation, research, and writing of the scientific paper, was performed by the candidate, C.J. le Roux. For the article presented in Chapter 3, P. Gans assisted with calculation of the stability constants and in all three articles (Chapter 3, Chapter 4 and Chapter 5) RJ Kriek (supervisor) made conceptual contributions. The original reference to the online article are presented in the beginning of each of the related chapters.

1.4 Methodology

The main focus of this study was to develop a dedicated and improved experimental procedure to successfully determine more accurate stability constants of different palladium(II) complexes. Previous authors made use of a batch-type experimental method, which produced a limited number of usable spectrophotometric data [23-38]. To improve the current speciation data for the systems in question, the number of spectrophotometric data that are used to calculate the formation constants had to be improved [39]. This improvement of experimental data was made possible by introducing an automated titration method which could generate large amounts of repeatable spectrophotometric data. The ideal titration condition was determined by simulation of the titration with HySS (Hyperquad Simulation and Speciation) which is part of the Hyperquad suit. HypSpec, a software program specially developed to calculate formation constants from spectrophotometric data, and also part of the Hyperquad suit [39, 40], was used to calculate the applicable formation constants and related molar absorbance spectra.

The first system that was investigated was palladium(II) thiocyanate. No stepwise formation data exists for this system, and the values that are available vary considerably. The next system of interest is palladium(II) chloride. Some speciation data is available for this system, however, there exists some uncertainty due to the amount of spectrophotometric data used in the calculations. The experimental method was then customized to generate more than 300 concentration variations to calculate formation constants for the palladium(II) bromide system for which even fewer speciation data exists. Finally, the method was adapted to determine stability constants of the mixed palladium(II) chloro-hydroxo and palladium(II) bromo-hydroxo complexes. Currently, no speciation data exits for the mixed palladium(II) bromo-hydroxo complexes.

1.5 References

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CHAPTER 2

PALLADIUM(II) SPECIATION METHOD REVIEW

Over the decades various methods were used to determine stability constants of metal complexes. The majority of these methods involved the preparation of individual samples with varying concentrations of the base metal, ligand or both. These techniques yielded only a few useable data points. In order to obtain reliable data more advanced speciation techniques were needed to ensure a large number of data points which could be repeated to ensure the legitimacy of the technique and calculated formation constants.

In all of the metal complexes palladium(II) was used as the metal. All the available literature values (excluding the published work from this thesis) for the metal complexes investigated in this study to date are shown in Table 2 emphasizing the lack in speciation data for the complexes in question.

Table 2: Published stepwise formation constants for the complexation of palladium(II) with monovalent anionic ligands

Complexation of palladium(II) with thiocyanate				
log β_1	log β_2	log β_3	log β_4	Reference
–	16.20	–	25.60	[1]
–	–	–	19.46	[2]
–	–	–	27.20	[3]
–	–	–	27.60	[4]
–	–	–	28.22	[5]
–	–	–	28.67	[6]
Complexation of palladium(II) with chloride				
log β_1	log β_2	log β_3	log β_4	Reference
4.47	7.76	10.17	11.54	[7]
4.40	7.74	10.08	11.46	[8]
4.47	7.80	10.18	11.53	[9]
Complexation of palladium(II) with bromide				
log β_1 / K_1	log β_2	log β_3	K_4	log β_4	Reference
5.17	9.42	12.7	2.20	14.9	[7]
–	–	–	2.23	–	[10]
–	–	–		13.05	[5]
–	–	–	2.16	–	[11]
–	–	–	2.20	–	[12]
4.37	–	–	3.50	–	[13]
Palladium(II) chloro-hydroxo and palladium(II) bromo-hydroxo complexes					
Complex	log β_{31}	log β_{22}	log β_{13}	log β_{04}	Reference
$[PdCl_p(OH)_q]^{2-}$	16.48	20.63	24.02	26.23	[9]
$[PdCl_p(OH)_q]^{2-}$	18.23	–	–	–	[14]
$[PdBr_p(OH)_q]^{2-}$	–	–	–	–	

p and *q* referring to the number of bromide and hydroxide ions in the complex

2.1 Palladium(II) thiocyanate speciation methods

In most speciation studies various types of batch methods are used where a number of samples with varying metal/ligand concentrations are prepared and analysed. One of these methods is the method of continuous variation, or Job's method which is used to determine the stoichiometry of a binding occurrence when only two species are present [1, 15, 16]. In this method, the total molar concentration of the metal and the ligand are held constant, but their mole fractions are varied. In the case of a competition reaction, a metal-ligand complex with a known stability constant is used to determine the stability constant of the new metal-ligand species after the original ligand was substituted. This method is mostly used where a stability constant is too large to be measured directly. The advantage of this method is its simplicity and in most cases a computer supported data fit is not necessary. The disadvantage of this method is that it is best applied if only one or at most two complexes are present in solution [15] and cannot be applied to a complete stepwise formation method as required. This method was used to determine stability constants for some of the palladium(II) thiocyanate complexes. For the determination of $\log\beta_2$ by Joshi *et al*. [3] a solution of palladium(II) with a known quantity of chloride as starting material was prepared. The complexation of Pd(II) with SCN^- was expressed as mixed complexes (Equation 1).

$$PdCl_m + nSCN^- \rightleftharpoons Pd(SCN)_nCl_{m-n} + nCl^- \quad (1)$$

The nature of the complexes was determined employing both Job's continuous variation method and the slope ratio method using different individual solutions that contained specific ratios of Pd(II) and SCN^- with an excess of Cl^-. For the latter method palladium chloride was used as a source of palladium and the chloride concentration was kept constant while the solution was titrated with thiocyanate. These methods enabled the authors to spectrophotometrically calculate both $\log\beta_2$ and $\log\beta_4$ for the complexation of palladium with thiocyanate.

Another experimental batch-type method that was employed to determine the stability constant of the tetrathiocyanatopalladate(II) was the competition method which mainly consisted of competition reactions between ligands having known stability constants with Pd(II) and thiocyanate [11 - 13]. This method was successfully used to determine the stability of the palladium(II) complexes with linear tetraamines [17]. By using this method as reference, a

rather complex competition method was developed by Harrington et.al [3] to determine the stability constant, log β_4, for the tetrathiocyanatopalladate(II) complex. A solution of $[Pd(SCN)_4]^{2-}$ and 2,2,2-tet was prepared at pH 2 and then titrated with a base until a transition pH was reached. The 2,2,2-tet complex was deprotonated and the red $[Pd(SCN)_4]^{2-}$ ion broken down to give the colourless $[Pd(2,2,2\text{-tet})]^{2+}$ complex which were used to calculate logβ_4 for the $[Pd(SCN)_4]^{2-}$ complex (Equations 2 and 3).

$$[Pd(SCN)_4]^{2-} + 2,2,2\text{-tet} + H^+ \rightleftharpoons [Pd(2,2,2\text{-tetH})SCN]^{2+} + 3SCN^- \quad (2)$$

$$[Pd(2,2,2\text{-tetH})SCN]^{2+} \rightleftharpoons [Pd(2,2,2\text{-tet})]^{2+} + SCN^- + H^+ \quad (3)$$

Although this method yielded good results, it can only be used to determine the stability constant for one palladium(II) thiocyanate complex.

2.2 Palladium(II) chloride speciation methods

The determination of stability constants for various palladium(II) chloride complexes was published by a number of authors [7-10, 14, 18-22]. Different methods of preparing palladium(II) solutions was used with the most common method of preparation being the precipitation of palladium hydroxide from chloride or nitrate followed by the dissolution of the washed hydroxide in perchloric acid [6-8, 12, 14, 19-21, 23]. The purity of the palladium(II) solutions and the analysis methods used resulted in uncertainty of the above mentioned published data.

The three studies of interest are that of Elding [7], Cruywagen and Kriek [9] and Weed [8]. Although Boily and Seward [22] also published stability constants for palladium(II) chloride complexes, the study was done at different temperatures. They made use of $PdCl_2$ to prepare a palladium(II) chloride stock solution and for the preparation of a chloride free palladium(II) solution, a solution of barium perchlorate was added to a solution of palladium(II) sulphate in identical equivalence in $HClO_4$ [22, 24]. Cruywagen and Kriek [9] also made use of $PdCl_2$ as a source of palladium(II) and hydrochloric acid and perchloric acid was used to vary the chloride concertation at a constant pH. Elding [7] made use of palladium sponge which was dissolved in a mixture of hot fuming nitric acid and perchloric acid to prepare a palladium(II) stock solution. The nitric acid was subsequently removed by several evaporations employing concentrated perchloric acid. In all of the above-mentioned studies of interest, a batch type

method where a number of individual solutions with varying metal/ligand concentrations were prepared and analysed, was employed. For these studies of interest, the ionic strength was kept constant at 1 M and the temperature constant at 25 °C. Authors used various software packages which included Letagrop [7], Hyperquad 2000 [9] and Gaussian98 [22, 24] to calculate the stability constants of the different palladium(II) complexes.

2.3 Palladium(II) bromide speciation methods

In contrast with palladium(II) chloride speciation, limited data are available in literature [5, 10-13] with Elding [7] being the only author that have reported four consecutive stepwise formation constants for the palladium(II) bromide system. Similar to the palladium(II) chloride speciation experiments, palladium sponge was dissolved in a mixture of hot fuming nitric acid and perchloric acid to prepare a palladium(II) stock solution. A total of 207 *individual* solutions was prepared by adding a constant volume of the palladium(II) stock solution and varying amounts of the bromide stock solution prepared from hydrobromic and perchloric acid. The ionic strength was kept constant at 1 M with perchloric acid as supporting electrolyte with the temperature kept constant at 25 °C. However, from the 207 *individual* solutions only 39 solutions, incorporating three different palladium concentrations, i.e. 4.76 $x10^{-5}$ M, 4.70 x 10^{-5} M and 4.70 x 10^{-3} M with varying bromide concentration, were employed to record the UV spectra. Elding used the same methods to calculate the stability constants as he did with the chloride system [7].

2.4 Palladium(II) chloro -and bromo-hydroxo speciation methods

Although published values for the hydrolysis of palladium(II) [14, 20, 21, 23, 25] at higher pH are available, limited data exists for mixed chloro-hydroxo complexes [9, 14, 20, 21, 23, 25], $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), while no data exists for the bromo-hydroxo complexes, $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) as shown in Table 2. Furthermore, a great deal of uncertainty exists with regard to the current published values, with the most complete study in terms of the stepwise formation of mixed chloro-hydroxo complexes being that of Cruywagen and Kriek [9]. Other authors focussed on the stability and kinetics of selected mixed chloro-hydroxo complexes [14, 22] presenting selected values and corresponding molar absorbances. Various authors [14, 21] also presented values for the mixed complex $[PdCl_3(OH)]^{2-}$ derived from the $[PdCl_4]^{2-}$ employing the following reaction:

$$[PdCl_4]^{2-} + H_2O \rightleftharpoons [PdCl_3(OH)]^{2-} + H^+ + Cl^- \quad (4)$$

The majority of the above-mentioned authors made use of a batch type experimental procedure whereby individual samples were prepared. Wood [20] dissolved palladium metal in a sodium hydroxide solution over a period of 465 days inside high-density polyethylene bottles which was stored in a water bath at 25 °C. After this period the solutions was analysed and the E_h and pH values determined and used to calculate the solubility of the various complexes. From here the stability constants was determined with a graphical procedure after the raw data was smoothed by least squares fitting of the simplest polynomial function. Boily and Steward [22] made use of $PdCl_2$ to prepare a palladium(II) stock solution as described in section 2.2. They also prepared individual samples containing palladium(II) and varied amounts of perchloric acid and used MORPHY98 with Gaussian98 [26] formatted wave function files to determine the different stability constants.

Cruywagen and Kriek [9] employed a double burette titration ensuring both the palladium and chloride concentrations were kept constant. A solution containing a mixture of $[PdCl_3(H_2O)]^-$ and $[PdCl_4]^{2-}$ (obtained by dissolving $PdCl_2$) was used as starting solution and titrated with sodium hydroxide. A similar blank titration was carried out to correct the spectra. Although this is the only complete stepwise formation study to date for $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), some uncertainty does exist as to the accuracy of the calculation of the formation constants as only a limited number of concentration variations were employed.

2.5 Conclusion

Different experimental methods was used to calculate the stability constants for the various palladium(II) complexes as mentioned above. In almost all of the experiments a batch type procedure was used by preparing a limited number of individual samples with varying metal and ligand concentrations. UV-vis spectra and pH measurements were used to analyse the different complexes and a variety of calculation methods and software programs were used to calculate the stability constants from the experimental data. When the all of the available stability constants to date of the various palladium(II) complexes are compared (Table 2), it is clear that not only a limited number of stability constants exists for the palladium(II) complexes in question, but that there is some uncertainty to the accuracy as to which it was calculated. For the bromo-hydroxo complexes no speciation data currently exists.

In order to improve on the current stability constants an automated experimental titration method, specifically designed for spectrophotometric data, is required. This titration method has to produce accurate repeatable spectrophotometric data over any predefined concentration range. If successful, this method can be applied to metal ligand complexes of which no speciation data currently exists.

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CHAPTER 3

PALLADIUM(II) THIOCYANATE SPECIATION

The article presented in Chapter 3 was published by the Journal of Coordination Chemistry, Volume 67, 2014, Pages 1520-1529, DOI: https://doi.org/10.1080/00958972.2014.918264. The formatting, figure and table numbers were changed to match the formatting of the rest of the thesis. An E_h-pH diagram was added to the chapter which was not part of the original publication.

3.1 Overview

Complex formation of Pd(II) with thiocyanate has been investigated by spectrophotometry at 25°C and an ionic strength of 1.0 M. The formation constants, β_n, for the palladium(II) thiocyanate complexes $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4), have been determined and the values are: log β_1 = 8.14, log β_2 = 15.46, log β_3 = 21.94, and log β_4 = 27.42. These complexes are generally accepted to be square planar. However, a five coordinated species, i.e. $[Pd(SCN_5]^{3-}$,

with a formation constant of log β_5 = 31.94, would seem to exist and is proposed to be square pyramidal. Molar absorption spectra for all the complexes in question have been obtained.

3.2 Introduction

Hydrometallurgical processes play an important part in the processing, refining and recycling of the platinum group metals and are typically divided into three general areas, leaching, solution purification and metal recovery. Subsequent to leaching, the leach liquor has to undergo concentration of the metal ions that are to be recovered. As some undesirable metals may have also been taken into solution during the leach process, the solution is often purified to eliminate these undesirable components. The two most common purification techniques employed are solvent extraction and ion exchange. With solvent extraction a mixture of an extractant in a diluent is used to extract a metal from one phase to another and with ion exchange chelating agents, natural zeolite, activated carbon, resins, and liquid organics impregnated with chelating agents are all employed to exchange cations or anions within the solution [1-4].

A crucial foundation for all of the above mentioned processes towards the development of any hydrometallurgical process is speciation, i.e. knowledge of the identity and distribution of specific metallic species in solution. This would involve, in part, the construction of E_h-pH-diagrams by which the stability regions of different metal complexes can be determined. To that regard information on the formation constants of both noble metals and base metals is imperative for the successful development of effective separation processes. Information on the formation constants of the platinum group metal complexes in solution is not readily available. The United States' NIST (National Institute of Standards and Technology) database of critically selected stability constants for metal complexes, as well as the IUPAC stability constants database, lists extremely limited data with regard to PGM-complexes [5-7].

The palladium thiocyanate system is one such system for which the stability constants are extremely limited. Only a few papers are available and they only report values for log β_2 and log β_4. Apart from the data being limited these values differ considerably. For log β_2 only one reported value of 16.20 [8] is available, whereas reported values for log β_4 are 19.46 [9], 25.6 [8], 27.20 [10], 27.60 [11], 28.22 [12], and 28.67 [13].

The determination of log β_2 by Joshi *et al*. [8] entailed the preparation of a solution of palladium(II) with a known quantity of chloride as starting material. The complexation of Pd(II) with SCN^- was expressed as mixed complexes (Equation 5).

$$PdCl_m + nSCN^- \rightleftharpoons Pd(SCN)_nCl_{m-n} + nCl^- \quad (5)$$

The nature of the complexes was determined employing both Job's continuous variation method and the slope ratio method using different individual solutions that contained specific ratios of Pd(II) and SCN^- with an excess of Cl^-. For the latter method palladium chloride was used as a source of palladium and the chloride concentration was kept constant while the solution was titrated with thiocyanate. These methods enabled the authors to spectrophotometrically calculate both log β_2 and log β_4 for the complexation of palladium with thiocyanate [8].

Other experimental methods employed mainly consisted of competition reactions between ligands having known stability constants with Pd(II) and thiocyanate [11-13]. This method limited the authors to calculate only one of the log β values due to the nature of the technique. The most recent literature on the complexation of palladium thiocyanate communicated a logβ_4 value of 27.20 [10]. The authors employed a rather complex competition reaction method where a solution of $[Pd(SCN)_4]^{2-}$ and 2,2,2-tet was prepared at pH 2 and then titrated with a base until a transition pH was reached. The 2,2,2-tet complex was deprotonated and the red $[Pd(SCN)_4]^{2-}$ ion broken down to give the colorless $[Pd(2,2,2\text{-tet})]^{2+}$ complex which were used to calculate log β_4 for the $[Pd(SCN)_4]^{2-}$ complex (Equations 6 and 7).

$$[Pd(SCN)_4]^{2-} + 2,2,2\text{-tet} + H^+ \rightleftharpoons [Pd(2,2,2\text{-tetH})SCN]^{2+} + 3SCN^- \quad (6)$$

$$[Pd(2,2,2\text{-tetH})SCN]^{2+} \rightleftharpoons [Pd(2,2,2\text{-tet})]^{2+} + SCN^- + H^+ \quad (7)$$

As yet no values for log β_1 and log β_3 have been reported.

In this study the aim was to use the palladium tetra-aqua complex $[Pd(H_2O)_4]^{2-}$ as starting material and titrate it with different volumes of a specifically prepared NaSCN solution to calculate the formation constants for the $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) system.

The expected reaction scheme is shown below (Equation 8):

$$[Pd(H_2O)_4]^{2+} + nSCN^- \rightleftharpoons [Pd(SCN)_n(H_2O)_{4-n}]^{2-n} \quad (n = 0 - 4) \quad (8)$$

The same procedure was employed as in our earlier determination of the formation constants for $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) and $[PdCl_p(OH)_q]^{2-}$ (p = 3 – 0 and q = 1 – 4) [14].

3.3 Experimental

All reagents (Sigma Aldrich) were of analytical grade and solutions were prepared with water obtained from a Millipore Milli-Q system. Perchloric acid was standardized indirectly against potassium hydrogen phthalate by titration with sodium hydroxide.

Palladium sponge was dissolved in a mixture of concentrated perchloric acid ($HClO_4$) and fuming nitric acid (HNO_3). The nitric acid was driven off by careful heating and the procedure repeated until all the palladium was dissolved with the palladium subsequently being oxidized to palladium(II). A stock solution of palladium(II) with a concentration of 3×10^{-3} M (confirmed by ICP analyses) and 1.0 M with regard to perchloric acid was prepared. From this solution an 8.0×10^{-5} M palladium solution was prepared which was 0.974 M with regard to $NaClO_4$ and 0.026 M with regard to $HClO_4$. A sodium thiocyanate (NaSCN) stock solution of 5.0×10^{-4} M was prepared that was also 0.974 M with regard to $NaClO_4$ and 0.026 M with regard to $HClO_4$, thereby ensuring constant pH and constant ionic strength (1.0 M) within the reaction vessel when palladium(II) and thiocyanate was titrated employing these two solutions.

Initial efforts to conduct the titration in a reaction vessel coupled to a ‘sipper system’, which pumped the solution by means of a small peristaltic pump through a flow-through cuvette, failed due to the fact that early precipitation was initiated as a result of stirring and pumping. As a result of this, due to the low solubility of $[Pd(SCN)_2(H_2O)_2]$ ($\log K_{sp} = -17.8$ [15]), a batch titration method was subsequently employed. A Metrohm 809.1 double burette auto-titrator was used to prepare 69 individual solutions containing 20 mL 8.0×10^{-5} M palladium solution and different volumes of the thiocyanate solution. This resulted in the thiocyanate concentration varying from 4.95×10^{-6} M to 2.80×10^{-4} M and the palladium concentration

varying from 7.92 x 10^{-5} M to 3.52 x 10^{-5} M as a result of dilution. This small change in concentration was accounted for when the different models were built and the formation constants calculated using HypSpec [16]. Absorption spectra were recorded immediately thereafter within the wavelength range 200 – 500 nm against water as reference at 25°C. An Analytic Jena SPECORD® S600 UV-Vis diode-array spectrophotometer, equipped with a quartz cuvette with a path length of 10 mm, was used for the absorption measurements. Equilibrium was reached instantaneously as no further change in the spectra of the solutions were observed over time and the precipitation of $[Pd(SCN)_2(H_2O)_2]$ only occurred after a few minutes. The end result of this method is the same as a normal titration and to that regard the absorption data, within HypSpec, is handled the same as with a normal titration.

Three initial titrations, with larger concentration change increments, were carried out to determine the concentration range and repeatability. This information was then used to subsequently conduct a further two titrations having smaller changes in the consecutive thiocyanate concentrations. A slight difference in the sigma value for the last two titrations was observed (8.94 x 10^{-3} and 8.23 x 10^{-3} respectively) and the best fitted data (lowest Sigma value) was used for the determination of the different stability constants with the standard deviations (from the HypSpec analysis) only calculated for this final titration data set.

Competition of H^+ for SCN^- and the subsequent formation of HSCN is negligible in that the pK_a of HSCN is –1.85 [15]. A high free thiocyanate concentration at the desired perchlorate concentration is therefore ensured.

3.4 Results and discussion

The two main difficulties that had to be overcome employing this approach was (i) the low solubility of $[Pd(SCN)_2(H_2O)_2]$, and (ii) obtaining reasonable absorbencies to calculate the corresponding log β values. To prevent the influence of precipitation having an effect on the calculation of the model individual samples were prepared simulating a titration (as explained above). The palladium concentration was kept below 8.0 x 10^{-5} M and to that regard the possibility of the formation of polynuclear palladium species is highly unlikely. Polynuclear species exhibit weak d-d bands in the UV-near-visible spectral region [17] and the fact that no change in the absorption spectra was observed within this region confirms that no polynuclear species were formed. The change in absorption spectra with increasing thiocyanate

concentration is shown in Figure 1. A number of observable changes in the absorption spectra together with the absence of an isosbestic point allude to the existence of 3 or more species.

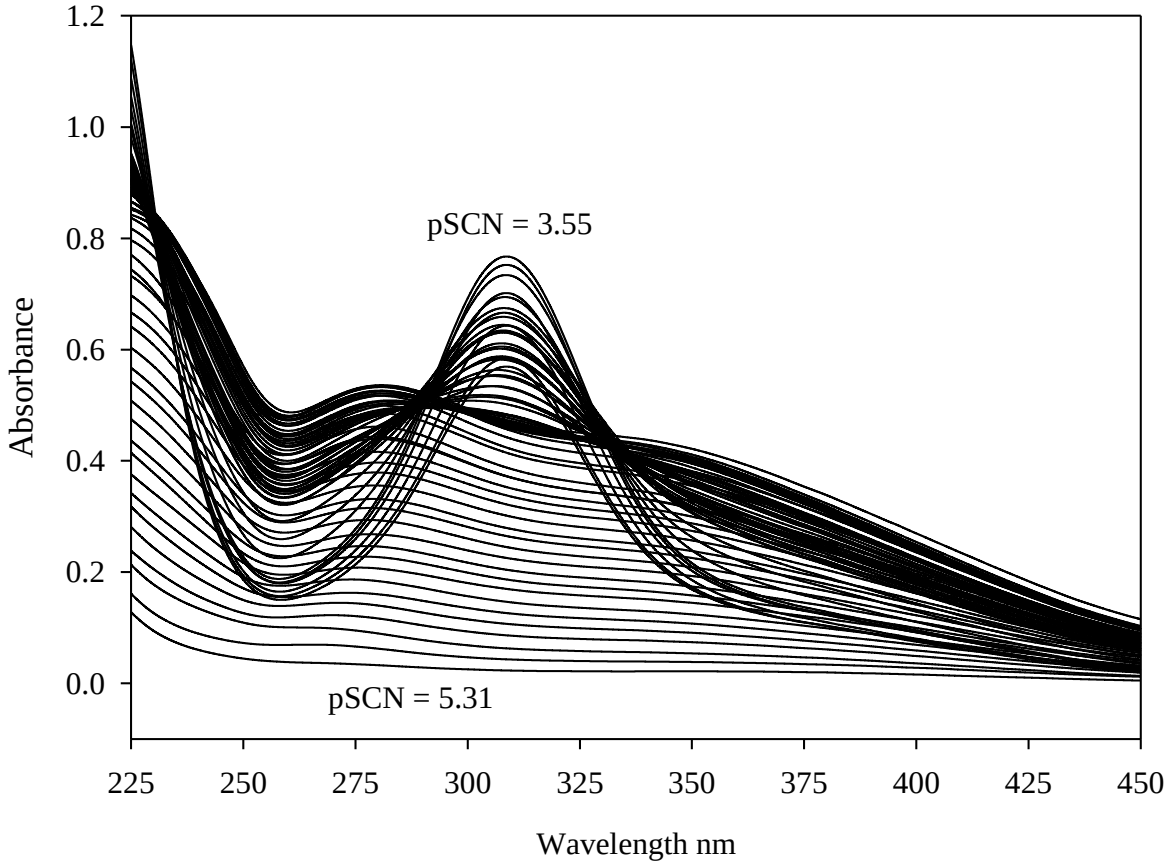

Figure 1: Change in absorption spectra with change in pSCN for $[Pd(H_2O)_{4-n}(SCN)_n]^{2-}$ (n = 0 – 4) and $[Pd(SCN)_5]^{3-}$, ionic strength 1.0 M and 25 °C.

Similar to Harrington *et al*. [10] reporting that the four coordinated $[Pd(SCN)_4]^{2-}$ exhibits a maximum absorption at a wavelength of 308 nm, we observed a major peak at 309 nm and therefore focussed our attention around this region. Up to date no recorded UV spectra or any molar absorbance spectra have been reported for the palladium thiocyanate system. Absorption data at every wavelength (every 0.5 nm) in the range 230 nm to 450 nm were treated with the program HypSpec 2009 to calculate equilibrium constants and absorption spectra for the initial complexes $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4). The molar absorption spectra for thiocyanate as well as for the aqua complex $[Pd(H_2O)_4]^{2+}$ were calculated independently under the same conditions (ionic strength and temperature) and were supplied as known spectra to HypSpec.

A measure of the overall quality of data refinement is indicated by the sigma (σ) value, derived from the squared residual r (Equation 9), where *m* is the number of data points, *n* the number of parameters, and *w* the weight as part of a least squared calculation. The weighting scheme accounts for the error in absorbance measurements and is specific to each spectrophotometer.

$$\sigma = \sqrt{\frac{\sum_i w_i r_i^2}{m-n}} \tag{9}$$

With a correct weighting scheme the value of the scaled sum of squares (σ) has an expected value of unity. An absolute weighting scheme with a linear weighting function (chosen within HypSpec) was employed as part of this study, which is appropriate for the Analytic Jena SPECORD® S600 UV-Vis diode-array spectrophotometer. A refinement is good if the calculated values agree with the observations within the limits of experimental error. Subsequent to repeated experimentation it was found that the model that fitted the data the best, judged by the lowest sigma value, includes the five coordinated $[Pd(SCN)_5]^{3-}$. Good correlation between the actual and calculated titration curves at 240nm, 260nm, 280nm and 309nm, where major changes in the spectra are observed, highlights the legitimacy of this five-coordinated model (Figure 2). Formation constants for models consisting of any number of complexes less than five could not be obtained as these models did not refine.

The values of the cumulative formation constants for the complexes $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) and $[Pd(SCN)_5]^{3-}$ are log β_1 = 8.14, log β_2 = 15.46, log β_3 = 21.94, logβ_4 = 27.42 and log β_5 = 31.94. The log β_2 and log β_4 values, calculated by us as part of the overall model, correspond well with those values obtained from literature and is therefore a very good indication of the reliability of the other overall model and formation constants, i.e. for $[PdSCN(H_2O)_3]^+$, $[Pd(SCN)_3H_2O]^-$, and $[Pd(SCN)_5]^{3-}$, and for the existence of these complexes under the experimental conditions, which is now reported for the first time. A summary of the different formation constants is presented in Table 3 together with the corresponding literature values. It is clear that a fair correlation exists between our value for log β_2 (15.55) and the only published value of 16.20 [8]. Furthermore, of the six values reported for log β_4 our value of 27.42 correlates well with two values reported, i.e. 27.20 [10] and 27.60 [11]. This provides further confirmation to the legitimacy of our model.

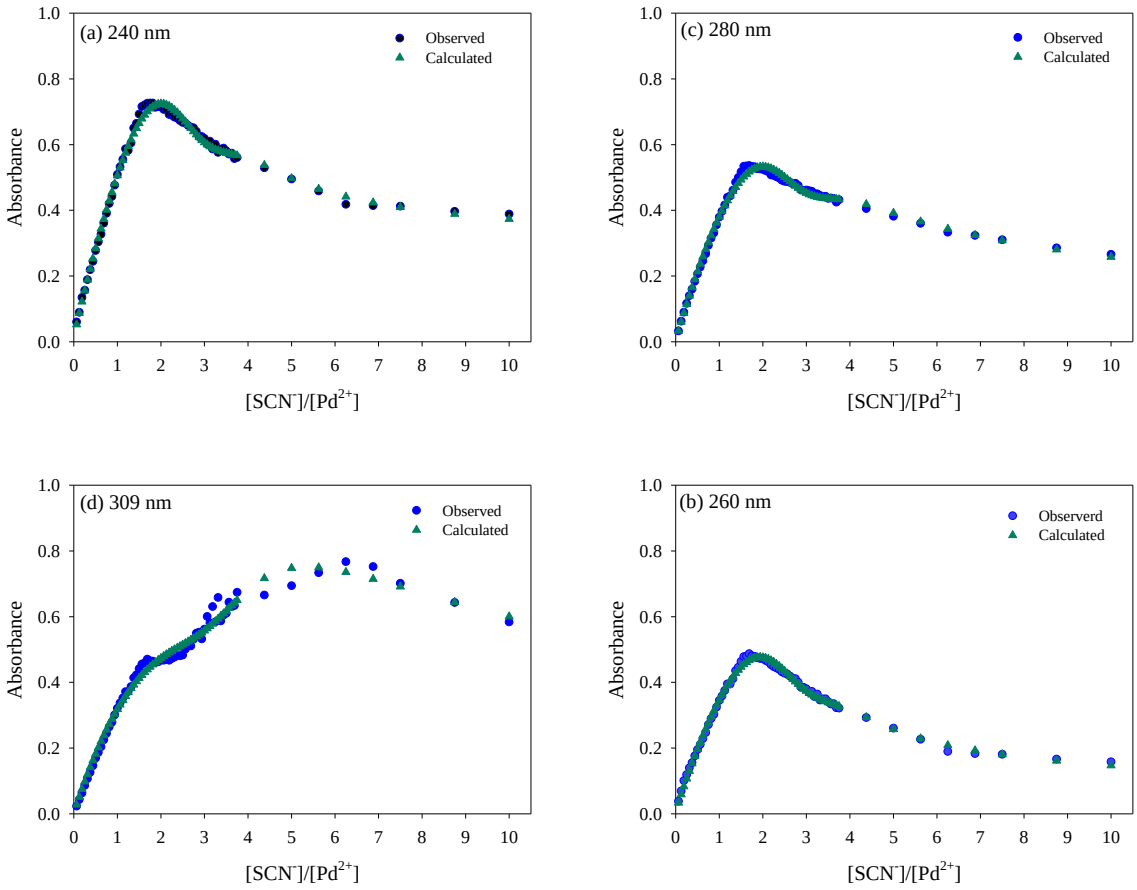

Figure 2. Actual/observed vs calculated titration curves at specific wavelengths

Table 3. Formation constants for $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ (n = 1 – 4) and $[Pd(SCN)_5]^{3-}$ at 1.0 M ionic strength and 25 °C (N/A = not available, σ = 8.23 x 10^{-3}).

n	Complex	Literature	log β_n
1	$[PdSCN(H_2O)_3]^+$	N/A	8.14 ± 0.026
2	$[Pd(SCN)_2(H_2O)_2]$	16.20 [8]	15.46 ± 0.024
3	$[Pd(SCN)_3(H_2O)]^-$	N/A	21.94 ± 0.096
4	$[Pd(SCN)_4]^{2-}$	19.46 [9], 25.60 [8], 27.20 [10] 27.60 [11], 28.22 [12], 28.67 [13]	27.42 ± 0.274
5	$[Pd(SCN)_5]^{3-}$	N/A	31.94 ± 0.277

From the equilibrium constants a distribution curve was constructed showing the complete speciation of the $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) system and $[Pd(SCN)_5]^{3-}$ employing a total Pd-concentration of 1M as an example (Figure 3). At the maximum thiocyanate concentration for this investigation, i.e. at 2.80 x 10^{-4} M, and at a palladium concentration of 3.52 x 10^{-5} M, in excess of 90% of the palladium is in the form of the pentathiocyanate complex $[Pd(SCN)_5]^{3-}$

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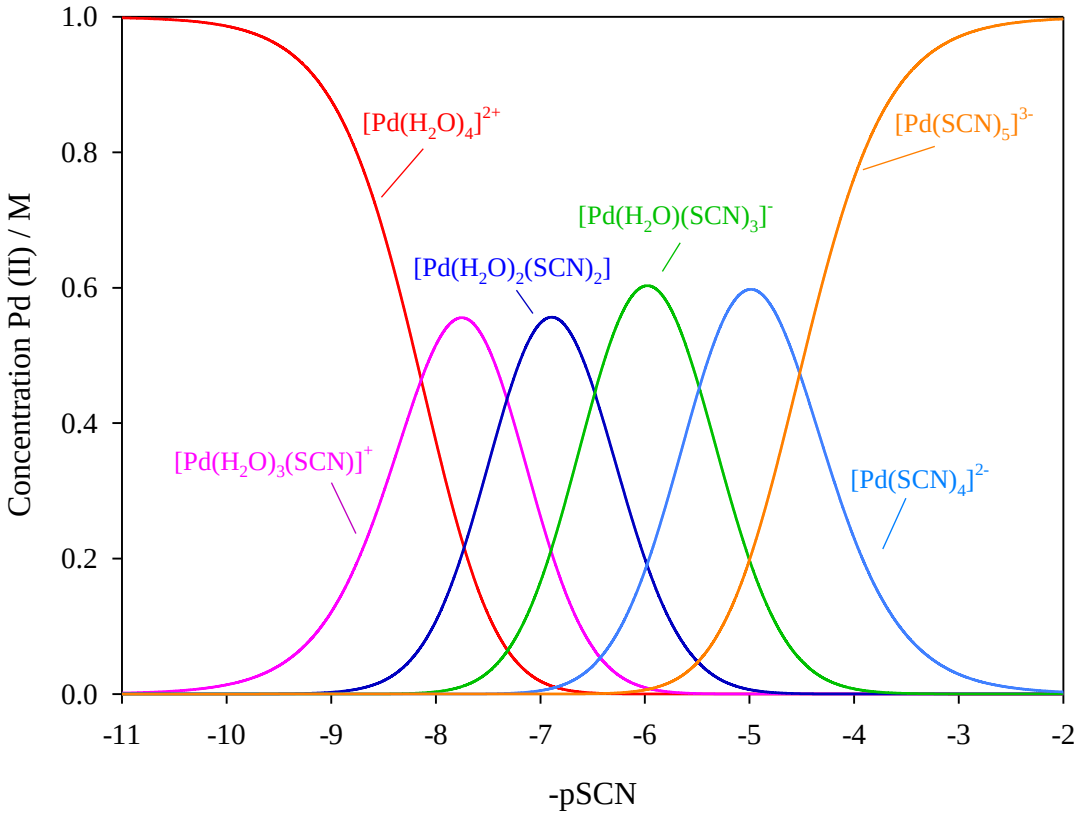

Figure 3: Distribution of $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) and $[Pd(SCN)_5]^{3-}$ species as a function of -pSCN.

In most cases palladium(II) complexes are known to be square planar [18-20], but some authors have suggested the possibility of palladium forming a five-coordinated trigonal-bipyramidal complex [21]. Desmarais *et al.* [22] have obtained a new class of palladium(II) olefin complex, which is five-coordinated, by using a specific nitrogen bidentate ligand. Similar work has been conducted by Albano *et al.* [23] who produced five-coordinated olefin complexes of palladium(II). In addition, Lopez-Torres *et al.* [24] investigated the reaction of cyclometalated halide-bridged palladium(II) complexes with a tertiary triphosphine ligand to produce a complex with a five-coordinated palladium atom as confirmed by spectroscopic and analytic

data. We modelled the five coordinated $[Pd(SCN)_5]^{3-}$ complex, employing Accelrys Materials Studio 5.5, starting out with the trigonal-bipyramidal structure and allowing it to stabilize. The structure changed from the trigonal-bipyramidal structure to a square pyramidal configuration (Figure 4) in both cases where the ligand binds to the metal through either nitrogen or sulphur. This was confirmed by modelling in Avogadro [25, 26] in that the trigonal-bipyramidal structure also stabilized in the square pyramidal configuration (Figure 5).

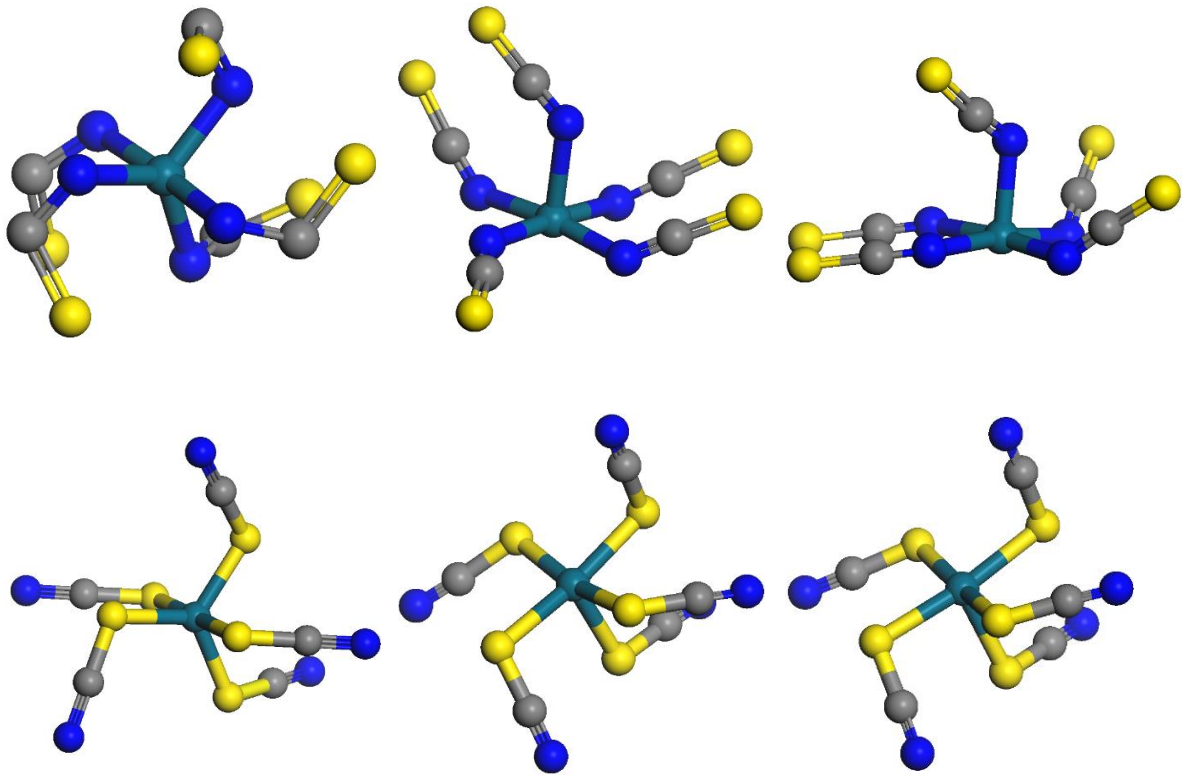

Figure 4: Modelled configurations of the five coordinated $[Pd(SCN)_5]^{3-}$ complex showing the change from trigonal-bipyramidal (at the left) to square pyramidal (to the right).

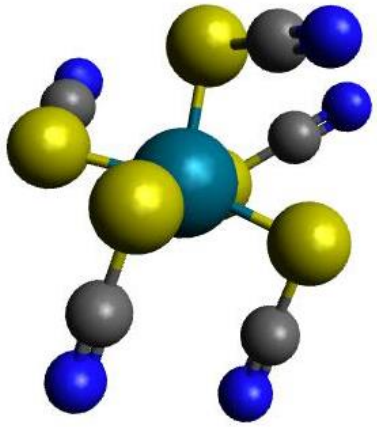

Figure 5: The stabilized five coordinated $[Pd(SCN)_5]^{3-}$ complex as modelled by Avogadro [25, 26].

The molar absorption spectra for all complexes are shown in Figure 6. $[Pd(SCN)_5]^{3-}$ have the strongest charge transfer band at 309nm.

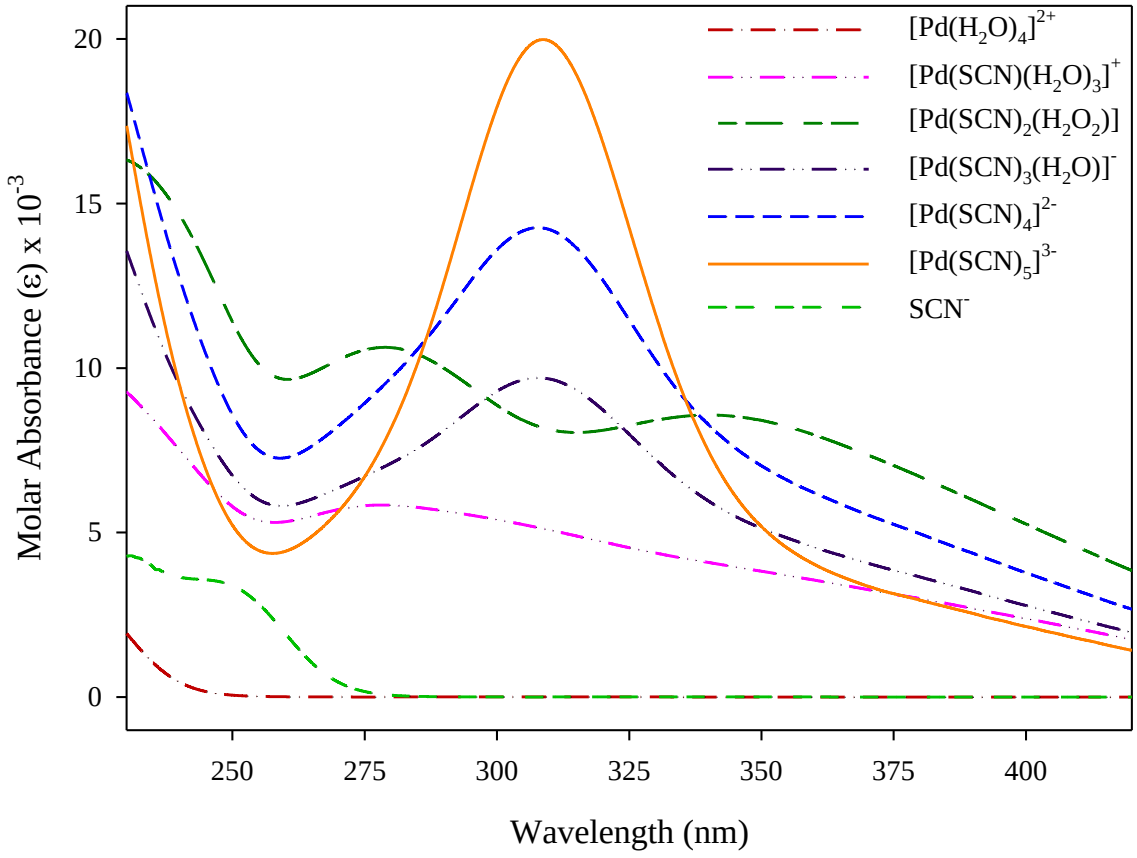

Figure 6: Calculated molar absorption spectra of $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) and $[Pd(SCN)_5]^{3-}$

In the case of the $[PdCl_n(H_2O)_{4-n}]^{2-n}$ system the charge transfer bands were shifted towards shorter wavelengths (higher energies) when chloride was substituted by water [14]. It is therefore expected that the charge transfer bands in the case of the $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) system, as well as for $[Pd(SCN)_5]^{3-}$, will also shift towards shorter wavelengths with the substitution of thiocyanate by water; in the present case even more so. Due to the pi-bonds present within the thiocyanate ligand one would expect it to be the main chromophore in the different complexes. This also explains why there is a similarity between the absorbance spectra of some of the complexes. The highest absorbance is for the most substituted complex, $[Pd(SCN)_5]^{3-}$ (Figure 6), which fits in well with the statement of SCN^- being the main chromophore.

A Pourbaix diagram was constructed for the Pd-C-N-S-H_2O system (Figure 7) employing the newly determined stability constants.

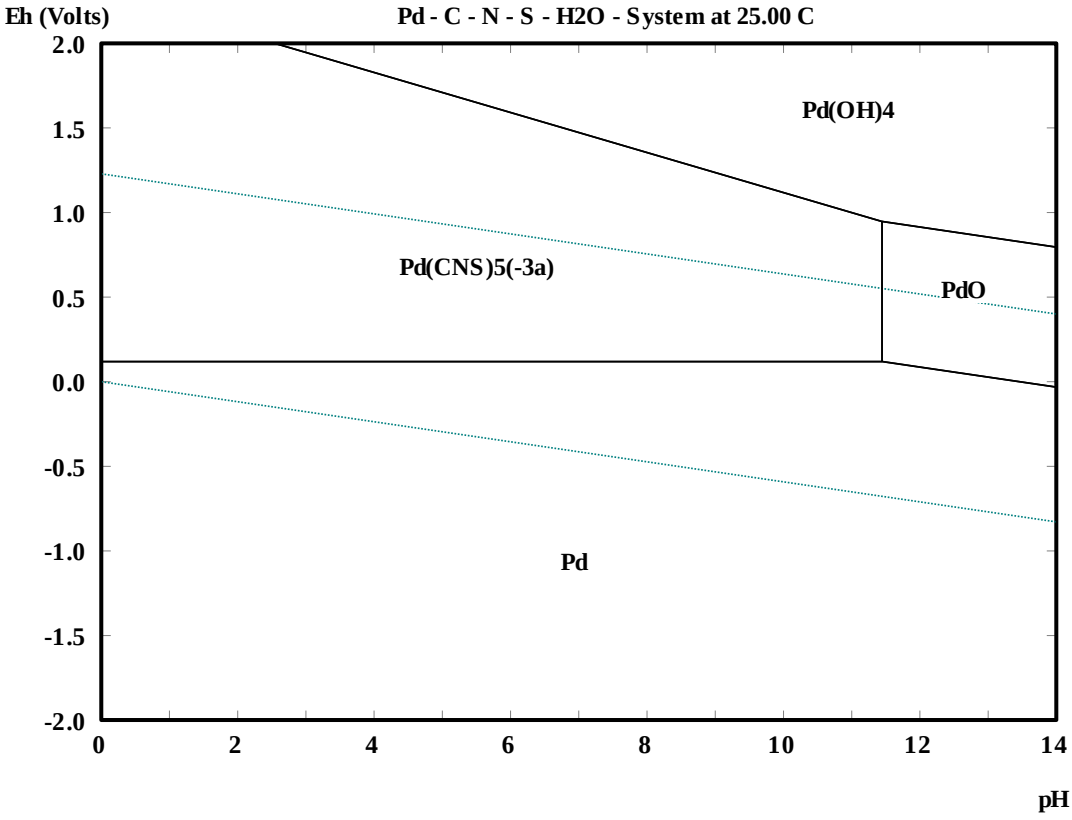

Figure 7: E_h-pH diagram for the Pd-C-N-S-H_2O system, ($[Pd^{2+}]$ = 1.0 mol/kg H_2O; $[SCN^-]$ = 0.1 mol/kg H_2O), constructed employing new stability constants listed in Table 3.

3.5 Conclusions

A successful spectrophotometric investigation into the complexation of palladium(II) with thiocyanate, i.e. obtaining a relevant and true sequential series of absorption spectra, modelling and proper data fitting, depended on preventing the precipitation of $[Pd(H_2O)(SCN)_2]$. This could not be accomplished by automated titration into a reaction vessel followed by circulation of the solution by means of a peristaltic pump through a flow-through cuvette as it was ascertained that mechanical stirring and pumping accelerated precipitation. This could be circumvented by making up individual solutions, also employing automated titration, and capturing the absorption spectrum immediately after proper mixing for each solution. The only model that fit the data involves the formation of five sequential complexes.

Values for the formation constants of the five palladium(II) thiocyanate complexes, i.e. $[Pd(SCN)(H_2O)_3]^+$, $[Pd(SCN)_2(H_2O)_2]$, $[Pd(SCN)_3(H_2O)]^-$, $[Pd(SCN)_4]^{2-}$ and $[Pd(SCN)_5]^{3-}$, have been determined at an ionic strength of 1.0 M and a temperature of 25°C. The formation constants are log β_1 = 8.14, log β_2 = 15.46, log β_3 = 21.94, log β_4 = 27.42 and log β_5 = 31.94, with formation constants for the one, three and five coordinated complexes being reported here for the first time. Within this five coordinated model our values of log β_2 (15.46) and log β_4 (27.42) are in good agreement with reported values, i.e. 16.20 [8] for the two coordinated complex and 27.20 [10] and 27.60 [11] for the four coordinated complex. This supports the legitimacy of this five coordinated model. Molecular modelling furthermore postulates that the five coordinated $[Pd(SCN)_5]^{3-}$ complex is square pyramidal.

3.6 Acknowledgement

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3.7 References

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CHAPTER 4

PALLADIUM(II) CHLORIDE AND -BROMIDE SPECIATION

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4.1 Overview

As the speciation of metal species, especially the noble metals, are crucial for recovery and separation purposes, the complex formation of Pd(II), with chloride and bromide respectively, has been investigated employing spectrophotometry at 25 °C and an ionic strength of 1.0 M Hyperquad Simulation and Speciation (HySS) was employed to determine the ideal titration conditions and an autotitrator (equipped with a flow-through cell) was used to accurately vary the chloride and bromide concentrations over an increased number of intervals, i.e. 128 and 300 respectively. All of these data points were used to calculate the formation constants of both palladium systems employing HypSpec (software specifically developed for the determination of

equilibrium constants from spectrophotometric data). The formation constants, β_n, for the palladium(II)-chloride and -bromide complexes, have been determined. For $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4), the log β values are: log β_1 = 4.49, log β_2 = 7.80, log β_3 = 10.18 and log β_4 = 11.54, while the log β values for $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4), are: log β_1 = 5.04, log β_2 = 9.12, log β_3 = 12.38 and log β_4 = 14.55. The formation constants for the palladium-chloride complexes agree well with the published data, while the formation constants for the bromide complexes differ somewhat from published data suggesting a different, but more accurate speciation. Molar absorption spectra for all the complexes in question have been obtained. Pourbaix diagrams were constructed from the new speciation data showing the predominant species for each system.

4.2 Introduction

Due to the excellent catalytic properties of the platinum group metals (PGMs), especially platinum, palladium and ruthenium, they are ideally suited for various applications that include fuel cell technology, industrial catalysts and catalytic converters, with the added benefit that they can be recycled [1-4]. Hydrometallurgical processes play a significant part in the processing, refining and recycling of the PGMs and are generally divided into three key areas, i.e. leaching, solution purification and metal recovery. During the process of leaching, which involves the use of aqueous lixiviant solutions to extract metal from metal bearing materials, some unwanted metals may have also been taken into solution and the solution is subsequently purified to eliminate these undesirable components. The two most common purification techniques that are currently used are solvent extraction and ion exchange. In the case of solvent extraction, a mixture of an extractant and a diluent is employed to extract a metal species/complex from one phase to another, while in the case of ion exchange natural zeolite, chelating agents, resins, activated carbon, and liquid organics impregnated with chelating agents are all employed to exchange cations or anions within the solution [5-16]. In many instances, chloride [5, 6, 9, 10, 16, 17] and in some cases bromide [5, 7, 9, 10], is used as a complexing agent. A vital basis for all of the above-mentioned processes, towards the development of any hydrometallurgical process, is speciation, i.e. knowledge of the identity and distribution of specific metallic species/complexes in solution. This would include, in part, the construction of distribution- and E_h-pH-diagrams by which the stability regions of different metal complexes can be determined.

The complexation equilibria of palladium(II) with chloride and bromide have been investigated by various authors and values for the formation constants have been determined. These complexes are assumed to be square planar and can be represented by the general formula $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) and $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) respectively. Information on the formation constants of the platinum group metal complexes in solution is not readily available, with the United States' NIST (National Institute of Standards and Technology) database of critically selected stability constants for metal complexes, as well as the IUPAC stability constants database, listing extremely limited data. This is true for palladium(II)-chloride and more so for palladium(II)-bromide.

From the published data, it is evident that different methods were used to prepare the palladium(II) 'starting' solution, where the most common method of preparation has been the precipitation of palladium hydroxide from chloride or nitrate followed by the dissolution of the washed hydroxide in perchloric acid [18-25]. So as to ensure the absence of any polynuclear hydrolysis products as well as colloidal species in the palladium(II) 'starting' solution palladium sponge was dissolved in hot fuming nitric acid with the nitric acid having been removed subsequently by several evaporations employing concentrated perchloric acid. This include our own work [26, 27] and that of Elding [28], which resulted in more satisfactory results. Various authors have presented values for formation constants for the complexation of palladium(II) with chloride [18-26, 28-31]. The majority of these values vary considerably with the best agreement having been obtained for formation constants determined more than 40 years ago by Elding [28] and Weed [31], and more recently (2006) by Cruywagen and Kriek [26] (see Table 4).

Table 4: Published stepwise formation constants for the complexation of palladium(II) with chloride

$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	Reference
4.47	7.76	10.17	11.54	[28]
4.40	7.74	10.08	11.46	[31]
4.47	7.80	10.18	11.53	[26]

All of the above-mentioned authors made use of a batch type experimental procedure whereby individual samples were prepared. The values presented by Weed [31] in his PhD thesis raises

some concerns as the wavelength range of recorded UV spectra, from which the stability constants were calculated, varied between 320 nm – 600 nm, which is out of the range of 'normal' investigations. All other published values where obtained from UV spectra with wavelengths ranging between 200 nm and 350 nm. Although good agreement has been obtained for the values calculated by Cruywagen and Kriek [26] and Elding [28], some uncertainty does exist as to the accuracy of the calculation of the formation constants as only a limited number of concentration variations were employed.

In the publication by Cruywagen and Kriek a series of only 24 *individual* solutions was prepared of which the chloride concentration was varied from 6 x 10^{-5} to 0.69 M by adding calculated amounts of a standardised hydrochloric acid stock solution. The palladium(II) concentration (3 x 10^{-5} M), ionic strength, temperature and acid concentration was kept constant for all solutions. A GBC 920 UV-Vis double beam spectrophotometer equipped with a Peltier thermos cell with a 1cm path length was used for the absorption measurements. Absorbance data were treated with the program HYPERQUAD 2000 [32] to calculate equilibrium constants and absorption spectra for the complexes $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4). In contrast, Elding also prepared a series of *individual* solutions (189 in total) for which both the palladium(II) and chloride concentrations were varied. From this set of solutions, however, only 30 solutions were employed to calculate the formation constants. The stability constants were calculated using the spectrophotometric version of Sillen's least squares programme Letagrop.

In comparison to the chloride complexes the formation constants for the palladium(II)-bromide complexes are even more limited with Elding [28] being the only author that have reported four consecutive stepwise formation constants for the $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) system. Other authors presented *K* values with some of them varying considerably. All available formation constants at the time of writing this paper are listed in Table 5.

The study by Elding [28] obviously proves to be the most complete speciation study to date presenting values for all four stability constants. The author prepared a total of 207 *individual* solutions by adding a constant volume of palladium(II) stock solution and varying amounts of the bromide stock solution prepared from hydrobromic and perchloric acid. The ionic strength was kept constant at 1 M with perchloric acid as supporting electrolyte with the temperature kept constant at 25 °C.

Table 5: Known stability constants for palladium (II) bromide

$\log \beta_1$ / K_1	$\log \beta_2$	$\log \beta_3$	K_4	$\log \beta_4$	Reference
5.17	9.42	12.7	2.20	14.9	[28]
–	–	–	2.23	–	[29]
–	–	–	–	13.05	[19]
–	–	–	2.16	–	[20]
–	–	–	2.20	–	[21]
4.37	–	–	3.50	–	[18]

However, from the 207 *individual* solutions only 39 solutions, incorporating three different palladium concentrations, i.e. 4.76 x10^{-5} M, 4.70 x 10^{-5} M and 4.70 x 10^{-3} M with varying bromide concentration, were employed to record the UV spectra. The stability constants were calculated using the same method as for the chloride system.

It is clear from the above that in all instances a batch experimental method, i.e. the making up of *individual* solutions, was employed to determine the formation constants with only a limited number of solutions (or data points) having been used. The aim of this study was to employ a more detailed and accurate experimental method that can produce and employ substantially more usable concentration variations within the desired ligand concentration range. This revised technique was first applied to the better known palladium(II)-chloride system so as to validate the technique against the published formation constants. Subsequently, this method was adjusted to accurately determine the various palladium(II)-bromide stability constants, employing HypSpec [32] (specifically designed for calculating stability constants). This program is part of the Hyperquad suite and shares some features with other programs within the suite and can be used to derive equilibrium constants from spectrophotometric data. The data may be in the form of one or more titration data sets, or single data points (batch data). The program combines the functionality of Hyperquad [32] and pHab [33], but with some simplifications.

4.3 Experimental

All reagents (Sigma Aldrich) were of analytical grade and solutions were prepared with water obtained from a Millipore Milli-Q system. Perchloric acid was standardized indirectly against potassium hydrogen phthalate by titration with sodium hydroxide. Hyperquad Simulation and Speciation (HySS) [34] software was used to determine the ideal titration conditions with a model having been specified by defining a set of equilibrium constants (equation 10).

$$\beta_{pq}.. = [A_pB_q.] / ([A]^p[[B]^q..) \quad (10)$$

The titration was subsequently simulated by specifying a set of titration conditions and calculating the concentrations of each complex species as the titration proceeds. The optimised titration conditions obtained is then used to calculate the ideal concentrations for the different solutions.

Palladium sponge was dissolved in a mixture of concentrated perchloric acid ($HClO_4$) and fuming nitric acid (HNO_3). The nitric acid was driven off and the procedure repeated until all the palladium was dissolved and oxidized to palladium(II). A stock solution of palladium(II) with a concentration of 3.0×10^{-3} M (confirmed by ICP analyses) and 1.0 M with regard to perchloric acid was prepared. From this solution a 1.05×10^{-4} M and a 1.02×10^{-4} M palladium solution was prepared, which was 0.966 M with regard to $NaClO_4$ and 0.034 M with regard to $HClO_4$. Sodium chloride (NaCl) and sodium bromide (NaBr) stock solutions of 0.02 M were prepared in a solution of $NaClO_4$ and $HClO_4$, which was 0.946 M with regard to $NaClO_4$ and 0.034 M with regard to $HClO_4$ thereby ensuring a constant pH and ionic strength of 1.0 M throughout all solutions.

For palladium(II)-chloride speciation 300 mL of the palladium stock solution (0.0315 mM) was added to a jacketed reaction flask that was thermostatically controlled at a fixed temperature of 25 °C employing a Julabo F12-ED refrigerated/heating circulator. A Metrohm 809.1 double burette auto-titrator was used to vary the chloride concentration over 128 intervals from 6.66×10^{-5} M to 8.00×10^{-2} M by adding precalculated volumes of the chloride containing solution. Although the palladium concentration slightly varied from 1.05×10^{-4} M to 6.30×10^{-5} M as a result of dilution, this is taken into account by HypSpec [32]. For palladium(II)-bromide speciation 200mL of the palladium stock solution (0.0204 mM) was

added to the temperature controlled reaction flask and the bromide concentration was varied over 300 intervals from 9.995 x 10^{-6} M to 1.204 x 10^{-2} M. Again, the palladium concentration slightly varied from 1.020 x 10^{-4} M to 4.06 x 10^{-5} M, which was accounted for by HypSpec [32].

An Analytic Jena SPECORD® S600 UV-Vis diode-array spectrophotometer, equipped with a quartz flow-through cuvette (10 mm path length), was used for the absorption measurements. This ensured uniform and constant intervals between successive ligand additions and the recording of the individual UV spectra. The solution inside the temperature controlled reaction cell was constantly circulated through the flow-through cuvette by means of a peristaltic pump ensuring effective mixing and temperature control of the solution after every addition. Equilibrium is reached instantaneously as no further changes in the spectra of the solutions were observed over time. Spectra were recorded every 200 seconds in the wavelength range 200 – 500nm against water as reference. The process of titration, mixing, flow-through and UV-spectra recording was fully automated employing a software program, Auto Mouse Clicker (with built-in timer).

Competition of H^+ for Cl^- and Br^-, with the subsequent formation of HCl and HBr, are negligible in that the pK_a of HCl and HBr is -9.0 and -11.0 respectively [35]. A high free chloride and bromide concentration at the desired ligand concentration is therefore ensured.

4.4 Results and discussion

4.4.1 Palladium(II) chloride complexation

The change in absorption spectra with increasing chloride concentration is shown in Figure 8. Absorption data at every wavelength (every 0.5 nm) in the range 206 nm to 350 nm were treated with the program HypSpec [32] to calculate equilibrium constants and molar absorption spectra for the complexes $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4). The molar absorption spectra for chloride as well as for the aqua complex $[Pd(H_2O)_4]^{2+}$ were determined independently at the same and constant ionic strength and temperature and supplied as known spectra to HypSpec [32]. By supplying these spectra, the calculation becomes less complex resulting in a more accurate result. After the different spectra were carefully examined the absorbance measurements below 206 nm were excluded from the calculations due to the high absorbance of chloride in this region.
A measure of the overall quality of data refinement is indicated by the sigma (σ) value, derived from the squared residual r (Equation 11), where *m* is the number of data points, *n* the number

of parameters, and *w* the weight as part of a least squared calculation. The weighting scheme accounts for the error in absorbance measurements and is specific to each spectrophotometer.

$$\sigma = \sqrt{\frac{\sum_i w_i r_i^2}{m-n}} \tag{11}$$

With a correct weighting scheme, the value of the scaled sum of squares (σ) has an expected value of unity. An absolute weighting scheme with a linear weighting function (chosen within HypSpec) was employed as part of this study, which is appropriate for the Analytic Jena SPECORD® S600 UV-Vis diode-array spectrophotometer. A refinement is considered accurate if the calculated values agree with the observations within the limits of experimental error.

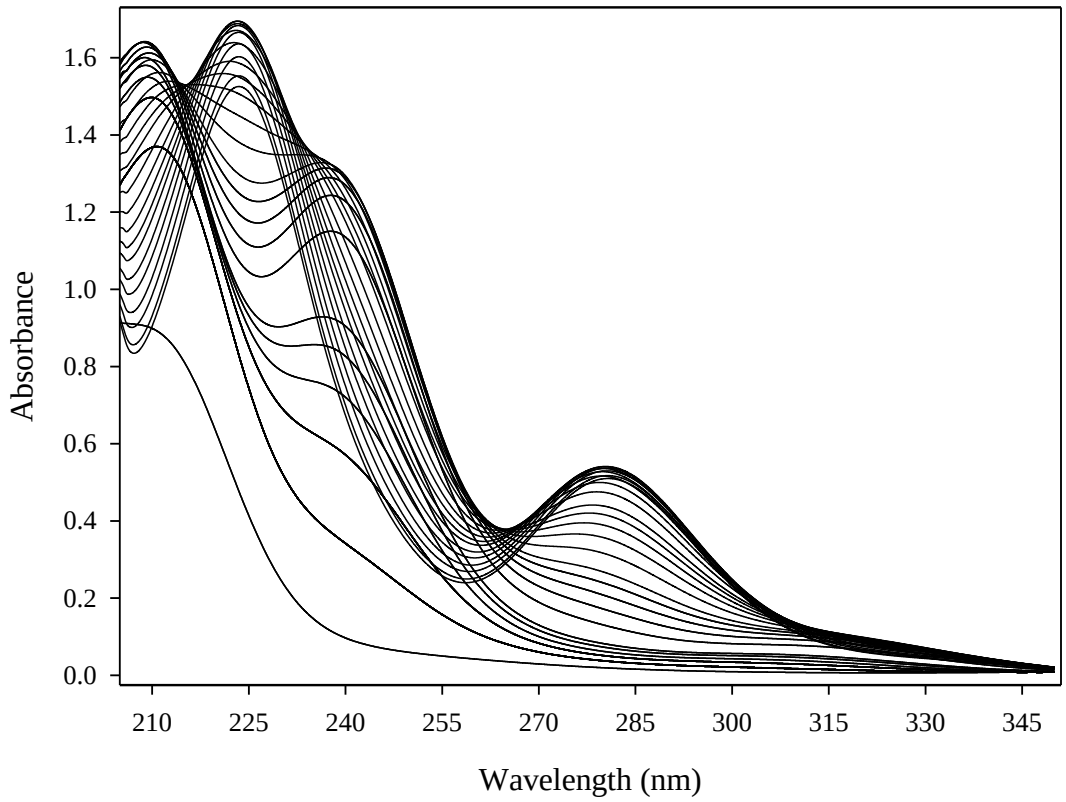

Figure 8: Change in absorption spectra with change in chloride concentration (every 5th absorption spectrum shown for improved visualisation)

Changes in the absorbance data can be observed at 208.5 nm, 223.5 nm, 238 nm and 280.5 nm. The calculated absorbance values and the observed absorbance values at these specific wavelengths are compared in Figure 9, highlighting the high accuracy of the experimental data and the excellent correlation between the experimental and calculated data. The molar

absorption spectra are shown in Figure 10. Similar to Elding [28] and Cruywagen and Kriek [26] the $[PdCl_4]^{2-}$ complex has the highest absorption band with a maximum absorbance at 224 nm and a lower absorption band at 282 nm. These charge transfer bands, caused by the transition of electrons from the chloride ligands to molecular orbitals localized primarily on palladium, are shifted towards shorter wavelengths with higher energies when chloride is substituted by water in the complexes. The characteristics of these bands have been investigated and discussed previously [28].

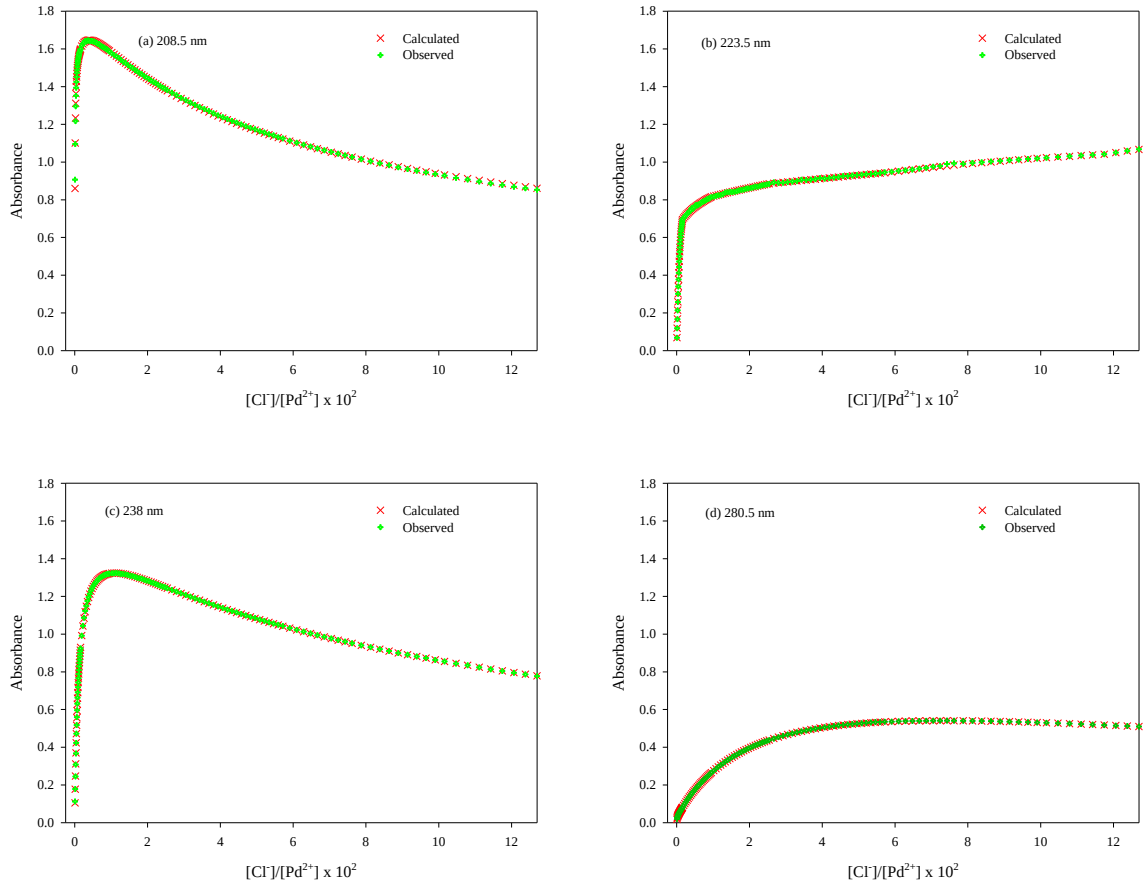

Figure 9: Actual/observed vs calculated absorbance at specific wavelengths for $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4).

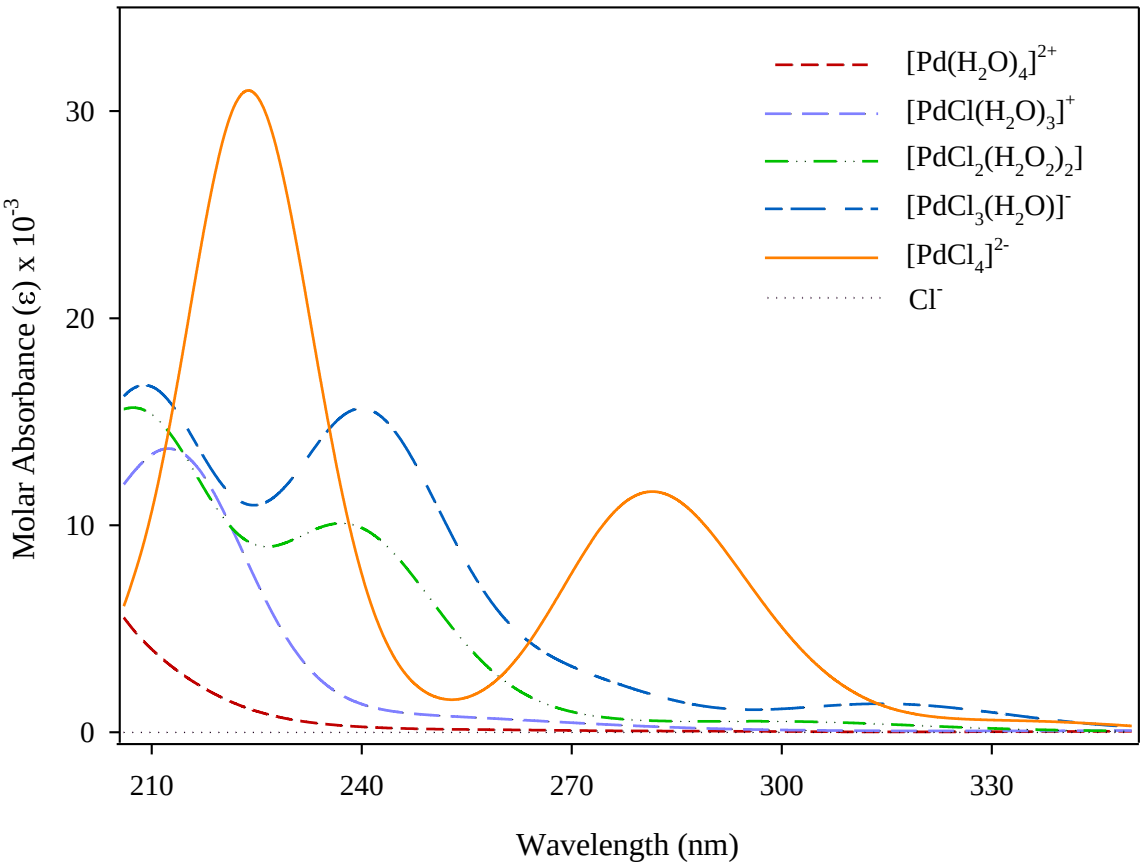

Figure 10: Calculated molar absorption spectra of $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4)

The calculated values of the cumulative formation constants (see Table 6) are in good agreement with the values reported by Elding [28] and more recently, Cruywagen and Kriek [26].

Table 6: Formation constants for $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 1 – 4) at 1.0 M ionic strength and 25 °C

n	log β_n (Titration 1)	log β_n (Titration 2)	log β_n (Titration 3)	log β_n (Average)
1	4.460 ± 0.001	4.499 ± 0.0013	4.497 ± 0.002	4.485 ± 0.001
2	7.817 ± 0.002	7.758 ± 0.002	7.817 ± 0.003	7.797 ± 0.002
3	10.187 ± 0.003	10.170 ± 0.004	10.187 ± 0.005	10.181 ± 0.004
4	11.541 ± 0.003	11.524 ± 0.004	11.535 ± 0.005	11.535 ± 0.004
σ	1.928 x 10^{-3}	2.228 x 10^{-3}	3.015 x 10^{-3}	2.390 x 10^{-3}

In contrast to the studies of these authors, the current investigation employed an additional fifteen data points at the lower end of the chloride concentration range, which together with the increased number of data points distributed over the rest of the chloride concentration range increased the accuracy in calculating the associated model. For comparative purposes our newly calculated formation constants are compared to that of the already published data (see Table 7) and it is evident that the data correlate well, which supports our methodological approach, although we would add more value to the current data due to the increased number of titration points (an increase of more than a factor of four).

Table 7: Comparative stepwise formation constants for the complexation of palladium(II) with chloride

log β_1	log β_2	log β_3	log β_4	Reference
4.47 ± 0.01	7.76 ± 0.04	10.17 ± 0.07	11.54 ± 0.09	[28]
4.47 ± 0.07	7.80 ± 0.11	10.18 ± 0.14	11.53 ± 0.15	[26]
4.485 ± 0.001	7.797 ± 0.002	10.181 ± 0.004	11.535 ± 0.004	This work

The distribution of the complexes as a function of log [Cl^-] is shown in Figure 11. In this study the chloride concentration was varied over 128 different concentration intervals from 6.30 x 10^{-5} M to 0.08 M. The first data point (at 6.30 x 10^{-5} M Cl^-) coincides with 53% of the Pd(II) being in the form of the monochloride complex $[PdCl(H_2O)_3]^+$, while the last data point (at 0.08 M Cl^-) coincides with 70% of the Pd(II) being in the form of the tetrachloride complex $[PdCl_4]^{2-}$, which attests to a representative range of chloride concentrations over which the solutions were made up and the model built.

HSC Chemistry® 6.0 from Outotec, a chemical reaction and equilibrium software package with an extensive thermochemical database, was used to construct a Pourbaix (E_h-pH) diagram from the speciation data (Figure 12). Our newly determined stability/formation constants for the $[PdCl_n(H_2O)_{4-n}]^{2-n}$ system (n = 0 – 4), together with the stability/formation constants of the mixed palladium(II) chloro-hydroxo complexes that were determined earlier [26], were employed to calculate the Gibbs free energies of formation for each complex and incorporated into the HSC Chemistry® 6.0 database.

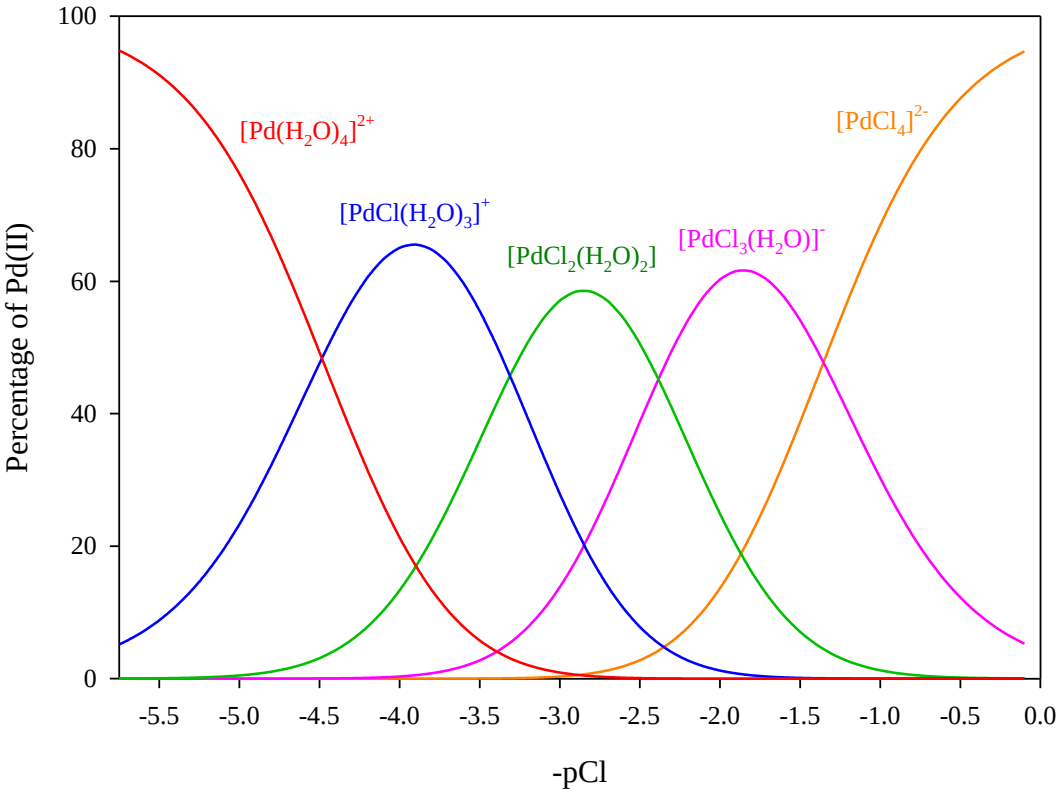

Figure 11: Distribution of $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) species as a function of -pCl

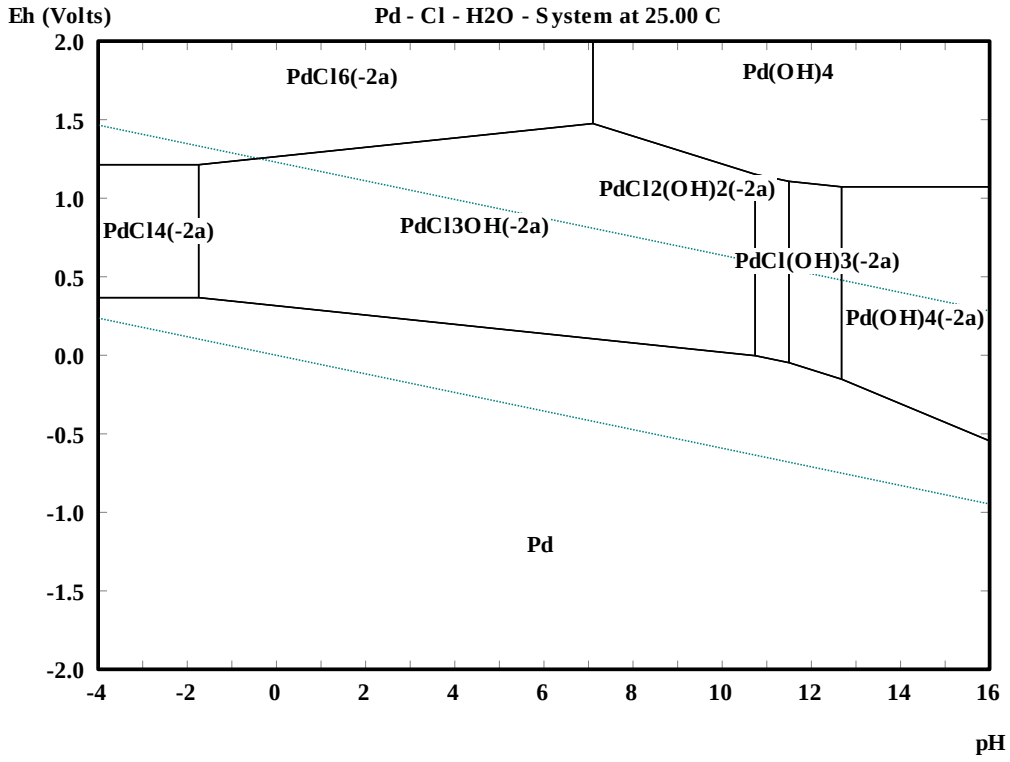

Figure12: E_h-pH diagram for the Pd-Cl-H_2O system, ($[Pd^{2+}]$ = 1mmol/kg H_2O; $[Cl^-]$ = 10 mol/kg H_2O)

4.4.2 Palladium(II) bromide complexation

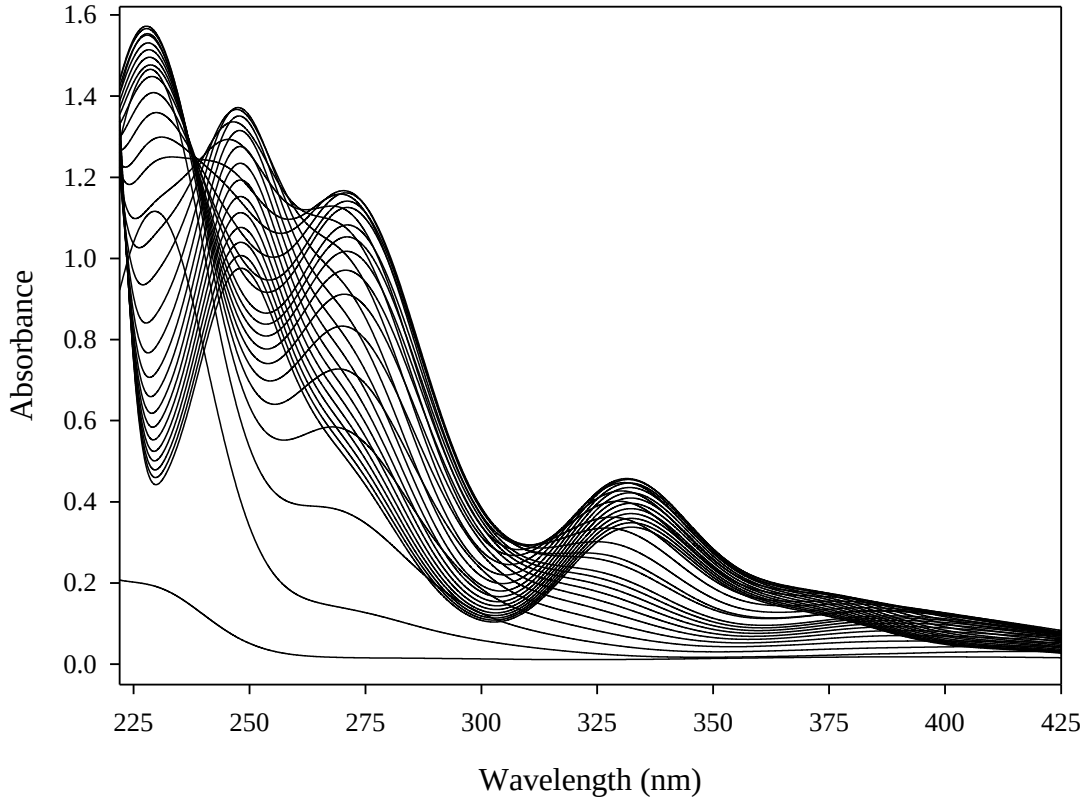

Figure 13: Change in absorption spectra with change in bromide concentration (every 10th absorption spectrum shown for improved visualisation)

Major peak changes occurred at 229.5 nm, 247 nm, 271 nm and 332 nm (Figure 13). Elding [28] focused on three corresponding wavelengths, i.e. 247 nm, 265 nm and 332 nm. As already mentioned only a limited number of recorded UV spectra and molar absorbance spectra have been reported for the palladium bromide system at present [28]. Initially the same number of concentration variations were employed (128 in total, similar to the palladium chloride investigation), however, satisfactory refinement of the model could not be obtained. Only after the number of concentration intervals were increased and varied over 300 intervals an accurate distinction between the transitions of the different species were obtained. This represents an increase of more than a factor of seven compared to the number of solutions employed by Elding [28]. Absorption data at every wavelength (every 0.5 nm) in the range 229.5 nm to 450 nm were treated with the program HypSpec [32] to calculate formation constants and absorption spectra for the complexes $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4). As in the case of chloride the molar absorption

spectrum for bromide was determined and supplied to HypSpec [32] as a known spectrum together with the already determined spectrum for the aqua complex $[Pd(H_2O)_4]^{2+}$. Similar to the chloride investigation the absorbance measurements below 229.5 nm were excluded from the calculations due to the high absorbance of bromide in this region. Again, the calculated absorbance values and the observed absorbance values at these specific wavelengths are compared in Figure 14, highlighting the high accuracy of the experimental data and the excellent correlation between the experimental and calculated data.

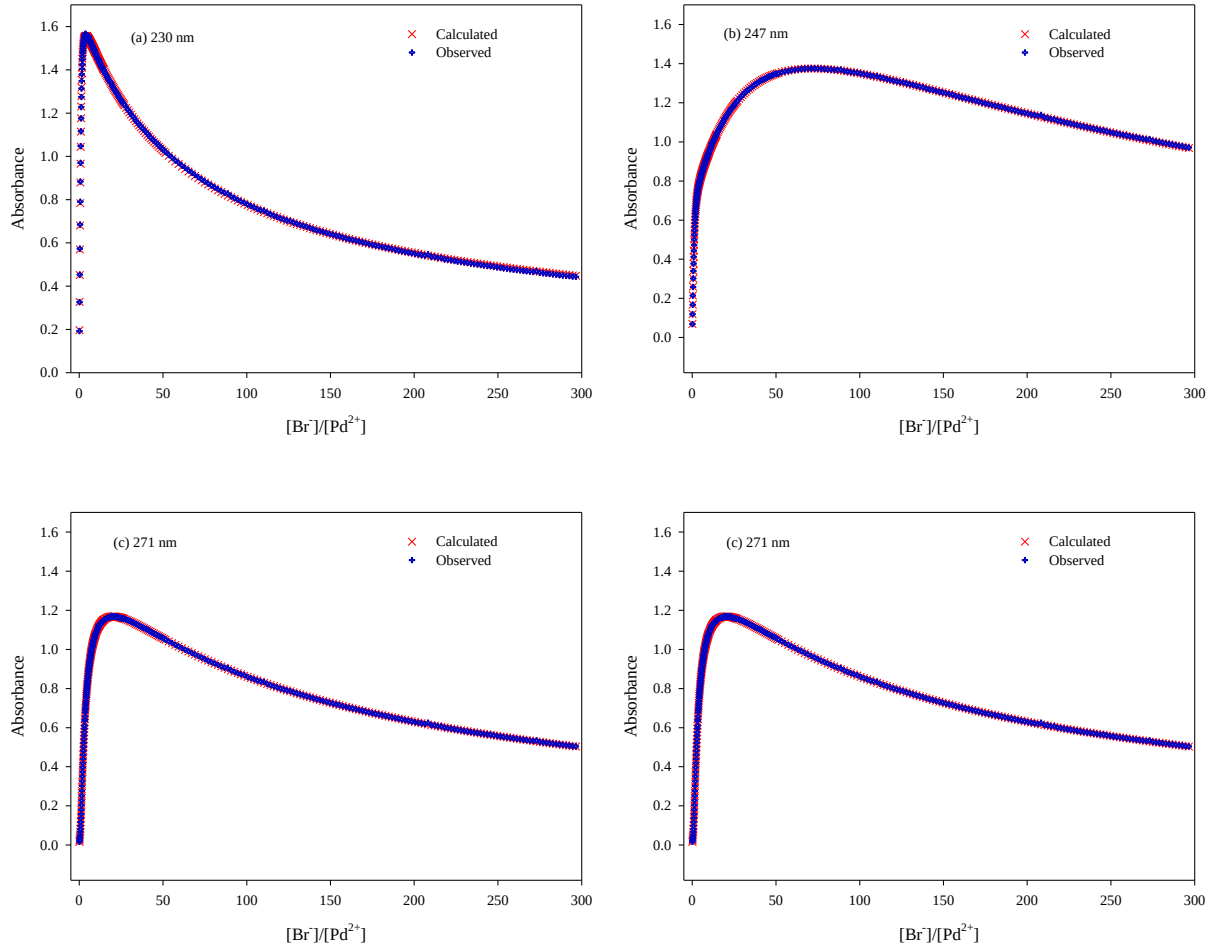

Figure 14: Actual/observed vs calculated absorbance at specific wavelengths for $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4)

The titration was repeated three times under the same conditions and the values of the cumulative formation constants for the complexes $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) are shown in Table 8 for the three individual titrations. The fact that we employed substantially more titration points,

compared to Elding's [28] limited number of individual solutions, is evident in that our calculated formation constants differ from that of Elding. The molar absorption spectra for all complexes are shown in Figure 15 with $[PdBr_4]^{2-}$ having the strongest charge transfer band at 248.5 nm with a secondary peak at 332 nm.

Table 8: Formation constants for $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 1 – 4) at 1.0 M ionic strength and 25 °C

n	log β_n (Elding [28])	log β_n (Titration 1)	log β_n (Titration 2)	log β_n (Titration 3)	log β_n (Average)
1	5.17 ± 0.02	5.040 ± 0.002	5.031 ± 0.002	5.041 ± 0.002	5.037 ± 0.002
2	9.42 ± 0.03	9.118 ± 0.004	9.120 ± 0.004	9.120 ± 0.003	9.119 ± 0.004
3	12.72 ± 0.06	12.369 ± 0.005	12.380 ± 0.004	12.381 ± 0.004	12.375 ± 0.004
4	14.94 ± 0.08	14.540 ± 0.004	14.544 ± 0.004	14.552 ± 0.005	14.545 ± 0.004
σ	N/A	1.829×10^{-3}	1.811×10^{-3}	1.829×10^{-3}	1.828×10^{-3}

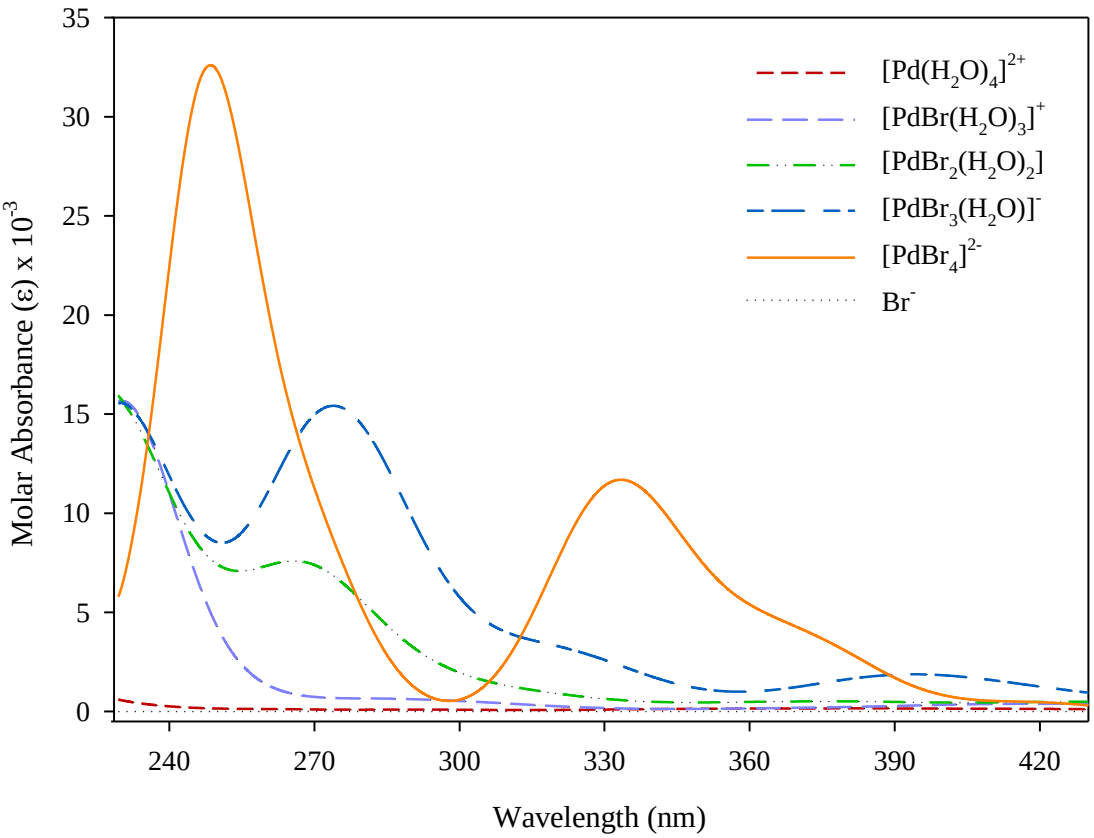

Figure 15: Calculated molar absorption spectra of $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 1 – 4)

In the case of the $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) system the charge transfer bands were shifted towards shorter wavelengths (higher energies) when chloride was substituted by water [31]. It is therefore expected that the charge transfer bands in the case of the $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4), will also shift towards shorter wavelengths with the substitution of bromide by water; in the present case, even more so. This is only the second proposed set of stepwise formation constants for $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 1 – 4) at 1.0 M ionic strength and 25 ºC. From the formation constants, a distribution diagram was constructed showing the complete speciation of the $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) system as a function of percentage palladium(II) (Figure 16). At the maximum bromide concentration for this investigation, i.e. at 1.204 x 10^{-2} M, and at a palladium concentration of 4.06 x 10^{-5} M, in excess of 80% of the palladium is in the form of the tetrabromide complex $[PdBr_4]^{2-}$. At the lowest concentration 48% of the Pd(II) is in the form of the mono bromide complex $[PdBr(H_2O)_3]^{+}$.

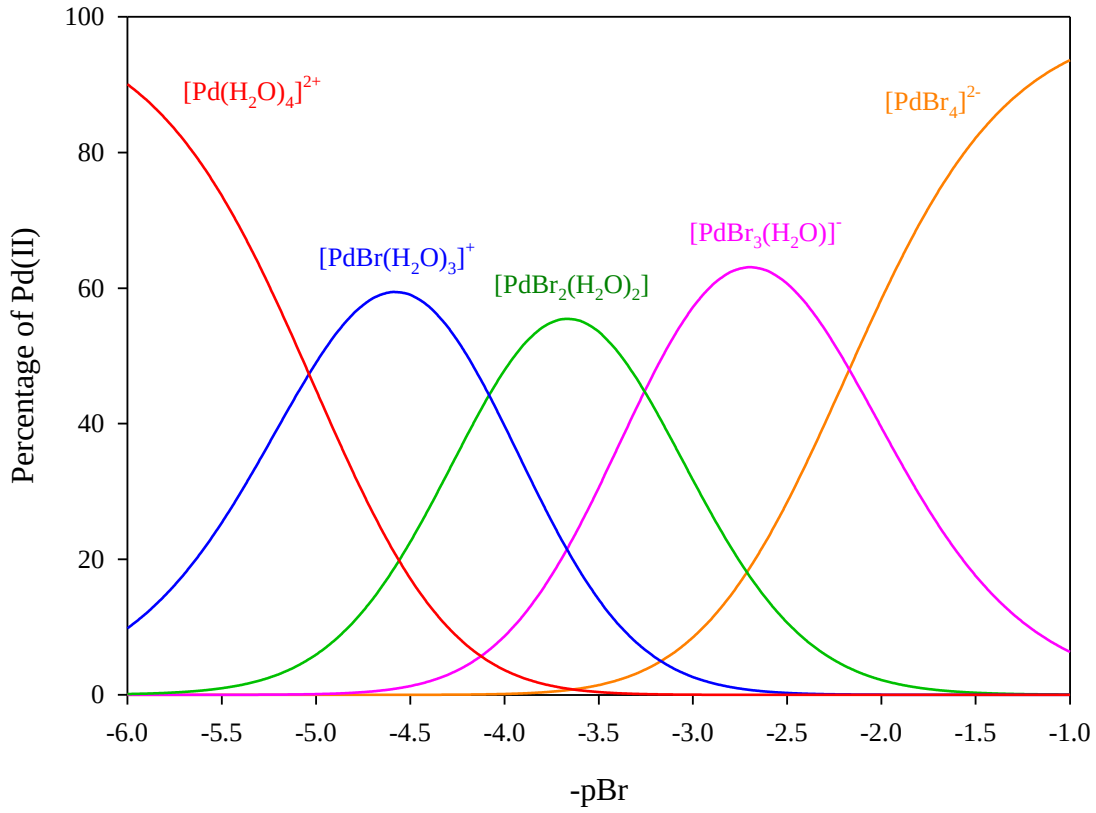

Figure 16: Distribution of $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) species as a function of -pBr

Similar to the palladium(II) chloride speciation a Pourbaix diagram was constructed employing the newly determined formation constants (Figure 17). To date, however, no speciation data exist for mixed palladium(II) bromo-hydroxo complexes (an investigation that we are currently busy with) as in the case of palladium(II) chloride. The lack of more complete speciation data for the Pd-Br-H_2O system is evident when the Pourbaix diagrams of the palladium(II) chloride and palladium(II) bromide systems are compared.

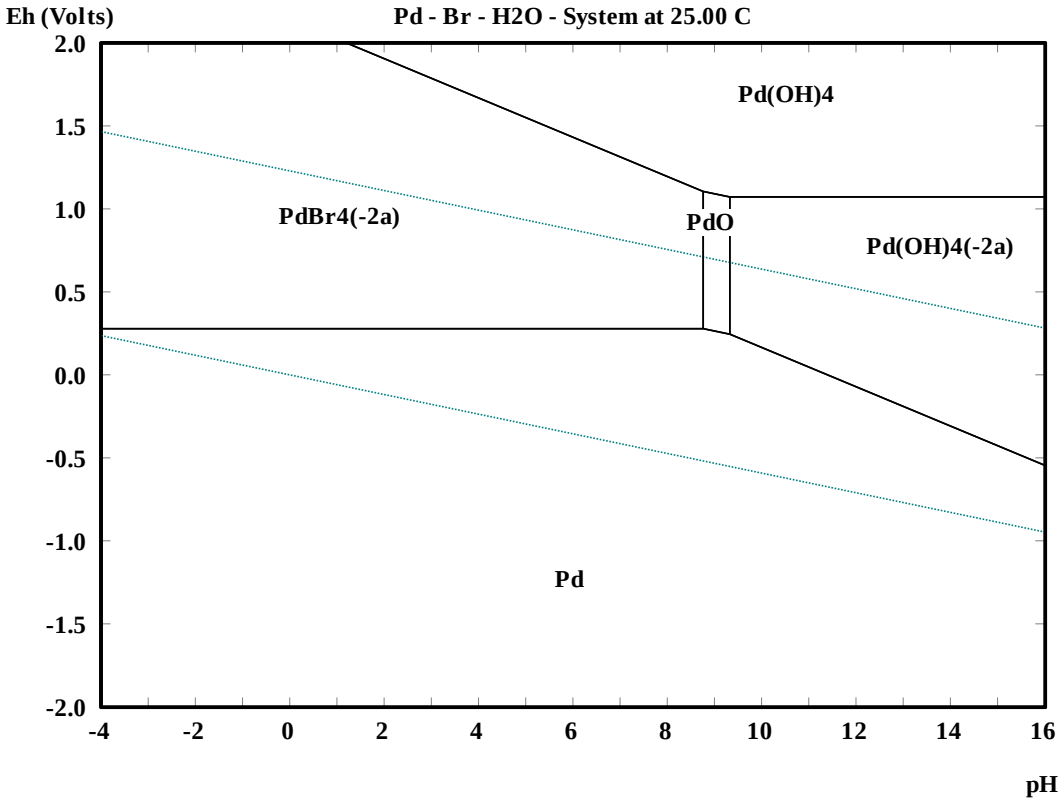

Figure 17: E_h-pH diagram for the Pd-Br-H_2O system, ([Pd^{2+}] = 1mmol/ kg H_2O; [Br^-] = 10 mol/kg H_2O)

Comparing the log β values (formation/stability constants) of the palladium(II) chloride and -bromide systems, it is evident that the log β values of the bromide system are larger than those of the chloride system. This points towards the fact that the formation of the different species of the palladium(II) bromide system takes place at lower ligand concentrations compared to the chloride system. This is in line with the data of the palladium(II) thiocyanate system [27] for which the log β values are almost double. The strength of interaction between the central palladium(II) ion and the bound ligands therefore increases in the order $Cl^- < Br^- < SCN^-$.

For this work, in contrast to the already published data, the experimental conditions employed, to determine the best fit for the data and calculate the formation constants and molar absorbances for the different complexes, were significantly more extensive as can be seen from Table 9. This include a vast increase in the number of wavelengths employed, i.e. smaller wavelength intervals, as well as a substantial increase in the number of concentrations that were employed. This was made possible by not making up individual solutions, but by conducting a single batch titration over the whole concentration range, which allowed for an improved fit of the data.

Table 9: Comparison of experimental conditions employed

	$[PdCl_n(H_2O)_{4-n}]^{2-n}$				$[PdBr_n(H_2O)_{4-n}]^{2-n}$	
	Elding [28]	Cruywagen & Kriek [26]	Weed [31]	This work	Elding [28]	This work
Wavelength range (nm)	210 – 300 305 – 605	203 – 325	320 – 600	206 – 350	210 – 300 305 – 605	229.5 – 450
Wavelengths	45 60	40	40	288	45 60	441
Wavelength interval (nm)	2.5 5	3	7	0.5	2.5 5	0.5
Concentration changes	30	24	40	128	39	300

In support of the above-mentioned models and associated formation constants the potential influence of any kinetic effects during the formation of the different complexes were considered. Consistent with our experimental approach a single batch titration was initiated and stopped at pCl = 4.50.

At this point scans were taken at every minute for 60 minutes, followed by a scan every hour for 23 hours. Subsequent to this ‘stationary’ event the titration was continued to pCl = 3.25 and the afore-mentioned sequence of scans was repeated. This was repeated for pCl = 2.40 and pCl = 1.40. From Figure 18 it is clear that overlays of all these scans do not show the existence of any kinetic effects.

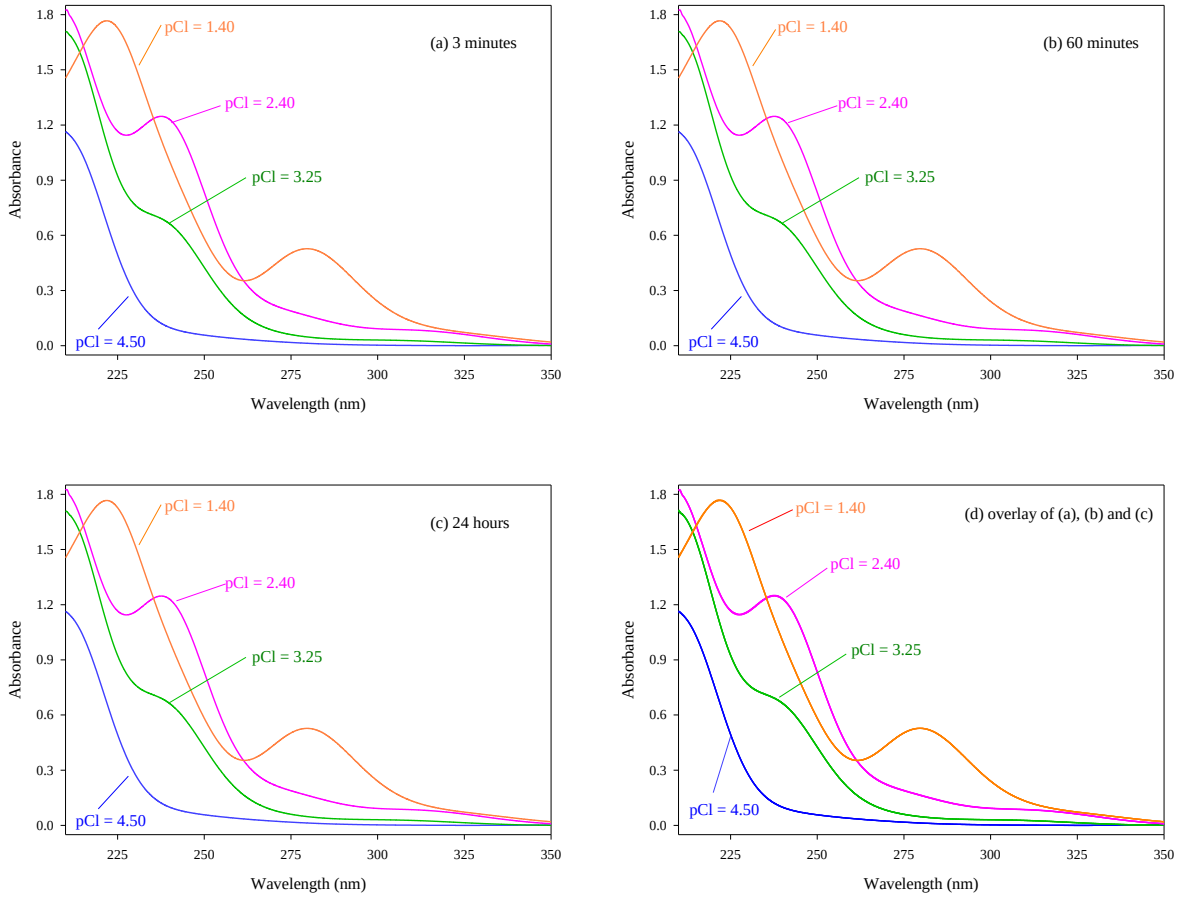

Figure 18: Change in UV Spectra at selected pCl-values after (a) 3 minutes, (b) 60 minutes, (c) 24 hours, with (d) being an overlay of (a), (b) and (c)

This was repeated for bromide (see Figure 19). It is evident that all scans, for chloride and bromide, overlay perfectly indicating that there is no change in the spectra over a 24-hour period, ruling out any kinetic effect during bond formation between palladium(II) and chloride and bromide respectively.

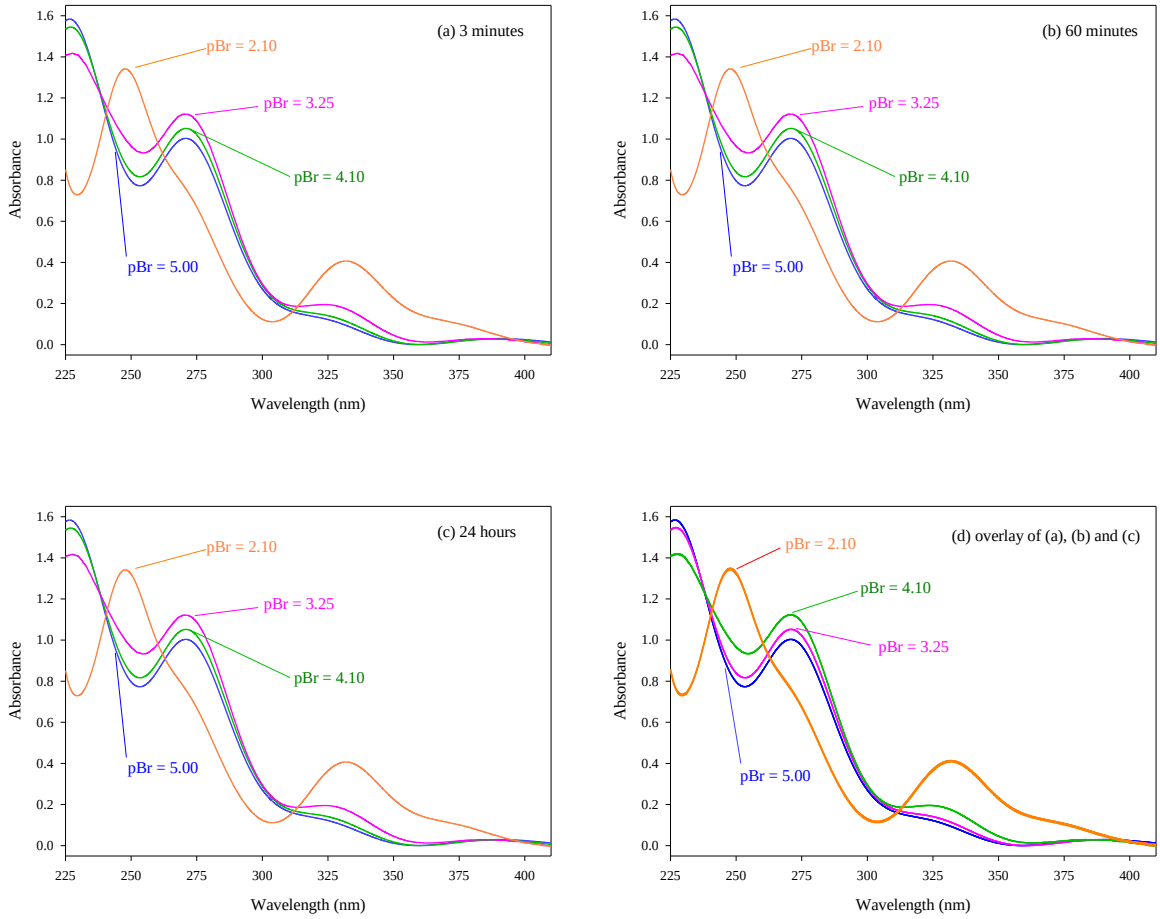

Figure 19: Change in UV Spectra at selected pBr-values after (a) 3 minutes, (b) 60 minutes, (c) 24 hours, with (d) being an overlay of (a), (b) and (c)

4.5 Conclusions

Hydrometallurgical processing of the PGMs, such as leaching, solvent extraction and ion exchange, require exact knowledge of the speciation of the specific metals involved. To this regard refined values for the stepwise formation constants of the palladium(II)-chloride system, i.e. $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4), have been determined spectrophotometrically at an ionic strength of 1.0 M and a temperature of 25 °C. Formation constants communicated for these two systems were based on a limited number of concentration variations, which entailed the making up of individual solutions that ranged between 24 and 30 solutions in total. The stepwise formation constants for the chloride system are: log β_1 = 4.485, log β_2 = 7.797, log β_3 = 10.181 and log β_4 = 11.535. The values obtained are still in good agreement with values published by

both Elding [28] and Cruywagen and Kriek [26]. After the titration method was successfully applied to the chloride system, it was customised and applied to the bromide system, $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4), for which the formation constants are: log β_1 = 5.037, log β_2 = 9.119, log β_3 = 12.375 and log β_4 = 14.546. These values differ from those published by Elding [28] and provides a new model for palladium(II)-bromide speciation. When the different methods to generate the absorbance data and consequently the formation constants are compared, it is evident that the increased number of data points, titration method, repeatable results and customised calculation software, without a doubt increased the legitimacy and accuracy of the calculated formation constants for both the chloride and bromide systems.

4.6 Acknowledgement

Our appreciation is hereby expressed to Anglo American Platinum Limited for the financial support that made this investigation possible.

4.7 References

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CHAPTER 5

PALLADIUM(II) CHLORO-HYDROXO AND -BROMO–HYDROXO SPECIATION

The revised article presented in Chapter 5 was resubmitted in Hydrometallurgy on the 30th of January 2019 and is currently under review from the 4th of February 2019.

5.1 Overview

Complex formation of mixed palladium(II) chloro-hydroxo and palladium(II) bromo-hydroxo complexes have been investigated employing spectrophotometry at 25 °C and an ionic strength of 1.0 M. Hyperquad Simulation and Speciation (HySS) was employed to determine the ideal titration conditions and an autotitrator (equipped with a flowthrough cell) was used to accurately vary the pH over 80 and 90 intervals respectively. The stability constants (log β_n) for the mixed chloro-hydroxo complexes $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), are: log β_1 = 18.36, log β_2 = 23.21, log β_3 = 26.91 and log β_4 = 29.68. These newly obtained values represent an improved speciation of the mixed palladium(II) chloro-hydroxo complexes. The same experimental procedure was employed to calculate, for the first time, the stepwise stability constants of the palladium(II) bromo-hydroxo system, $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), i.e. log β_1 = 18.73, log β_2 = 22.25, log β_3 = 25.58 and log β_4 = 28.47. Molar absorption spectra for all the complexes in question have been obtained. For both systems, complete Pourbaix diagrams

were constructed from the new speciation data showing the predominant species for each system.

5.2 Introduction

Hydrometallurgical processing of platinum group metals (PGMs) require exact knowledge of the speciation of the specific metals involved. Both chloride [1-6] and bromide [1, 4, 6, 7] anions are investigated for their application in hydrometallurgical processes as complexing agents.

As mentioned previously [8, 9] the speciation of a specific system, i.e. the identity and distribution of specific metallic species/complexes in solution as characterised by the stability constants (also known as formation constants), is essential in developing, improving and understanding dedicated hydrometallurgical processes. The stability constants convert into Gibbs free energies that, when different, result in a shift of the stability regions of different complexes which is illustrated by a Pourbaix diagram. For example, an investigation into the rapid liquid-liquid extraction of palladium(II) employing hexadecylpyridinium bromide (HDPB), the extraction was studied as a function of several parameters, which included pH [10]. The extraction efficiency of palladium(II) was carried out over the pH range 1 – 10 and it was possible to successfully extract palladium(II) at pH values as high as 5, while extraction decreased significantly at higher pH values. In addition, an investigation into the sorption-based recovery of palladium(II), employing the commercial basic anion exchanger Lewatit MonoPlus SR-7, the importance of knowing the speciation of palladium(II) in solution has been deemed crucial to determine the affinity of palladium(II) for binding sites [11]. Although platinum group metal (PGM) recovery is generally carried out in strong acidic media, the exact knowledge of platinum group metal ion speciation in more basic solutions facilitates the possibility to develop hydrometallurgical extraction processes in a wider pH range. This was illustrated in a leaching study conducted on the recovery of PGMs from gasoline and diesel fuel catalysts at eight predefined pH-static set points (pH = 2 - 9) [12]. Knowledge of the speciation of metal ions in solution is largely dependent on pH, metal concentration and the presence of ligands [13]. It therefore follows that a change in the pH of a solution can have a dual interaction effect on sorption performance due to the influence of the acidity/basicity together with the presence of halide ions.

The complexation equilibria of palladium(II) with only chloride and bromide, at low pH values, have been investigated by a number of authors and values for the formation constants have been determined [9, 14-23]. These complexes can be represented by the general formula $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) and $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) respectively. In contrast, at higher pH values, published formation constant values for the hydrolysis of palladium(II) [24-28] are available, however, limited data exists for mixed chloro-hydroxo complexes [16, 24-28], $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), while no data exists for the bromo-hydroxo complexes, $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4).

Furthermore, a lot of uncertainty exists with regard to the current published formation constant values, with the most complete study in terms of the stepwise formation of mixed chloro-hydroxo complexes being that of Cruywagen and Kriek [16]. Other authors focussed on the stability and kinetics of selected mixed chloro-hydroxo complexes [15, 24] presenting selected values and corresponding molar absorbances. Various authors [24, 28] also presented values for the mixed complex $[PdCl_3(OH)]^{2-}$ derived from $[PdCl_4]^{2-}$ employing reaction 12:

$$[PdCl_4]^{2-} + H_2O \rightleftharpoons [PdCl_3(OH)]^{2-} + H^+ + Cl^- \qquad (12)$$

The majority of the above-mentioned authors made use of a batch type experimental procedure whereby individual samples were prepared. Cruywagen and Kriek [16] employed a double burette titration ensuring both the palladium and chloride concentrations were kept constant. A solution containing a mixture of $[PdCl_3]^-$ and $[PdCl_4]^{2-}$ (obtained by dissolving $PdCl_2$) was used as starting solution and titrated with sodium hydroxide. A similar blank titration was carried out to correct the spectra. Although this is the only complete stepwise formation study to date, some uncertainty does exist as to the accuracy of the calculation of the formation constants as only a limited number of concentration variations were employed.

As part of previous investigations an automated titration and data collection setup was employed with great success [8, 9]. This automated experimental method was appropriately customized to accurately determine the stepwise formation constants for both palladium(II) chloro-hydroxo and palladium(II) bromo-hydroxo mixed complexes. For this study a solution containing $[PdCl_4]^{2-}$ was prepared by adding chloride to a stock solution of palladium(II) so as to ensure that this was the only initial species present. The concentration of both palladium(II) and chloride were kept constant with the only change that of the hydroxide concentration.

Similar to previous investigations [8, 9], the same software program, HypSpec [29], was used to derive equilibrium constants from spectrophotometric data. The same experimental method was customised to determine the stability constants for palladium(II) bromo-hydroxo mixed complexes. A full set of stability constants for the palladium(II) bromo-hydroxo mixed complexes is reported here for the first time.

5.3 Experimental

5.3.1 Experimental design

For the first time two specialized analytical apparatus, a Metrohm 809.1 double burette auto-titrator and an Analytic Jena SPECORD® S600 UV-Vis diode-array spectrophotometer equipped with a quartz flow-through cuvette, were combined by means of a software program to work as a dedicated speciation apparatus.

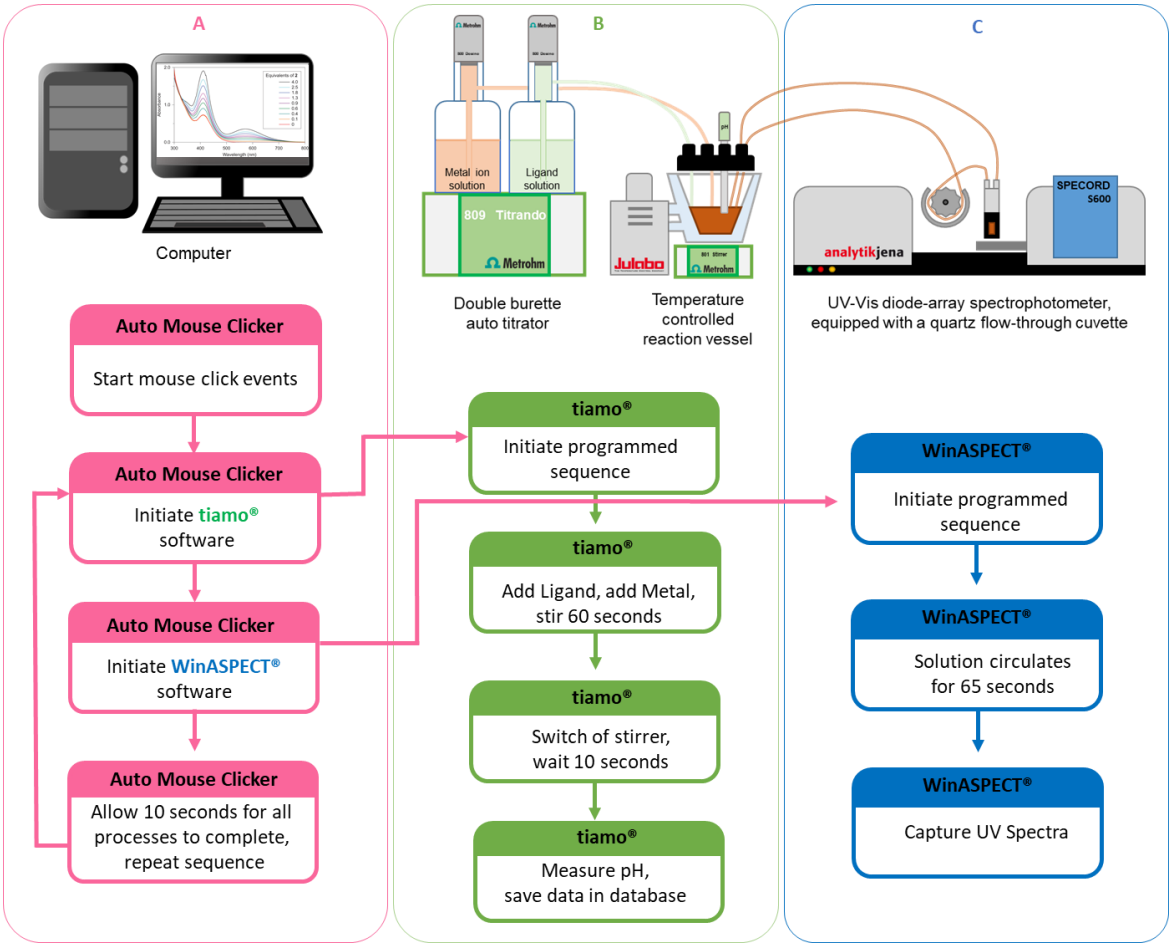

Figure 20: Detailed schematic diagram of the experimental procedure followed

The jacketed reaction flask was thermostatically controlled at a fixed temperature of 25 °C employing a Julabo F12-ED refrigerated/heating circulator. It was now possible to automatically vary the ligand concentration over various intervals ensuring a very accurate and consistent set of absorbance data. A detailed schematic diagram is presented in Figure 20.

The experimental procedure can be divided into three parts. Section A is represented by the computer and Auto Mouse Clicker software program. In section B the tiamo® software is in charge of controlling the Metrohm 809.1 double burette auto-titrator, which is responsible for the addition (dosing) of the metal/ligand solutions, magnetic stirrer and the pH measurements. Finally, WinASPECT® controls the Analytic Jena SPECORD® S600 UV-Vis diode-array spectrophotometer as seen in C.

The Auto Mouse Clicker program (A) controls the other two software packages and once it is activated the procedure continues automatically. First, it will activate the tiamo software package (B), which will then continue executing the programmed sequence set. A short time interval of 5 seconds was set within the Auto Mouse Clicker program to ensure an adequate mixture of the solution inside the jacketed reaction flask before the WinASPECT® software is activated (C). The Analytic Jena SPECORD® S600 has a peristaltic pumping system (sipper) which circulates the solution from the reaction flask through the quartz flow-through cuvette. The time interval for the sipper system is controlled inside the WinASPECT® software and will execute before each UV measurement. The temperature of the reaction flask is controlled by setting a fixed temperature value on the Julabo F12-ED refrigerated/heating circulator.

The time intervals within all three software programs are set to ensure effective mixing in the reaction flask (B) and circulation of the solution through the flow-through cuvette (C). It also allows for the solution inside the reaction flask to settle for 10 seconds before the pH is measured (B). Once all the steps are completed, the procedure will be repeated as required.

The 809 Titrando high-end titrator has the option of connecting a large range of intelligent electrodes. In order to ensure accurate pH measurements, which is compulsory for determining the hydroxide concentration during the titration, the Metrohm Solitrode Pt 1000 electrode (6.0228.000) was employed. It was calibrated with standard pH buffers from Metrohm (4,7 and 9) before each titration. No special buffers or calibration was required as the pH range was

between 4 and 13. Equilibrium is reached instantaneously as no further changes in the spectra of the solutions were observed over time. Spectra were recorded every 90 seconds in the wavelength range 200 – 500 nm for palladium(II) chloro-hydroxo mixed complexes and 240 – 550 nm for palladium(II) bromo-hydroxo mixed complexes against water as reference. For each speciation study a background titration that contained no palladium was done and the absorbance spectra was then subtracted from the original absorbance spectra. Competition of H^+ for Cl^- and Br^-, with the subsequent formation of HCl and HBr, are negligible in that the pK_a of HCl and HBr is -9.0 and -11.0 respectively [30].

For the $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) system absorption data at every wavelength (every 0.5 nm) from 220 nm to 320 nm (Table 10), within the pH range 4 – 12, were treated with the program HypSpec [29] to calculate the stability constants (β_n) and molar absorption spectra. As discussed and motivated earlier [9] the absorbance data below 220 nm were excluded from the calculations. For the $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) system absorption data at every wavelength (every 0.5 nm) between 240 nm and 425 nm (Table 10), coinciding with a pH range of 8 < pH < 12, were treated with the program HypSpec [29] to calculate stability constants and absorption spectra for the complexes. For the palladium(II) chloro-hydroxo speciation the number of datapoints (or concentration changes) increased to 71, compared to the earlier study that only investigated 17 concentration changes. For the palladium(II) bromo-hydroxo study a total of 80 concentration changes could be accommodated.

Table 10: Comparison of experimental conditions employed for $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) and $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4)

	$[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4)		**$[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4)**
	Cruywagen & Kriek [16]	This work	This work
Wavelength range (nm)	230 – 325	220 – 320	240 – 425
Wavelengths	32	220	370
Wavelength interval (nm)	3	0.5	0.5
Concentration changes	17	71	80
pH	4 < pH < 12	4 < pH < 12	8 < pH < 12

5.3.2 Solution preparation and titration

All reagents were of analytical grade and solutions were prepared with ultra-pure water obtained from a Millipore Milli-Q system. A stock solution of palladium(II), with a concentration of 3.0 x 10^{-3} M (confirmed by ICP analyses) in 1.0 M perchloric acid, was prepared [8]. From this stock solution, a palladium(II) chloride solution (6.0 x 10^{-5} M) was prepared by adding a suitable amount of NaCl (0.964 M total), while ensuring an ionic strength of 1.0 M. According to the stability constants previously published [9], palladium(II) chloride will be for all intents and purposes in the four-coordinated form, i.e. $[PdCl_4]^{2-}$. A 0.6 M sodium hydroxide solution, having an ionic strength of 1 M (by adding $NaClO_4$), was used to vary the pH for both chloride and bromide experiments.

An 80 mL sample of a palladium(II) chloride starting solution ($[Pd^{2+}]$ = 3 x10^{-5} M, $[Cl^-]$ = 0.482 M, I = 1.0 M) was added to the jacketed reaction flask that was thermostatically controlled at a fixed temperature of 25 °C (employing a Julabo F12-ED refrigerated/heating circulator). Equal amounts of the Palladium(II) chloride and sodium hydroxide solutions were dispensed from the double burette auto-titrator (see Figure 20), spread over 80 intervals, ensuring that both the palladium(II) and chloride concentration were constant throughout the titration. Initially, large amounts of both solutions (23 mL) had to be added to the palladium(II) chloride solution contained in the reaction vessel so as to ensure a significant change in the absorbance spectra. After this point was reached, small amounts (0.04 mL – 2.0 mL) were titrated simultaneously from both burettes in order to generate as many absorbance data as possible. A total of 2.40 mL of the 0.6 M NaOH solution was needed to vary the pH from 3.35 to 10.33 over 60 intervals and an additional 22 mL was spread over 20 intervals to obtain a maximum pH of 11.58.

For the palladium(II) bromo-hydroxo speciation 80 mL of a palladium(II) bromide starting solution ($[Pd^{2+}]$ = 3 x10^{-5} M, $[Br^-]$ = 0.482 M, I = 1.0 M) was added to the temperature-controlled reaction vessel. Once a noticeable change in the absorbance spectra was observed (26 mL) smaller amounts was titrated to again ensure the spread of a maximum number of data points over the desired pH range. A total of 1.6 mL of the 0.6 M NaOH solution was needed to vary the pH from 3.50 to 10.05, over 40 intervals, and an additional 32 mL was spread over 50 intervals to reach a maximum pH of 11.57.

5.3.3 Calculation of stability constants

The stability constants and molar absorbance spectra are determined from the spectrophotometric data by employing a software program HypSpec [29], which is specifically designed to derive equilibrium constants from spectrophotometric data and is part of the Hyperquad suit. The stability constants are calculated by a non-linear refinement process during which stability constant values are optimized. During the refinement three constraints are applied, i.e. the equations of mass-balance are always satisfied, the molar absorbance values are obtained by linear least-squares fitting of the absorbance values according to the Beer-lambert law: $A = l \Sigma \varepsilon c$, where c is a species concentration and the stability constants must have positive values. A measure of the overall quality of data refinement is indicated by the sigma (σ) value, which was explained as part of a previous publication [9].

In HypSpec a special convention is used for the hydroxide ion. Because of the self-ionization equilibrium ($H^+ + OH^- \rightleftharpoons H_2O$), HypSpec does not regard the hydroxide ion as a ligand, or competing species/reagent as is the case with the chloride ion (Cl^-). The amount of bound OH^- is determined from the pH-values, which points towards the free H^+ and free OH^- and are taken into consideration as per equations 13 – 15. For a general metal complex $[ML_n(OH)_{4-n}]$, where *M* is the metal, *L* the ligand and *n* the number of bonded ligands, we can write the following expression:

$$[ML_n(OH)_{4-n}] = \beta_{n,4-n}[M][L]^n[OH]^{4-n} \quad (13)$$

$$\text{Since } [H^+][OH^-] = K_w,$$

$$\text{and } [OH] = K_w[H]^{-1}$$

$$[ML_n(OH)_{4-n}] = \beta_{n,4-n}[M][L]^n K_w^{4-n}[H]^{n-4} \quad (14)$$

$$= \beta_{n,4-n} K_w^{4-n} [M][L]^n [H]^{n-4}$$

$$= {}^*\beta_{n,4-n}[M][L]^n[H]^{n-4} \quad (15)$$

The concentration of the hydroxide ion is now related to the concentration of the reagent H^+. Because of this convention the formation constants of hydrolysed species will appear to be on a different scale, which are reported in literature as log $^*\beta$ (equation 16). For the two systems

presented in this paper the relationship between log β (normally reported in literature) and log $^*\beta$ are as follow:

$$\log {}^*\beta_{n,\,4-n} = \log \beta_{n,4-n} + (4-n) \log K_w \qquad (16)$$

Hyperquad Simulation and Speciation (HySS) software, which is also part of the Hyperquad suit, [31] was used to determine the ideal titration conditions with a model having been specified by defining a set of equilibrium constants (equation 17).

$$\beta_{pq}.. = [M_pL_q.] / ([M]^p[[L]^q..) \qquad (17)$$

The titration was subsequently simulated by specifying a set of titration conditions and calculating the concentrations of each complex species as the titration proceeds. The optimised titration conditions obtained are then used to calculate the ideal concentrations for the different solutions.

In order to construct Pourbaix (E_h-pH) diagrams from the determined speciation data, HSC Chemistry® 6.0 (Outotec) was used. The enthalpy (H), entropy (S) and heat capacity (C_p) values of elements and compounds are stored in the database together with a variety of additional information. HSC Chemistry® also has the option to save additional species into its database to be used across all calculation modules.

5.4 Results and discussion

5.4.1 Palladium(II) chloro-hydroxo complexation

The change in absorption spectra, with change in pH, is shown in Figure 21.

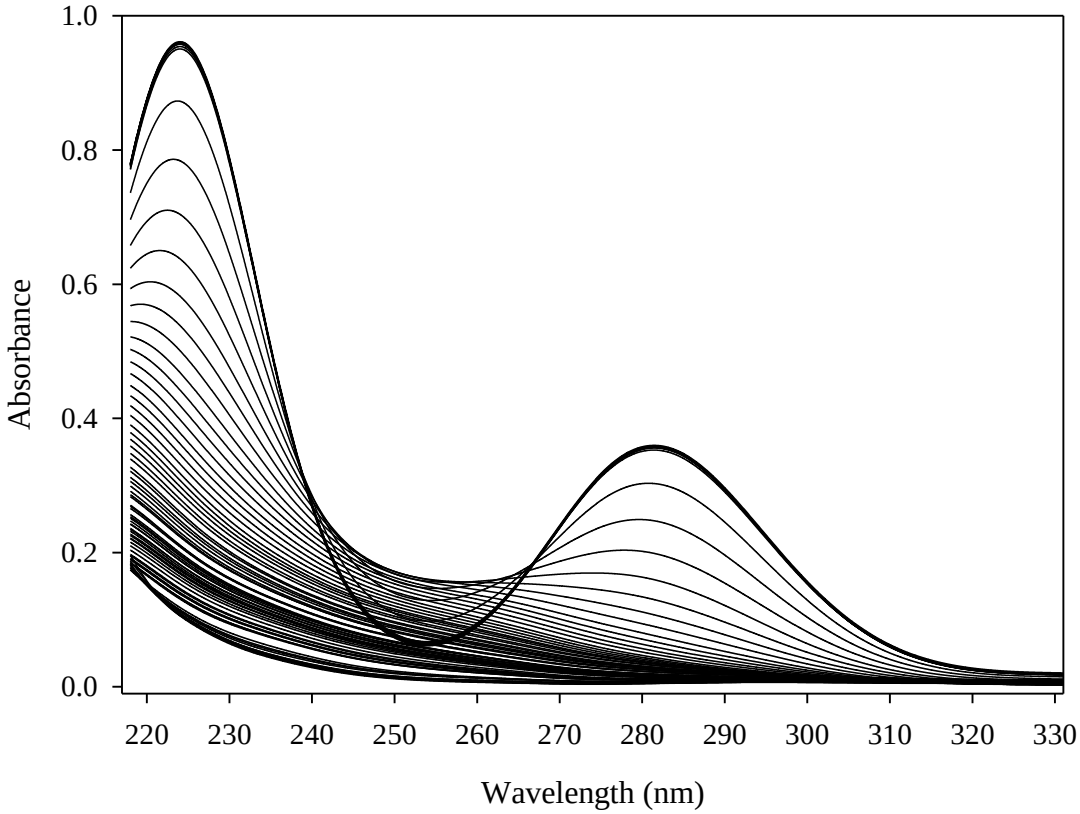

Figure 21: Change in absorption spectra with change in pH for $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), ionic strength 1.0 M and 25 °C.

Similar to results reported by Cruywagen and Kriek [16], noticeable changes in the absorbance spectra occurred at 224 nm and 282 nm. Employing the same model (as determined by Cruywagen and Kriek [16]) as initial input, together with the aid of HypSpec's factor analysis tool, as well as the fitting/correlation of the experimental and calculated data (Figure 3), it was ascertained that the same number of species were present. This also confirmed the dominance of the $[PdCl_4]^{2-}$ species at the start of the titration, and it was furthermore ascertained that the model did not change subsequent to including $[PdCl_3]^-$ as a known reagent, and it ($[PdCl_3]^-$) was subsequently excluded as a reagent from the final model. Similar to previously published works [8, 9] the observed and calculated absorbance data, as a means of verifying the model, were compared at the above-mentioned wavelengths and excellent agreement was obtained.

This, in line with the small sigma-value obtained and the confirmation of the presence of four chloride complexes, supports the legitimacy of the proposed model.

The calculated values of the cumulative stability constants for $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), as per the convention used by HypSpec, are displayed in Table 11. The titration was repeated three times and the average value converted as per equation 5 (pK_w = 13.74 for 1 M NaCl/$NaClO_4$ [32, 33]) to compare it to existing literature values (see discussion in Section 2.3).

Table 11: Stability constants for $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) at 1.0 M ionic strength and 25 °C

n	log $*\beta_n$ (Titration 1)	log $*\beta_n$ (Titration 2)	log $*\beta_n$ (Titration 3)	log $*\beta_n$ (Average)	log β_n (pK_w = 13.74)
0	-	-	-	-	11.54 ± 0.01 [9]
1	4.41 ± 0.01	4.67 ± 0.01	4.78 ± 0.02	4.62 ± 0.19	18.36 ± 0.19
2	-4.52 ± 0.01	-4.22 ± 0.01	-4.06 ± 0.02	-4.27 ± 0.74	23.21 ± 0.74
3	-14.72 ± 0.01	-14.17 ± 0.01	-14.04 ± 0.03	-14.31 ± 0.36	26.91 ± 0.36
4	-25.29 ± 0.02	-24.76 ± 0.07	-25.80 ± 0.13	-25.28 ± 0.52	29.68 ± 0.52
σ	3.13 x 10^{-3}	3.92 x 10^{-3}	7.31 x 10^{-3}	4.78 x 10^{-3}	4.78 x 10^{-3}

To date, the only other complete speciation study of mixed palladium(II) chloro-hydroxo complexes was that of Cruywagen and Kriek [16]. Van Middlesworth and Wood [24] determined the stability constants of various palladium(II) hydroxide and hydroxy-chloride complexes, typically present in seawater. They reported a stability constant (log β_1) for $[PdCl_3(OH)]^{2-}$ of = 18.36 at the same reaction conditions but by employing different solubility methods. When comparing the newly proposed values to that of Cruywagen and Kriek [16] one of the major differences is the value of log β_1 = 18.36 (this work) vs log β_1 = 16.48 [16]. Furthermore, the newly determined absorbance spectra (Figure 22) now includes data for the wavelength region 220 – 230 nm, which did not form part of the earlier investigation [16].

Similar to an earlier investigation on the complexation of palladium(II) with chloride and bromide [9], the experimental conditions employed for the present investigation were

expressively more extensive so as to determine the best fit for the data and accurately calculate the formation constants and molar absorbances for the different mixed complexes (see Table 11). This includes a vast increase in the number of wavelengths employed, i.e. smaller wavelength intervals, as well as a substantial increase in the number of concentrations that were employed. This was made possible by accurately dispensing a minimum volume of 0.004 mL. A summary of the relevant calculated overall (β_n) formation constants is shown in Table 12.

Table 12: Summary, and comparison with literature data, of overall formation constants (β_n) for mixed palladium(II) chloro-hydroxo complexes

Mixed Pd(II) chloro-hydroxo complexes				Literature	Experimental
$[PdCl_3(OH)]^{2-}$	$[PdCl_2(OH)_2]^{2-}$	$[PdCl(OH)_3]^{2-}$	$[Pd(OH)_4]^{2-}$	Reference	Conditions
16.12	-	-	26.4	[28]	25 °C, I = 0.75 M
18.23	-	-	-	[24]	25 °C, I = 1.0 M
-	-	-	26.4	[26]	17 °C, I = 0.1 M
16.48	20.63	24.02	26.23	[16]	25 °C, I = 1.0 M
18.36	23.12	26.91	29.68	This work	25 °C, I = 1.0 M

This investigation includes not only more absorbance spectra over the whole pH-range studied, but also more absorbance data at lower wavelengths (below 230nm). This results in a 2 – 3 order of magnitude difference in the newly determined overall formation constants (β_n) when compared to the previously determined values [16]. This is a direct result of an approximately two-order of magnitude difference in the first stepwise formation constant (K_1) for the formation of $[PdCl_3(OH)]^{2-}$ out of $[PdCl_4]^{2-}$ (Table 13).

Table 13: Summary of stepwise formation constants (K_n) for mixed palladium(II) chloro-hydroxo complexes

Mixed Pd(II) chloro-hydroxo complexes					Literature
$[PdCl_4]^{2-}$	$[PdCl_3(OH)]^{2-}$	$[PdCl_2(OH)_2]^{2-}$	$[PdCl(OH)_3]^{2-}$	$[Pd(OH)_4]^{2-}$	Reference
11.54 [9]	6.69	-	-	-	[24]
11.54 [9]	4.94	4.15	3.39	2.21	[16]
11.54 [9]	6.82	4.76	3.79	2.77	This work

From Table 13 it is clear that the biggest difference is evident for the first stepwise formation constant (K_1) as this work allowed for more data points in the low pH-value region where $[PdCl_3(OH)]^{2-}$ formed out of $[PdCl_4]^{2-}$. Although being slightly higher, subsequent stepwise formation constants (K_n), for n = 2 – 4, are in line with the earlier work. Our K_1-value is furthermore in line with the work of Van Middlesworth [24].

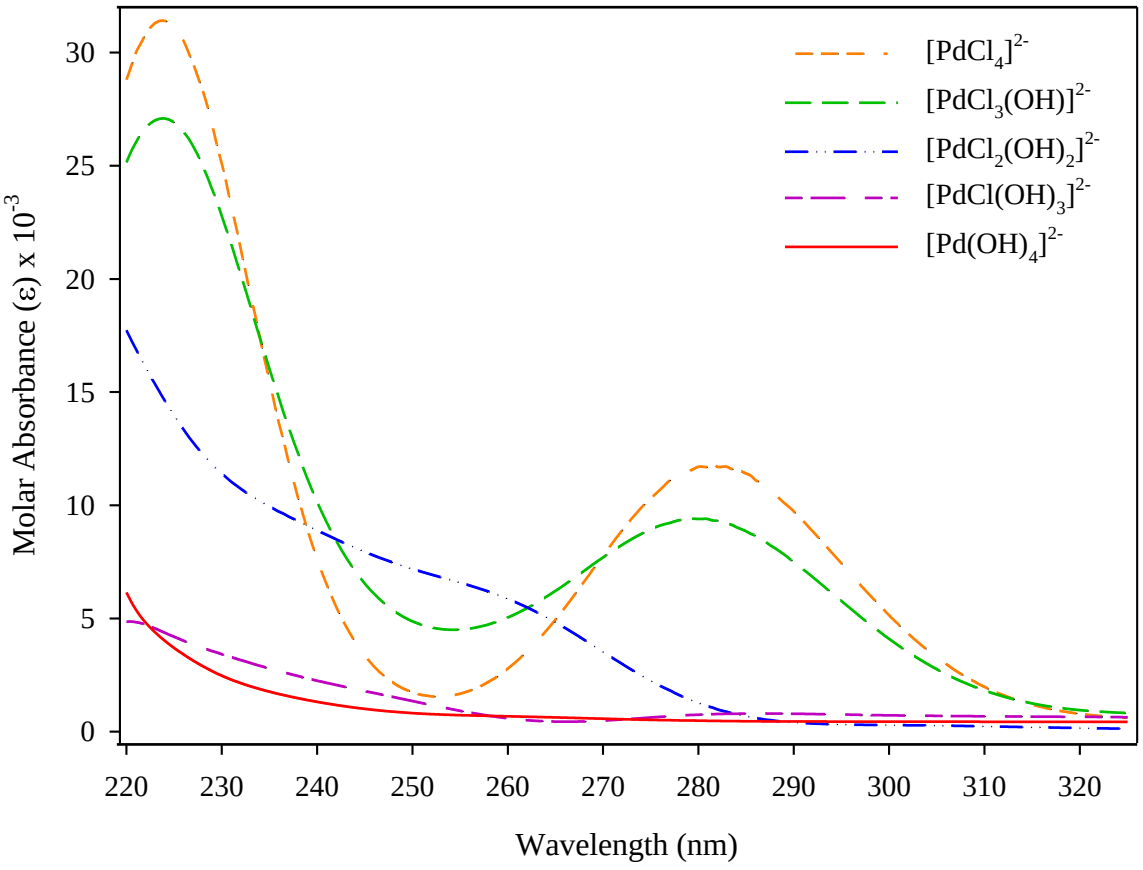

Figure 22: Calculated molar absorption spectra of $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4).

From Figure 22 it is evident that there is a considerable change in absorbance data values between 220 nm and 230 nm, as noticeable changes in the absorbance spectra occurred at 224 nm. In an effort to compare our data to that of Cruywagen and Kriek [16], absorbance data generated below 230 nm was excluded, which resulted in us not being able to obtain a refinement of the model or to conduct a manual fitting of the data. Although there was a slight difference in the stability constants of the three titrations, the trend was similar. As chloride is substituted by hydroxide, with an associated increase in pH, a decrease in absorbance is evident due the shift in bands towards the shorter wavelengths.

The software program HySS, which is part of the Hyperquad Suite, was used to calculate the distribution of the complexes from the newly determined formation constants (Table 11) as a function of pH and is shown in Figure 23. It is evident that $[PdCl_3(OH)]^{2-}$ is the most dominant mixed ligand complex at pH 6.5 – 8.5, which coincides with a study conducted by Van Middlesworth and Wood [24] on the stability of palladium(II) hydroxide and palladium(II) chloro-hydroxo complexes.

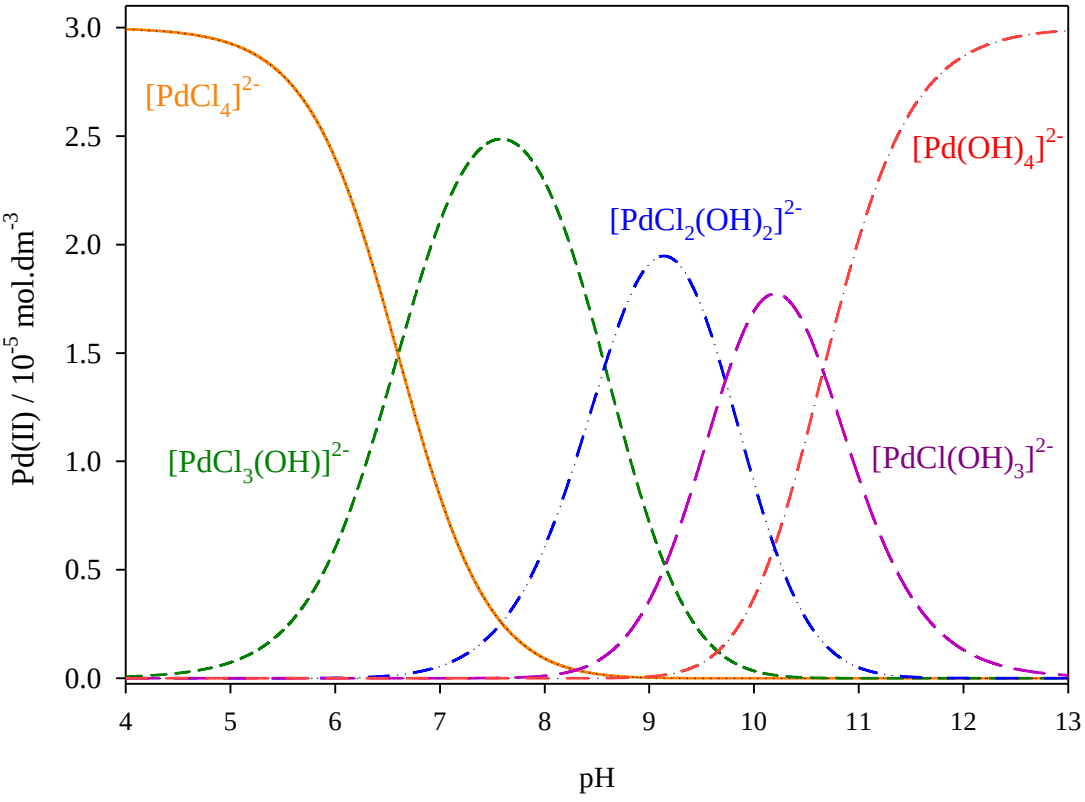

Figure 23: Distribution of $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) species as a function of pH at 25 °C. $[Pd^{2+}] = 3 \times 10^{-5}$ M, $[Cl^-] = 0.482$ M, ionic strength 1.0 M.

This complex is present in the pH-range 5 – 10 and has its strongest presence at pH = 7.5. The other mixed complexes are dominant in the range 8 < pH < 11, after which palladium (II) hydroxide dominates at pH-values above 10.5.

HSC Chemistry® 6.0 from Outotec, was used to construct a Pourbaix (E_h-pH) diagram from the speciation data (Figure 24). Our newly determined stability constants for the mixed palladium(II) chloro-hydroxo complexes $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), together with the stability constants of the $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) system that were determined earlier [9] were employed to calculate the Gibbs free energies of formation for each complex that was subsequently incorporated into the HSC Chemistry® 6.0 database and used to construct the Pourbaix diagram.

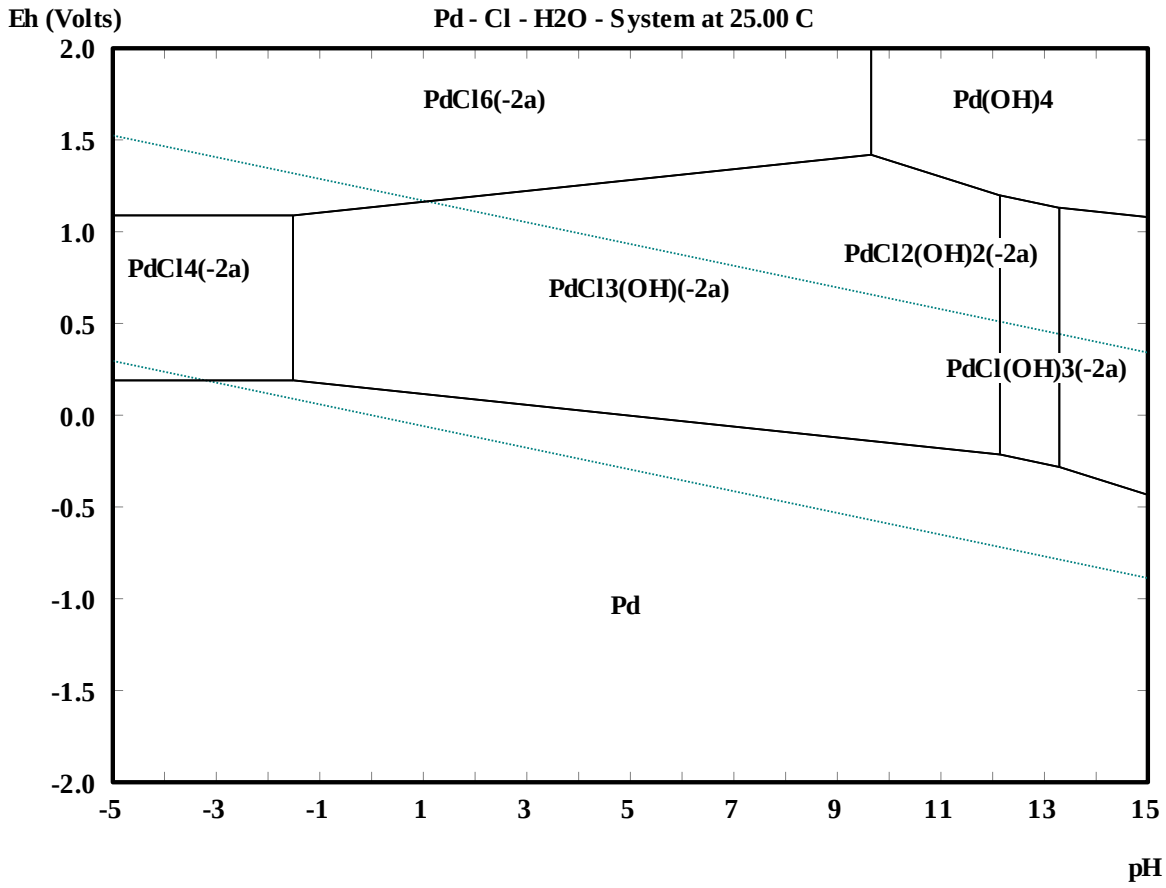

Figure 24: E_h-pH diagram for the Pd-Cl-H_2O system, ($[Pd^{2+}]$ = 1mmol/kg H_2O; $[Cl^-]$ = 1000 mol/kg H_2O), constructed employing new stability constants listed in Table 12 and reference [9]

5.4.1 Palladium(II) bromo-hydroxo complexation

The change in absorption spectra, with a change in pH, for mixed palladium(II) bromo-hydroxo complexes are shown in Figure 26. When the absorption spectra are compared to that of the palladium(II) chloro-hydroxo absorption spectra (Figure 21) it is evident that most of the changes in speciation took place in solutions of pH > 8. As a result, it was experimentally easier to obtain more data points as the majority of the changes in speciation took place after the neutralisation point of NaOH and $HClO_4$. Major peak changes occurred at 249 nm and 334 nm as the absorbance decreased with the substitution of bromide by hydroxide.

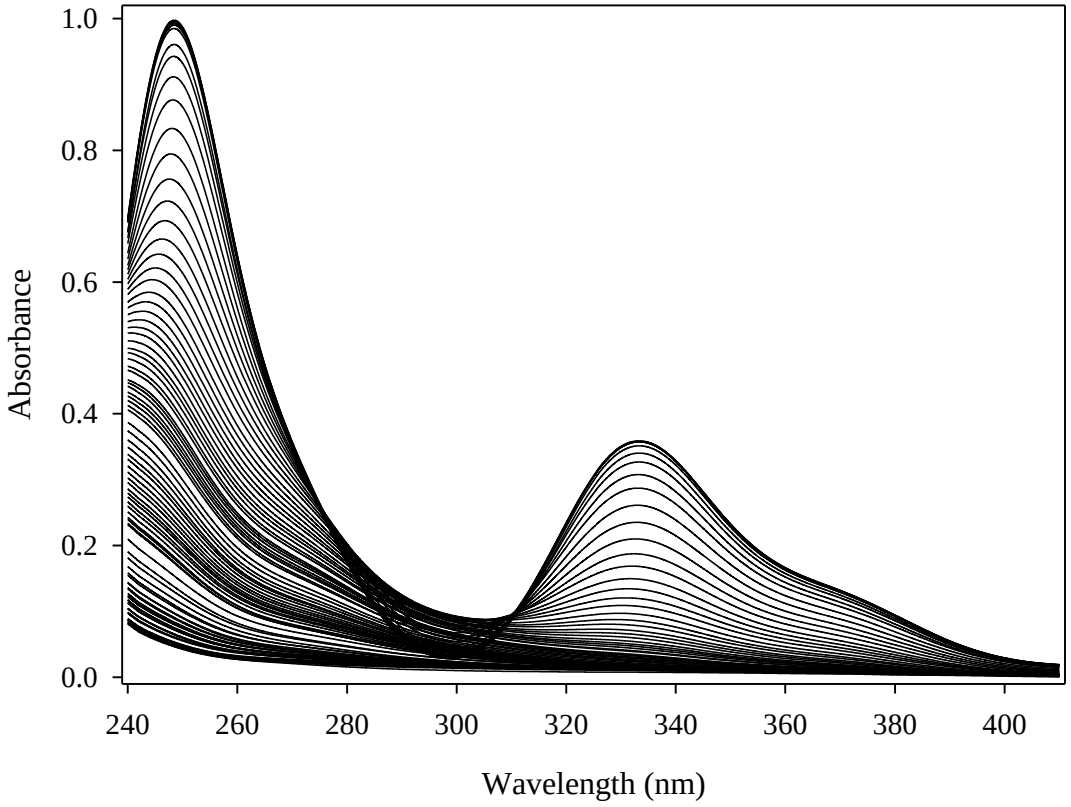

Figure 25: Change in absorption spectra with change in pH for $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), ionic strength 1.0 M and 25 °C.

Similar to the chloro-hydroxo investigation, the excellent agreement between the calculated and observed absorbances at these two wavelengths, together with the small sigma value after successful refinement confirms the legitimacy of the proposed formation constants. All possible tools within HypSpec [29] was used to ensure the legitimacy of the proposed model. The built-in factor analysis tool in HypSpec [29], for calculating the number of coloured species, confirmed the presence of five coloured species. The absorbance measurements below

240 nm were excluded from the calculations due to the high absorbance of bromide and hydroxide in this region. The titration was repeated three times under the same conditions and the values of the cumulative formation constants for the complexes $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) are shown in Table 14 for the three individual titrations.

Table 14: Formation constants for $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) at 1.0 M ionic strength and 25 ºC

n	log $*\beta_n$ (Titration 1)	log $*\beta_n$ (Titration 2)	log $*\beta_n$ (Titration 3)	log $*\beta_n$ (Average)	log β_n (pK_w = 13.745)
0	-	-	-	-	14.55± 0.01 [9]
1	5.01 ± 0.01	4.92 ± 0.01	5.01 ± 0.01	4.99 ± 0.05	18.73 ± 0.05
2	-5.20 ± 0.01	-5.37 ± 0.01	-5.20 ± 0.01	-5.24 ± 0.10	22.35 ± 0.10
3	-15.58 ± 0.02	-15.85 ± 0.02	-15.58 ± 0.02	-15.66 ± 0.16	25.58 ± 0.16
4	-26.39 ± 0.03	-26.76 ± 0.03	-26.37 ± 0.04	-26.51 ± 0.22	28.47 ± 0.22
σ	2.46×10^{-3}	2.46×10^{-3}	2.48×10^{-3}	2.47×10^{-3}	2.47×10^{-3}

This is, to date, the only available set of formation constants for $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4). The calculated molar absorbance spectra for the mixed palladium(II) bromo-hydroxo complexes are presented in Figure 26.

When the individual log β values of the palladium(II) chloro-hydroxo and the palladium(II) bromo-hydroxo are compared, it is evident that the log β values of the bromide system are slightly smaller than those of the chloride system. Bromide is a slightly stronger ligand than chloride [9] and as a result it will be more difficult for hydroxide to displace the bromide ion bonded in the palladium(II) complex. This is also the reason why most of the mixed palladium(II) bromo-hydroxo species only exist at higher pH values compared to that of the mixed palladium(II) chloro-hydroxo complexes.

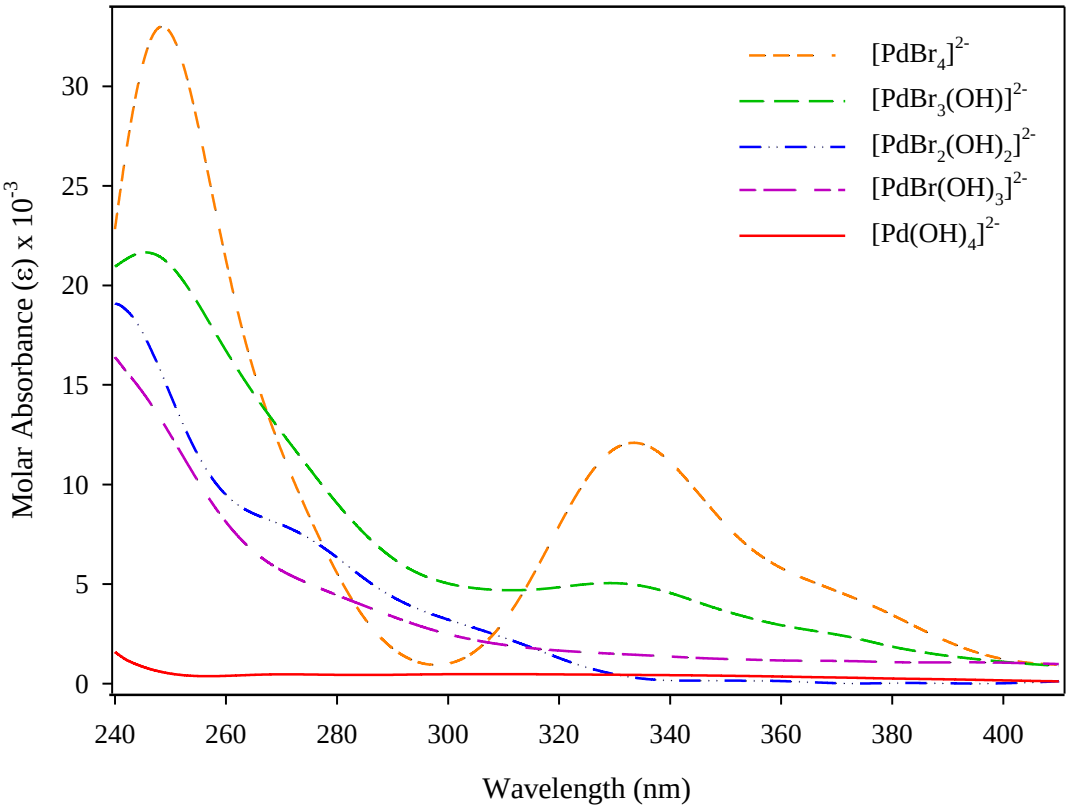

Figure 26: Calculated molar absorption spectra of $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4)

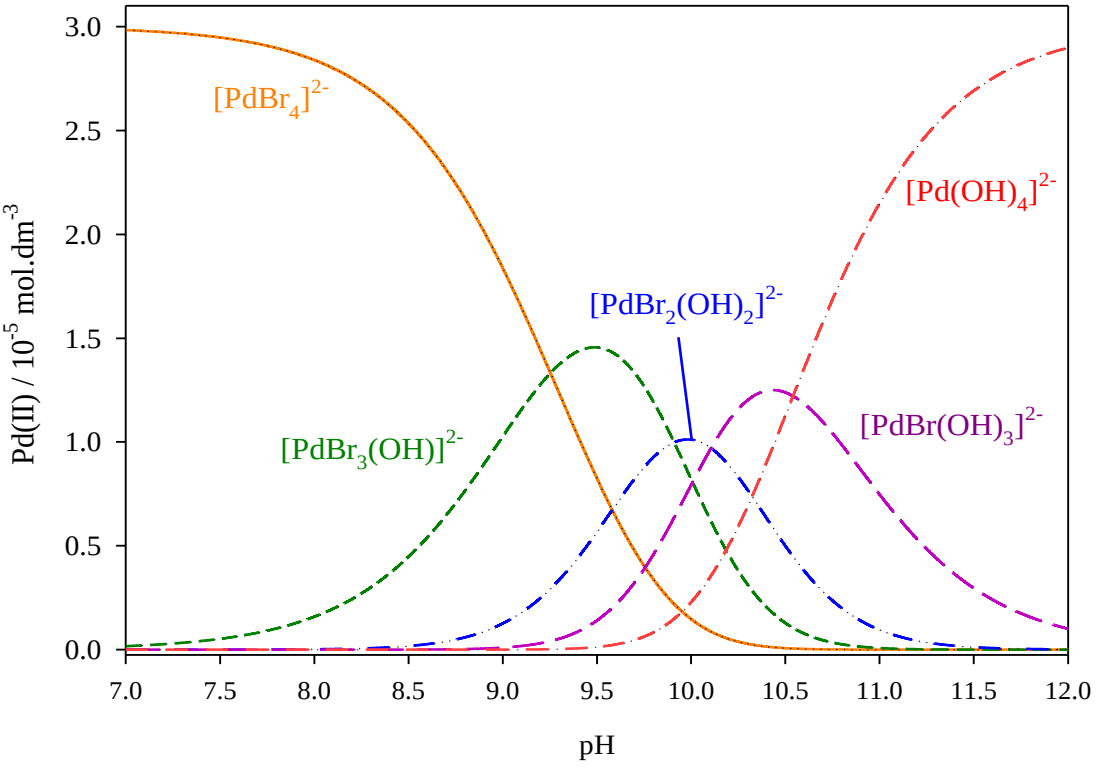

Figure 27: Distribution of $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) species as a function of pH at 25 °C. $[Pd^{2+}] = 3 \times 10^{-5}$ M, $[Br^-] = 0.482$ M, ionic strength 1.0 M

From the formation constants, a distribution diagram was constructed showing the complete speciation of the $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) system as a function of concentration palladium(II) (Figure 27). From the distribution diagram, it is evident that $[PdBr_3(OH)]^{2-}$ is the dominant mixed palladium(II) bromo-hydroxo complex, similar to that of the palladium(II) chloro-hydroxo speciation.

A Pourbaix diagram was also constructed for the Pd-Br-H_2O system (Figure 28) employing the newly determined stability constants. Previously, no speciation data existed for the mixed palladium(II) bromo-hydroxo complexes [10], however, with the introduction of the newly obtained stability constants one is now able to construct a more complete Pourbaix diagram including all of the mixed complexes. When the Pourbaix diagram of the palladium(II) bromo-hydroxo system is compared to that of the palladium(II) chloro-hydroxo system it is evident that $[PdBr_3(OH)]^{2-}$ has a smaller region of stability, while the mono bromide mixed complex, $[PdBr(OH)_3]^{2-}$ is more stable at higher pH values.

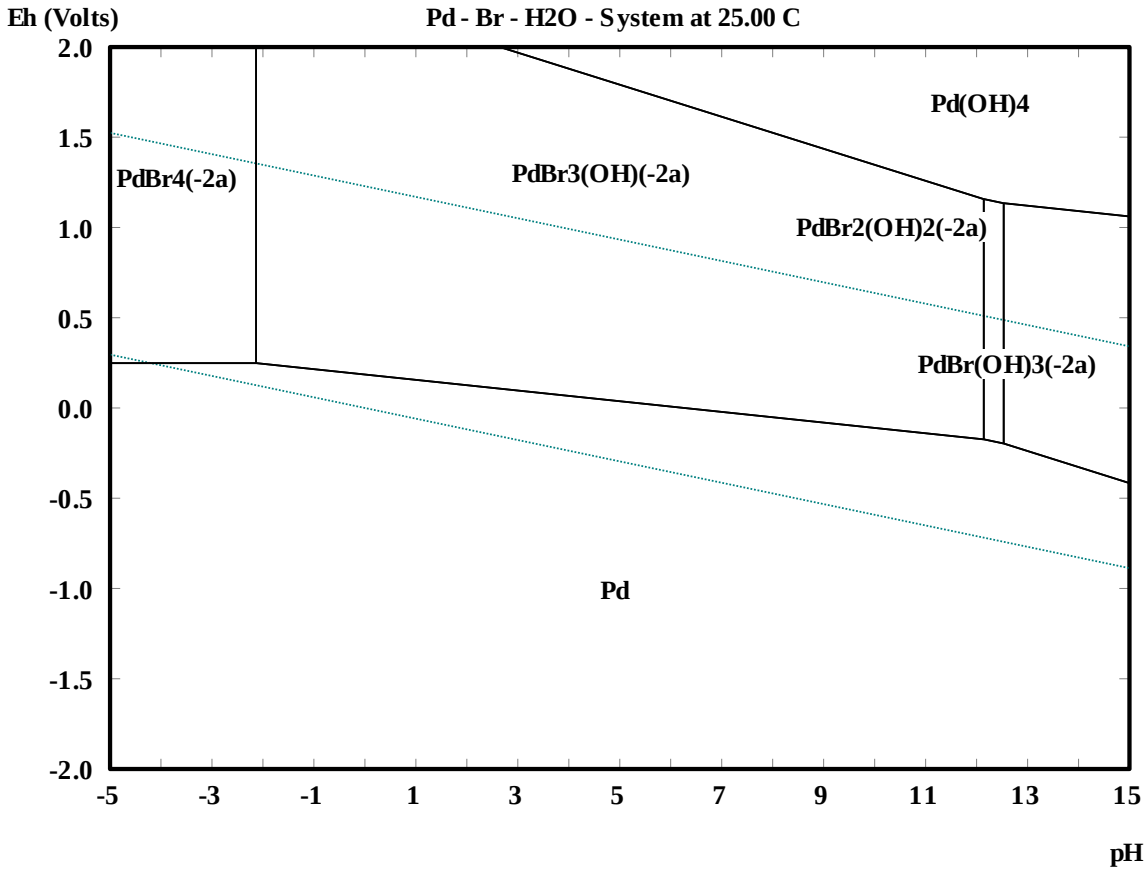

Figure 28: E_h-pH diagram for the Pd-Br-H_2O system, ($[Pd^{2+}]$ = 1mmol/kg H_2O; $[Br^-]$ = 10 mol/kg H_2O), constructed employing new stability constants listed in Table 14 and reference [9]

5.5 Conclusions

As mentioned previously, hydrometallurgical processing of PGMs require exact knowledge of the speciation of the specific metals involved. In a previous study values for the overall stability constants of the palladium(II)-chloride system, i.e. $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4), have been determined spectrophotometrically at an ionic strength of 1.0 M and a temperature of 25 °C [9].

The same experimental method was customised and employed to accurately determine the overall stability constants of the mixed palladium(II) chloro-hydroxo system, i.e. $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), of which limited data are available in literature. The average values determined for the stability constants, β_n, $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), are: log β_1 = 18.36, log β_2 = 23.21, log β_3 = 26.91 and log β_4 = 29.68. These values differ somewhat from those published by Cruywagen and Kriek [16], but provides a refined model for the mixed palladium(II) chloro-hydroxo complexes. After the titration method was successfully applied to the palladium(II) chloro-hydroxo system, it was customised and applied to the palladium(II) bromo-hydroxo system, $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4). These stability constants are: log β_1 = 18.73, log β_2 = 22.25, log β_3 = 25.58 and log β_4 = 28.47, which represent the first known full set of stability constants for this system. Our automated titration method, that allows for an increased number of data points, together with the customised calculation software, provided us with repeatable results and without a doubt increased the legitimacy and accuracy of the calculated stability constants; in the first instance for the known mixed palladium(II) chloro-hydroxo system, and as a consequence for the palladium(II) bromo-hydroxo system as well.

Chloride is already used as a complexing agent for the leaching of the PGMs, and the refined stability constants for $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) provides a more precise model of this system. Should bromide be investigated as complexing agent for the leaching of the PGMs, a precise model for the $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) system as well as the associated E_h-pH diagram is now available.

5.6 Acknowledgements

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CHAPTER 6
AUTOMATED SPECIATION METHOD

In this study, two very different apparatus were programmed to work together to serve as an effective automated speciation setup. This chapter will give all the relevant information in detail about the various techniques used to generate all the stability constants, how these techniques were developed and how they were customised and automated to work for all of the different systems. It will also provide the necessary information on the software packages, including all the settings specific to each speciation study, that were used.

6.1 Techniques Development

As discussed in Chapter 2, various batch experimental techniques was used to determine the stability constants of the palladium(II) complexes. In order to pursue a more accurate approach for this study, two specialized analytical apparatus were combined. These apparatuses

included, a Metrohm 809.1 double burette auto-titrator and an Analytic Jena SPECORD® S600 UV-Vis diode-array spectrophotometer equipped with a quartz flow-through cuvette.

The Metrohm 809.1 double burette auto-titrator can accurately add volumes as small as 0.002 ml and has the option of connecting a large range of intelligent electrodes. For pH measurements, the Metrohm Solitrode Pt 1000 electrode (6.0228.000) was used and was calibrated with standard pH buffers from Metrohm before each titration. The pH buffers 4, 7 and 9 were used, and the pH electrode was dispersed in each buffer for 30 seconds before the buffer was measured. Before each calibration, and after each titration, the electrode was cleaned by stirring it in deionized water for 15 minutes. In all of the calibrations, the calibration slope was more or equal to 99.6%. For the mixed halide hydroxide complexes, the concentration of the free hydroxide (OH^-) is calculated from the pH measurements.

The Analytic Jena SPECORD® S600 was used to generate the UV spectra of the different complexes. The polychromator systems are designed to work without any movable components and have high-precision optics which consist of an aberration-corrected grating, a mechanical slit and a diode array detector. All of these components are concealed in a rugged quartz-ceramic body which is insensitive to external influences. It has the ability to take a measurement within 12 milliseconds from a spectral range of UV to NIR.

The combination was done via a software program, Auto Mouse Clicker (with a built-in timer), to work as a dedicated speciation apparatus. A jacketed reaction flask was used as a reaction vessel and was thermostatically controlled at a fixed temperature of 25 °C employing a Julabo F12-ED refrigerated/heating circulator. It was now possible to automatically vary the ligand concentration over various intervals ensuring a very accurate and consistent set of absorbance data. A detailed schematic of the system is presented in Figure 29.

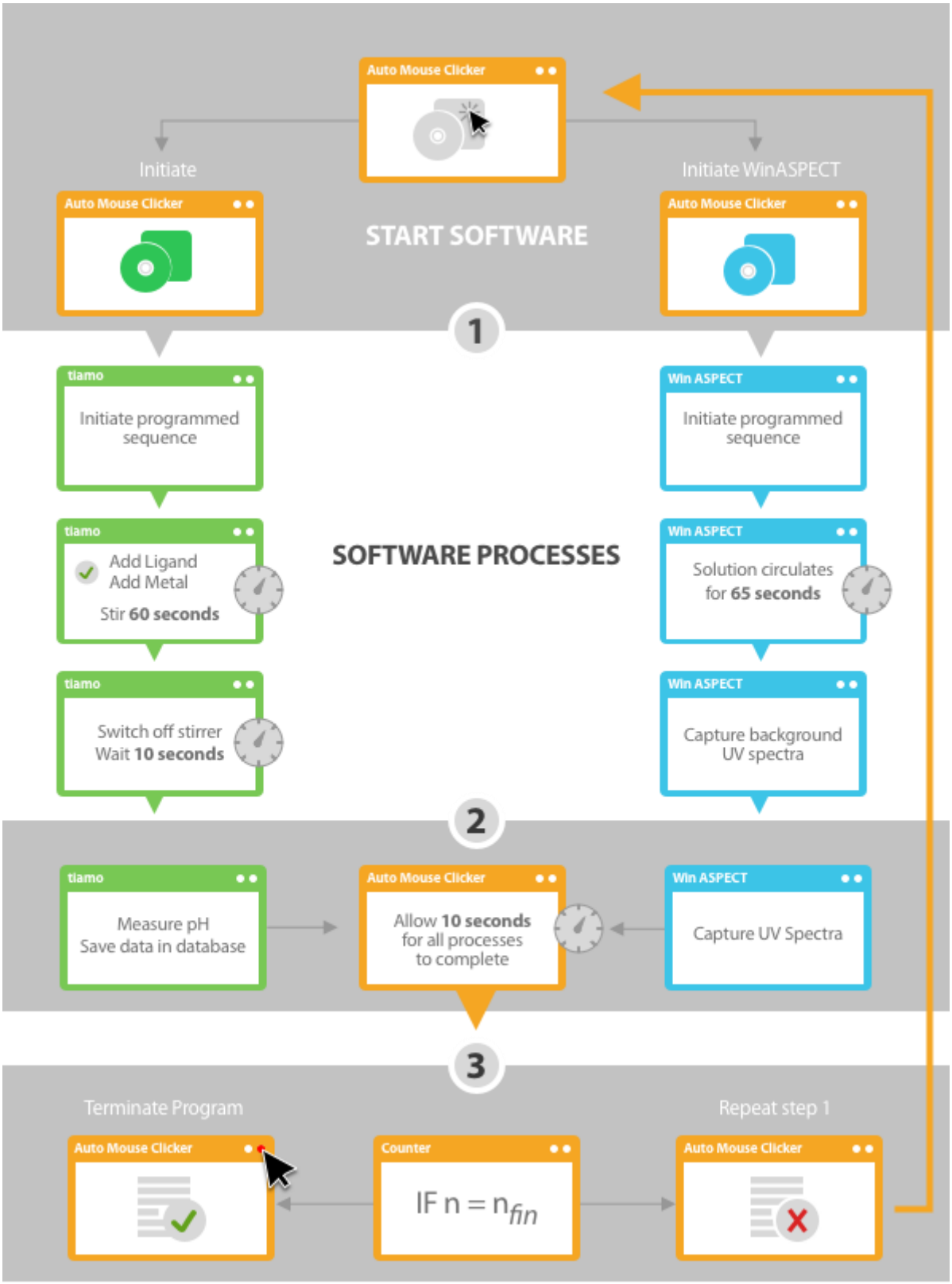

Figure 29: Detailed schematic of the fully automated experimental procedure

The experimental procedure can be divided into three parts. Section 1 is the software process which controls both the tiamo® software and the WinASPECT® software via the Auto Mouse Clicker software program. Once initiated, the tiamo® software will start the Metrohm 809.1 double burette auto-titrator which is responsible for the addition (dosing) of the metal/ligand solutions, magnetic stirrer and the pH measurements. Shortly after this process is started the WinASPECT® software, which controls the Analytic Jena SPECORD® S600 UV-Vis diode-array spectrophotometer, was initiated.

A short time interval of 5 seconds is set within the Auto Mouse Clicker program to ensure an adequate mixture of the solution inside the jacketed reaction flask before the WinASPECT® software is activated. The Analytic Jena SPECORD® S600 has a peristaltic pumping system (sipper) which circulates the solution from the reaction flask through the quartz flow-through cuvette. The time interval for the sipper system are controlled inside the WinASPECT® software and will execute before each UV measurement. The temperature of the reaction flask is controlled by setting a fixed temperature value on the Julabo F12-ED refrigerated/heating circulator. The time intervals within all three software programs are set to ensure effective mixing in the reaction flask and circulation of the solution through the flow-through cuvette. It also allows for the solution inside the reaction flask to settle for 10 seconds before the pH is measured.

In Section 2, both pH and UV measurement takes place simultaneously. In order to ensure that all processes are completed, a waiting period of 10 seconds is used. A predetermined amount of automatic repetitions is programmed at the start of the experiment. As shown in section 3, the method will repeat until the predetermined amount of repetitions is reached whereby the method will then automatically terminate. All of the analytical apparatuses were calibrated and optimised for each speciation investigation. The most relevant settings are shown in a number of screenshots to give a detailed explanation of how the data was generated. These settings and information are essential for the duplication and improvement of the presented absorbance data.

In Figure 30 the layout of the three software programs are shown, i.e. Auto Mouse Clicker (A), tiamo® (B) and WinASPECT® (C). For the particular example shown in Figure 30, there are four mouse events programmed (A), each with its (own) time interval. Both the tiamo® (B) and WinAspect® (C) are controlled by selecting the on-screen coordinates of their respective

start buttons. The layout of the screen should be the same for the whole experiment to ensure that the correct buttons were activated as required.

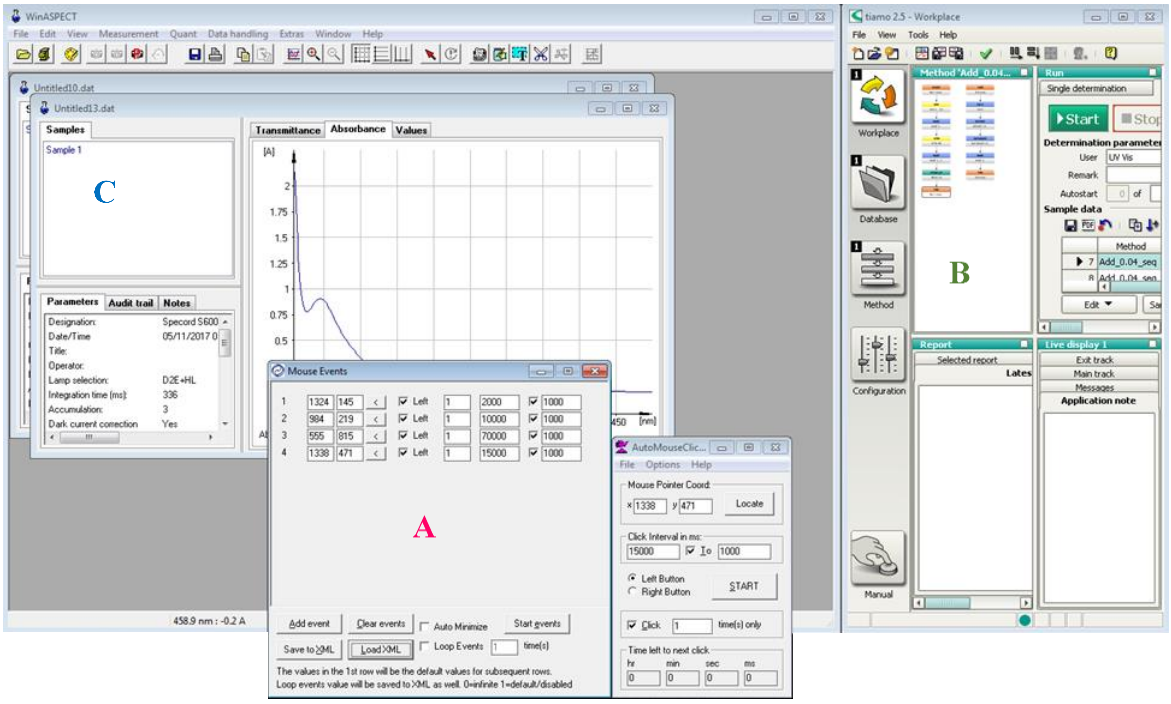

Figure 30: Screenshot of the software programs layout on the PC screen

All three the software packages have built-in timers and were programmed to ensure that the required sequence of events was followed. At the end of each experimental run, the number of data points of both programmes must be the same. If this is not the case, the method should be scanned for errors. The tiamo® software has a built-in database with a date stamp for each entry. By comparing the data in the database to the spectra generated in WinASPECT®, one can determine if the data collected was correct and if each spectrum linked to each dosing and pH step.

The spectrophotometric data together with the pH data are combined in a text file and imported into a software program HypSpec, which is specially developed to calculate formation constants from spectrophotometric data. More detail on how the software works will be discussed later in this chapter. Within the WinASPECT® software there are endless options and settings to adjust as needed. The most important settings are shown in Figure 31. Depending on the makeup of the solution used, the integration time (the time the shutter is open) can be set manually or automatically within the software. By using the *Monitor* mode (Figure32), you can automatically search for the integration time for the given wavelength

region. One can also set the number of repetitions of each measurement (accumulation). The measured values of the selected spectral regions are averaged from the total number of individual measurements and the obtained result displayed. The accumulation of individual measurements serves to improve the signal-to-noise ratio.

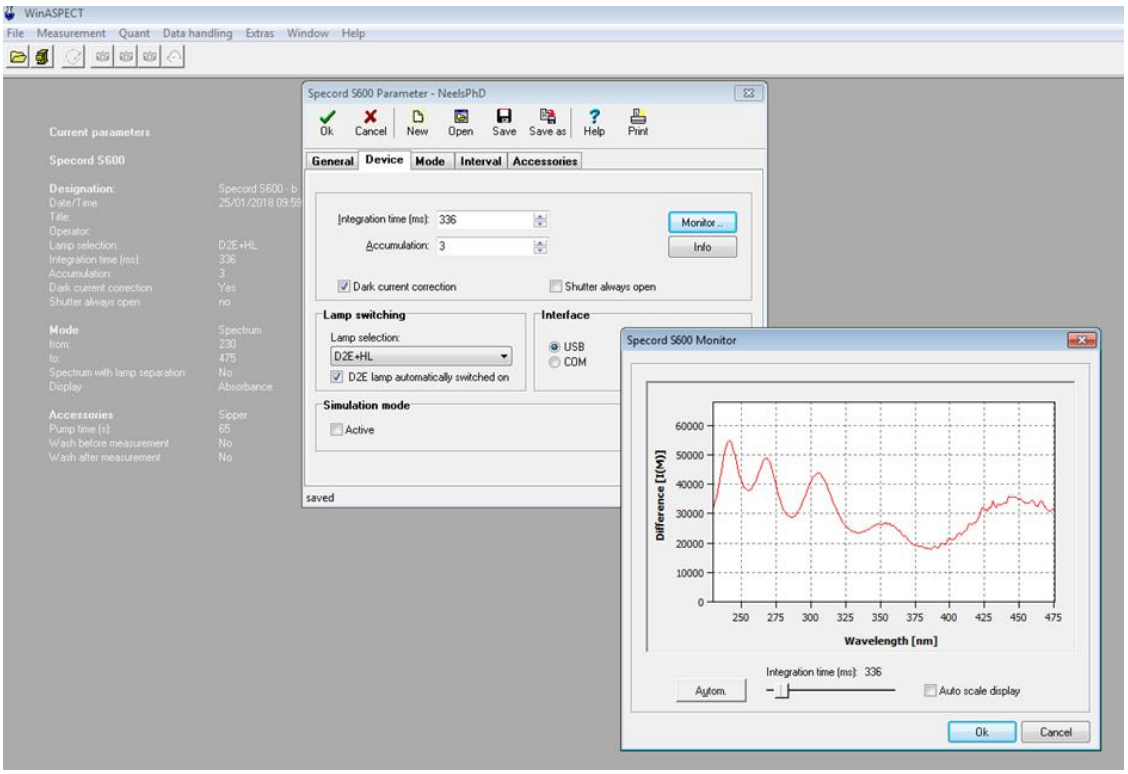

Figure 31: Settings within the WinASPECT software

A typical programmed sequence (method) for the Metrohm 809.1 double burette auto-titrator is shown in Figure 32. This method can be adjusted as required, depending on the experimental needs.

As previously mentioned, the tiamo® software controls the Metrohm 809.1 double burette auto-titrator which controls the ligand/metal dosing sequences as well as pH measurements. The software has a number of built-in commands, and for our methods, the most common commands that were used included ADD, WAIT, STIR, MEAS pH, CALC, REPORT and DATABASE. Depending on the software used to calculate the formation constants, the values of the pH measurements can either be in pH values or milli Volts.

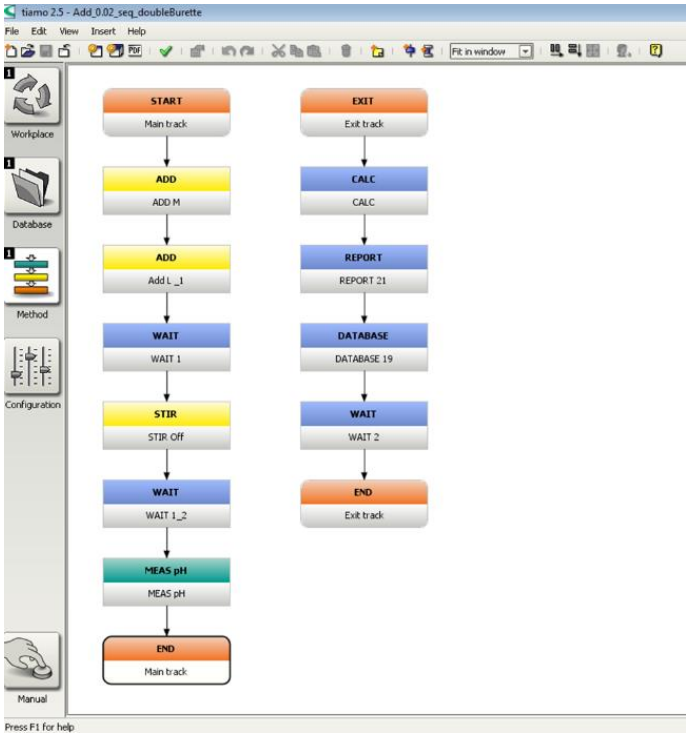

Figure 32: Typical programmed sequence for the Metrohm 809.1 double burette auto-titrator

Depending on the concentration changes required, a single dosing procedure can be repeated or if there is more than one dosing instruction the *Determination Series* option can be used as illustrated in Figure 33.

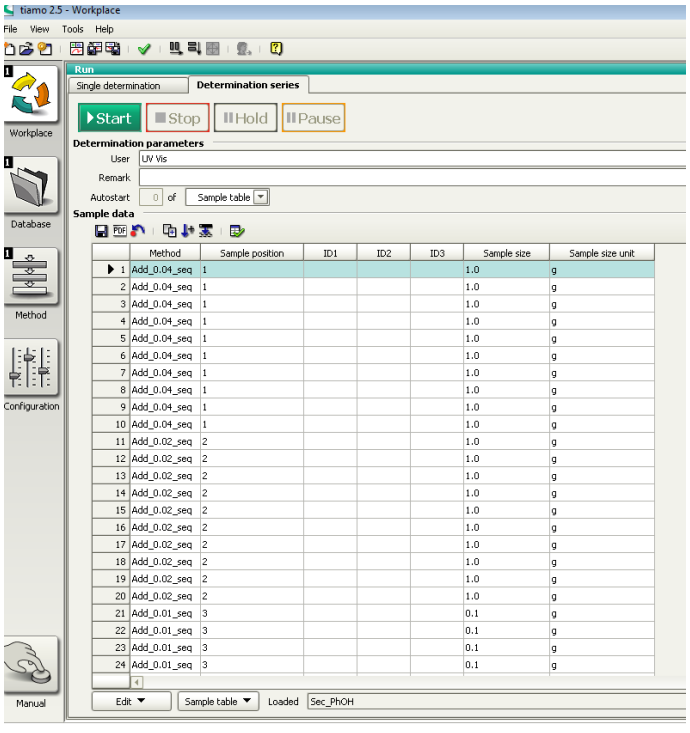

Figure 33: Determination series option for varying dosing options

This option is used when an auto-sample system is attached to the Metrohm 809.1. Each line in the sample table can have a different method which can be repeated any amount of times. In this example, three different volumes were added, i.e. 0.04 ml, 0.02 ml and 0.01 ml. Thus, by using this option, various dosage amounts can be programmed to control both the metal and ligand concentrations accurately.

The advantage of this option, when more than one dosing volume is required, is the way it is written in the database as illustrated in Figure 34. For each line, the relevant data is displayed in a column format which can easily be copied to Microsoft Excel (or similar program) for the data to be analysed and processed as required. It is important to make sure that the values that must be written to the database are specified and that the correct calculation method (CALC) is used. It is also possible to have more than one calculation command in one method resulting in various output formats from a single measurement.

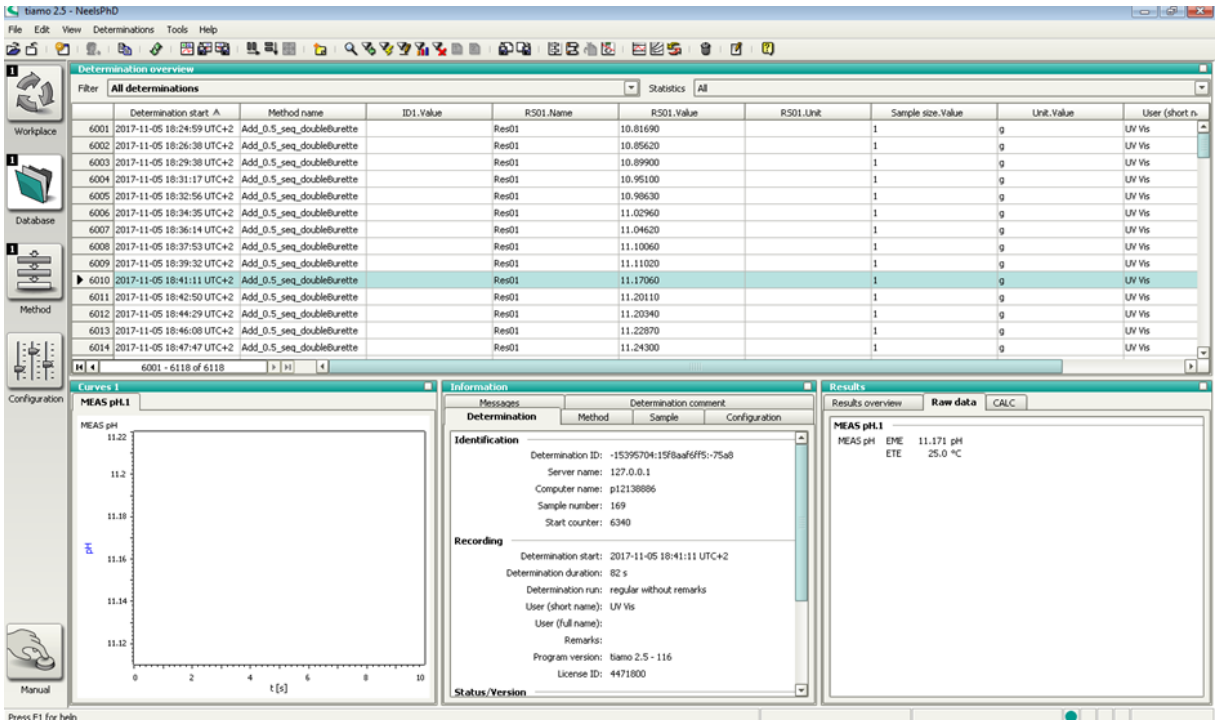

Figure 34: Screenshot of the tiamo® database

6.2 Hyperquad software: HypSpec and HySS

The two software packages that were used to assist with the titration setup and calculation of the formation constants and related graphs were Hyperquad Simulation and Speciation (HySS) and HypSpec, both part of the Hyperquad suit [1, 2]. HySS software was used to determine the ideal titration conditions for a specific model having been specified by defining a set of equilibrium constants calculated with equation 1.

$$\beta_{pq}.. = [M_pL_q.] / ([M]^p[[L]^q..) \quad (18)$$

The titration was simulated by specifying a set of titration conditions and calculating the concentrations of each complex species as the titration proceeded. The optimised titration conditions obtained were then used to calculate the ideal concentrations for the different solutions. The stability constants and molar absorbance spectra were calculated from the spectrophotometric data by employing HypSpec which is specifically designed to derive equilibrium constants from spectrophotometric data. A live screenshot of the program's main window is shown in Figure 35.

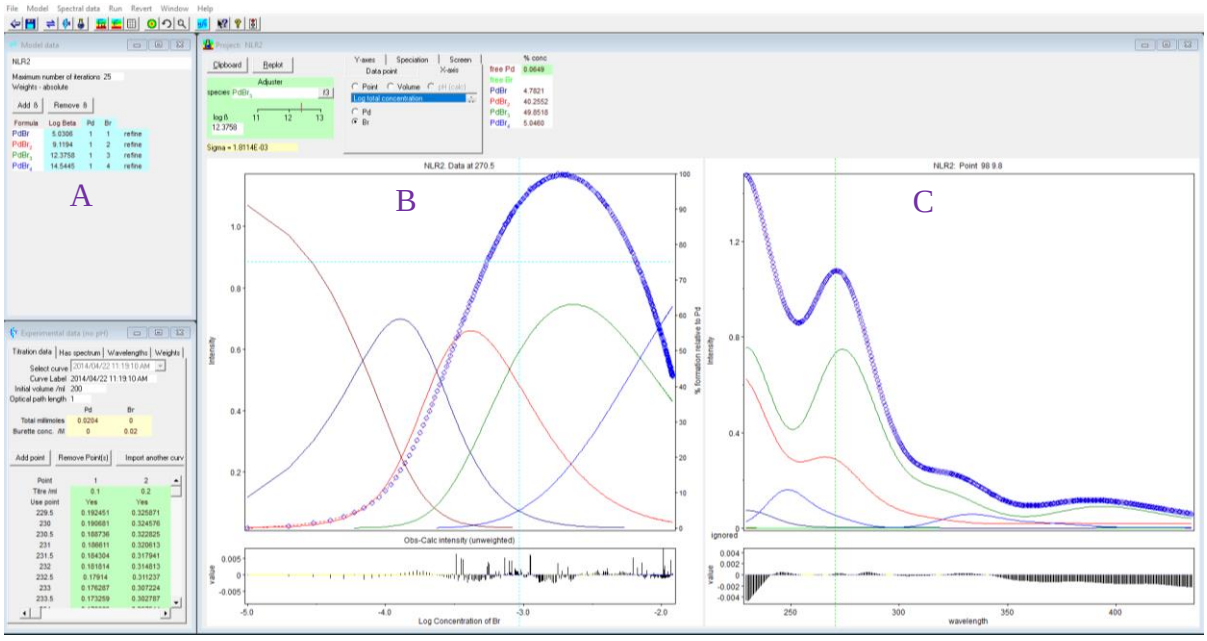

Figure 35: Screenshot of the HypSpec program workspace sheet

On the top left side (A) the possible formation constants are provided for each specie. A live output of the speciation calculated from the specified formation constants is displayed in the

Obs-Calc intensity window (B). The dotted blue and red lines are an indication of the quality of the data. When there is little to no difference between these two lines, the data quality/accuracy is good. The window on the right-hand side (C) shows the makeup of the observed UV spectra. The observed UV spectra (blue and red line) is the sum of the individual species as observed in window C.

The stability constants are calculated by a non-linear refinement process in which stability constant values are optimized. During the refinement, three constraints are applied. The equations of mass-balance are always satisfied, the molar absorbance values are obtained by linear least-squares fitting of the absorbance values according to the Beer-lambert law: $A = l \Sigma \varepsilon c$, where c is a species concentration and the stability constants must have positive values.

In equation 19 a measure of the overall quality of data refinement is indicated by the sigma (σ) value, derived from the squared residual r, where *m* is the number of data points, *n* the number of parameters, and *w* the weight as part of a least squared calculation. The weighting scheme accounts for the error in absorbance measurements and is specific to each spectrophotometer.

$$\sigma = \sqrt{\frac{\sum_i w_i r_i^2}{m-n}} \tag{19}$$

With a correct weighting scheme, the value of the scaled sum of squares (σ) has an expected value of unity. Due to the high accuracy of the Analytic Jena SPECORD® S600 UV-Vis diode-array spectrophotometer, an absolute weighting scheme with a linear weighting function (chosen within HypSpec) was employed as part of this study. A refinement is considered accurate if the calculated values agree with the observations within the limits of experimental error.

As mentioned previously, palladium(II) halide hydroxo complexes were investigated. In HypSpec, a special convention is used for the hydroxide ion. Due to the self-ionization equilibrium ($H^+ + OH^- \rightleftharpoons H_2O$), the hydroxide ion is regarded as a species rather than as a reagent.

Therefore, for a general metal complex $[ML_n(OH)_{4-n}]$, where *M* is the metal, *L* the ligand and *n* the number of bonded ligands, the following expression can be written:

$$[ML_n(OH)_{4-n}] = \beta_{n,4-n}[M][L]^n[OH]^{4-n} \quad (20)$$

$$\text{Since } [H^+][OH^-] = K_w,$$

$$\text{and } [OH] = K_w[H]^{-1}$$

$$[ML_n(OH)_{4-n}] = \beta_{n,4-n}[M][L]^n K_w^{4-n}[H]^{n-4} \quad (21)$$

$$= \beta_{n,4-n} K_w^{4-n} [M][L]^n [H]^{n-4}$$

$$= {}^*\beta_{n,4-n}[M][L]^n[H]^{n-4} \quad (22)$$

The concentration of the hydroxide ion is now related to the concentration of the reagent H^+. Because of this convention, the formation constants of the hydrolysed species will appear to be on a different scale which are reported in the literature as log $*\beta$. For the two systems presented in this paper the relationship between log β (normally reported in the literature) and log $*\beta$ can be expressed as:

$$\log {}^*\beta_{n,\,n-4} = \log \beta_{n,4-n} + (4-n) \log K_w \quad (23)$$

6.3 Solution preparation

A single palladium(II) stock solution of 3.0×10^{-3} M was prepared by dissolving palladium sponge in a mixture of concentrated perchloric acid ($HClO_4$) and fuming nitric acid (HNO_3). The nitric acid was driven-off by careful heating, and the procedure was repeated until all the palladium was dissolved with the palladium subsequently being oxidized to palladium(II). The concentration of the palladium(II) was confirmed by ICP analysis and diluted as required. The total ionic strength of all the solutions used was fixed at 1.0 M. Sodium perchlorate ($NaClO_4$, anhydrous) and perchloric acid ($HClO_4$) were used to adjust the ionic strength and acid concentration as required.

6.4 Experimental method for palladium(II) thiocyanate speciation

The first system that was investigated was that of palladium(II) thiocyanate. The only stability constants that were available were that of log β_2 and log β_4. The continuous variation method and a rather complex competition reaction were used to determine these values[3, 4]. After completing a few trail titrations, we found that the precipitation of $[Pd(SCN)_2(H_2O)_2]$ (K_{sp} = -17.8) occurs after ten minutes. However, HypSpec requires all species to be in solution to successfully calculate the applicable formation constants.

Therefore, in an attempt to overcome the precipitation of $[Pd(SCN)_2(H_2O)_2]$, the Analytic Jena SPECORD® S600 was modified to accommodate an in-house built flow-through cell with a pathlength of 10 cm, which would enable us to work at very low concentrations to try and eliminate precipitation. The concentration of the palladium(II) was diluted to concentrations as low as 3.0×10^{-8} M to avoid any precipitation. Although no precipitation was noticed when various fractions of the palladium(II) thiocyanate was prepared in individual flasks, this option also proved to be unsuccessful. Early precipitation was initiated as a result of stirring and pumping because the reaction vessel was coupled to a 'sipper system', which pumped the solution by means of a small peristaltic pump through a flow-through cuvette. The only way to overcome the precipitation of $[Pd(SCN)_2(H_2O)_2]$ was by employing a batch titration method.

A batch titration was done with the Metrohm 809.1 double burette auto-titrator. With the auto-titrator, 69 individual solutions were prepared containing 20mL 8.0×10^{-5} M palladium solution and different volumes of the thiocyanate solution. Once a solution was prepared, the spectra was taken as soon as possible to avoid any precipitation. This makeup of various solutions was done one by one for each of the 69 prepared solutions.

The thiocyanate concentration was varied from 4.95×10^{-6} to 2.80×10^{-4} M and the palladium concentration varying from 7.92×10^{-5} to 3.52×10^{-5} M as a result of dilution. Equilibrium was reached instantaneously as no further change in the spectra of the solutions were observed over time, and the precipitation of $[Pd(SCN)_2(H_2O)_2]$ only occurred after a few minutes. The (end) result of this method is the same as a normal titration and within HypSpec the absorption data is handled the same way as with a normal titration.

6.5 Experimental method for palladium(II) chloride –and bromide speciation

Various authors have presented values for formation constants for the complexation of palladium(II) with chloride by employing a batch type experimental procedure whereby individual samples were prepared [5-8]. However, because all of the complexes were in solution at the required conditions, the automated titration method could effortlessly be applied to this system. This titration method resulted in a more detailed and accurate experimental method that could produce and employ substantially more usable concentration variations within the desired ligand concentration range. A fixed amount of palladium(II) solution was added to a 550 ml jacketed reaction flask. NaCl was dispensed from the auto-titrator burette over various intervals to ensure a constant change in the absorbance data. The pH was constant at less than 3, ensuring an acidity environment. This revised technique was first applied to the familiar palladium(II)-chloride system to validate the technique against the published formation constants. Subsequently, this method was adjusted to accurately determine the various palladium(II)-bromide stability constants. The reaction parameters for both systems are summarised in Table 15 and Table 16 below:

Table 15: Summary of reaction parameters for $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4)

	palladium(II) chloride system
Description	**Experimental values**
Concentration Pd(II) (M)	1.02×10^{-4}
Burette concentration of Cl^- (M)	2.0×10^{-2}
Change in concentration of Pd(II) (M)	$1.05 \times 10^{-4} \rightarrow 6.30 \times 10^{-5}$
Change in concentration of Cl^- (M)	$6.66 \times 10^{-5} \rightarrow 8.00 \times 10^{-2}$
pH	Constant ≤ 3
Ionic strength (M)	1.0
Starting volume Pd(II) in reaction vessel	200 ml
Titration sequence (added volume variations)	25 x 0.1 ml 25 x 0.5 ml 25 x 1.0 ml 25 x 2.0 ml 10 x 3.0 ml 10 x 4.0 ml 8 x 5.0 ml

The slight change in the concentration of palladium(II) due to dilution is accounted for within HypSpec. In both systems the ionic strength and pH were kept constant, and only the ligand (Cl^- and Br^-) was added in a series of volume steps as shown in Table 15 and Table 16.

Table 16: Summary of reaction parameters for $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4)

	palladium(II) bromide system
Description	**Experimental values**
Concentration Pd(II) (M)	1.05×10^{-4}
Burette concentration of Br^- (M)	2.0×10^{-2}
Change in concentration of Pd(II) (M)	$1.020 \times 10^{-4} \rightarrow 4.06 \times 10^{-5}$
Change in concentration of Br^- (M)	$9.995 \times 10^{-6} \rightarrow 1.204 \times 10^{-2}$
pH	Constant ≤ 3
Ionic strength (M)	1.0
Starting volume Pd(II) in reaction vessel	300 ml
Titration sequence (added volume variations)	100 x 0.1 ml 25 x 0.2 ml 25 x 0.5 ml 25 x 1.0 ml 125 x 2.0 ml

For the palladium(II) bromide system a total of 305 different concentration variations were needed to obtain a successful refinement within HypSpec.

6.6 Experimental method for mixed palladium(II) chloro -and bromo-hydroxo speciation

From the previous investigation it was evident that the titration method for the pure complexes worked well with the HypSpec software. Therefore, it was modified and also applied to the mixed palladium(II) chloro hydroxo – and bromo hydroxo systems. In the previous methods the pH were kept constant, but for the investigation of the palladium(II) halide, the concentration was kept constant, and the pH was varied by adding NaOH. The concentration of the palladium(II) halide inside the reaction flask has to be half of that in the burette, but the ionic strength should always be constant at 1.0 M. Therefore, the palladium(II) halide solution inside the burette was diluted to exactly half of that of the burette concentration in the reaction flask at the beginning of the titration by adding a buffer $NaClO_4$ solution ensuring a constant ionic strength of 1.0 M. For both chloride and bromide investigations a 0.6 M sodium

hydroxide solution, having an ionic strength of 1 M (by adding $NaClO_4$), together with a 6.0 x 10^{-5} M palladium(II) halide in 0.02 M $HClO_4$ were used to vary the pH.

To ensure that the concentration of palladium(II) and halide was always constant, equal amounts of the palladium(II) halide and sodium hydroxide solutions were dispensed from the double burette auto-titrator. At the start of the titration, larger amounts of the two solutions were added until a change in the absorbance spectra was noticed. A summary of the reaction parameters of both systems is shown in Table 17 and Table 18. For both systems, the palladium(II) and halide concentration were kept constant. For the palladium(II) chloro-hydroxo system the pH range of interest is different to that of the palladium(II) bromo-hydroxo system, making it difficult to obtain more UV spectra in that region due to the neutralisation of $HClO_4$ by NaOH.

Table 17: Summary of reaction parameters for $[PdCl_n(OH)_{4-n}]^{2-}$ (n = 0 – 4)

	palladium(II) chloro-hydroxo system
Description	**Experimental values**
Burette concentration Pd(II) (M)	6.00 x 10^{-5}
Burette concentration of Cl^- (M)	9.64 x 10^{-1}
Concentration Pd(II) (M)	Constant at 3.00 x 10^{-5}
Concentration of Cl^- (M)	Constant at 4.82 x 10^{-1}
pH	4.0 to 13
Ionic strength (M)	1.0
Titration sequence (added volume variations)	60 x 0.04 ml 10 x 0.2 ml 10 x 2.0 ml

Similar to the palladium(II) bromo system, more data points were required to calculate a reliable model.

Table 18: Summary of reaction parameters for $[PdBr_n(OH)_{4-n}]^{2-}$ (n = 0 – 4)

	palladium(II) bromo-hydroxo system
Description	**Experimental values**
Burette concentration Pd(II) (M)	6.00×10^{-5}
Burette concentration of Br^- (M)	9.64×10^{-1}
Concentration Pd(II) (M)	Constant at 3.00×10^{-5}
Concentration of Br^- (M)	Constant at 4.82×10^{-1}
pH	8.7 to 11.6
Ionic strength (M)	1.0
Titration sequence (added volume variations)	40 x 0.04 ml 20 x 0.1 ml 20 x 0.5 ml 10 x 2.0 ml

6.7 Conclusion

The combination of the various analytical hardware and software resulted in an automated speciation experimental procedure which could generate a large amount of speciation data. Not only was the generated data accurate, but it was also repeatable. This method is not only dedicated for the complexes discussed in this study but can be applied to any speciation investigation.

6.8 References

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CHAPTER 7

CONCLUDING REMARKS

As shown in Chapter 2, the amount of speciation data available for the five speciation systems which were investigated i.e. palladium(II) thiocyanate, palladium(II) chloride, palladium(II) bromide, palladium(II) chloro – hydroxo mixed complexes and palladium(II) bromo – hydroxo mixed complexes is limited. It was further shown that the methods that were used mainly consisted out of batch-type experiments, and in some cases complex competition reactions were used. Due to the experimental methods employed, a limited amount of data points were produced which were used to calculate the corresponding formation constants.

7.1 Conclusions

In this study, a new fully automated speciation titration method was successfully developed and applied. The combination of the Metrohm 809.1 double burette auto-titrator and Analytic Jena SPECORD® S600 UV-Vis diode-array spectrophotometer equipped with a quartz flow-through cuvette, proved to serve as a dedicated speciation apparatus which could be applied to different speciation systems.

The first metal-ligand system that was investigated was that of palladium(II) thiocyanate. The success of the speciation data depended on the prevention of the precipitation of $[Pd(H_2O)(SCN)_2]$. The fully automated speciation method could not be fully employed as the mechanical stirring and pumping accelerated precipitation of $[Pd(H_2O)(SCN)_2]$. The method was modified to obtain valid speciation data, by applying the titration method to generate individual solutions, and to capture the absorption spectrum immediately after proper mixing of each solution to prevente the precipitation of $[Pd(H_2O)(SCN)_2]$. The only model that fits the data involved the formation of five sequential complexes. The formation constants for the one, three and five coordinated complexes are reported in this study for the first time. Furthermore, molecular modelling postulates that the five coordinated $[Pd(SCN)_5]^{3-}$ complex is square pyramidal.

The automated experimental procedure was applied to the better-known palladium(II) chloride system, i.e. $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4), and because all of the palladium(II) chloride complexes was in solution under the experimental conditions, the automated experimental method could be fully employed. The values obtained in this study were in good agreement with values published by both Elding [1] and Cruywagen and Kriek [2] and confirmed the legitimacy of the experimental method. Again, the method was customized and applied to the bromide system, i.e. $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4). However, these values differed from those published by Elding [1] and provided a new model for palladium(II) bromide speciation.

The experimental method was modified and employed to accurately determine the overall formation constants of the mixed palladium(II) chloro-hydroxo system, i.e. $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), for which limited data were available in the literature. The new method not only produced more absorbance spectra over the whole pH-range studied, but also generated more absorbance data at lower wavelengths (220nm - 230nm). The newly determined overall formation constants (β_n) differed (2 – 3 order of magnitude) when compared to the values determined by Cruywagen and Kriek [2]. The main difference was in the first stepwise formation constant (K_1), for the formation of $[PdCl_3(OH)]^{2-}$ out of $[PdCl_4]^{2-}$, as the new automated experimental method allowed for more data points in the pH-value region where $[PdCl_3(OH)]^{2-}$ formed out of $[PdCl_4]^{2-}$. However, the K_1-value was in line with the value determined by Van Middlesworth and Wood [3]. The subsequent stepwise formation constants (K_n), for n = 2 – 4, are in line with earlier work [2].

Finally, the titration method was successfully applied to the palladium(II) bromo-hydroxo system, $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), and the values obtained represented the first known full set of formation constants for this system.

From the experimental data, palladium(II) formed four-coordinated complexes at high ligand concentrations with bromide, chloride and hydroxide that is in line with the literature. There was no evidence that suggested the existence of a five- or six-coordinated complex for the experimental data generated. However, for palladium(II) thiocyanate, the only model that fit the experimental data, implicated the formation of five sequential complexes, which included the five-coordinated complex, $[Pd(SCN)_5]^{3-}$. The thiocyanate (SCN^-) ligand has the ability to bind from either the nitrogen or the sulphide side. The nature of the exact binding mechanism did not form part of the scope of this study, which was aimed at determining the stability constants of various metal complexes.

All of the calculated formation constants mentioned above are summarized in Table 19

Table 19: Summary of calculated stability constants

Complexation of palladium(II) with thiocyanate					
Complex	log β_1	log β_2	log β_3	log β_4	log β_5
$[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ and $[Pd(SCN)_5]^{3-}$	8.14	15.46	21.94	27.42	31.94
n = 1 – 4					
Complexation of palladium(II) with chloride and bromide					
Complex	log β_1	log β_2	log β_3	log β_4	
$[PdCl_n(H_2O)_{4-n}]^{2-n}$	4.49	7.80	10.18	11.54	
$[PdBr_n(H_2O)_{4-n}]^{2-n}$	5.04	9.12	12.38	14.55	
n = 1 – 4					
Palladium(II) chloro-hydroxo and palladium(II) bromo-hydroxo complexes					
Complex	log β_{31}	log β_{22}	log β_{13}	log β_{04}	
$[PdCl_p(OH)_q]^{2-}$	18.36	23.21	26.91	29.68	
$[PdBr_p(OH)_q]^{2-}$	18.73	22.35	25.58	28.47	
p and *q* referring to the number of bromide and hydroxide ions in the complex					

The newly developed automated titration method that allows for an increased number of data points, together with the customised calculation software provided repeatable results. Therefore, as shown in Table 19, the legitimacy and accuracy of the calculated formation constants were increased. The automated experimental method proved to produce accurate, repeatable data and was successfully applied to five different speciation systems. In all of these systems, palladium(II) was used as the metal.

7.2 Recommended future work

The newly developed experimental procedure can furthermore be applied to complexation studies with other PGM metals of interest, providing much-needed speciation data to ultimately improve the recycling processes of PGM's. Furthermore, the exact binding mechanism of thiocyanate in the five-coordinated complex $[Pd(SCN)_5]^{3-}$ can be investigated by an in-depth molecular modelling study and supporting experimental procedures.

7.3 References

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ATTACHMENTS

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Complexation of palladium(II) with thiocyanate – a spectrophotometric investigation

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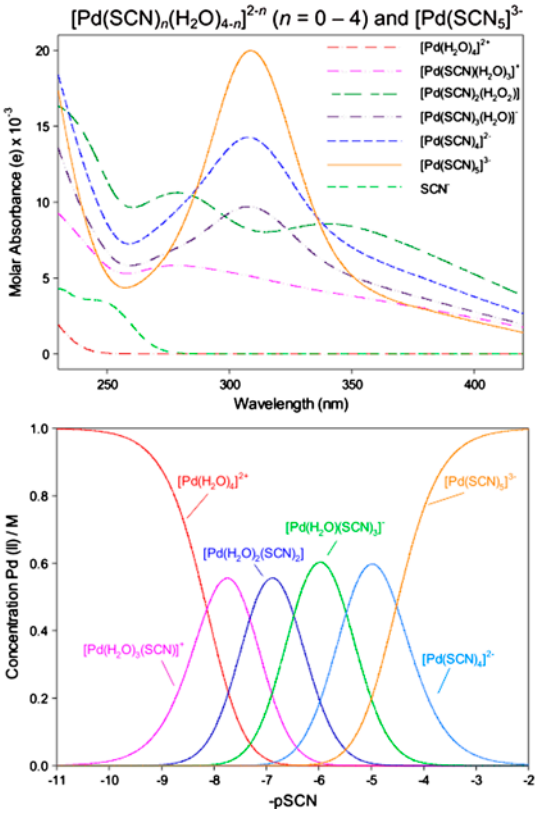

A spectrophotometric investigation into the complexation of palladium(II) with thiocyanate revealed the existence of five coordinated palladium(II) complexes. Molar absorbance spectra as well as formation constants were calculated for all five complexes.

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Complex-formation of Pd(II) with thiocyanate has been investigated by spectrophotometry at 25 °C and an ionic strength of 1.0 M. The formation constants, β_n, for the palladium(II) thiocyanate complexes $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4), have been determined and the values are: $\log\beta_1 = 8.14$, $\log\beta_2 = 15.46$, $\log\beta_3 = 21.94$, and $\log\beta_4 = 27.42$. These complexes are generally accepted to be square planar. However, a five-coordinate species, i.e. $[Pd(SCN_5)]^{3-}$, with a formation constant of $\log\beta_5 = 31.94$ seems to exist and is proposed to be square pyramidal. Molar absorption spectra for all the complexes in question have been obtained.

Keywords: Palladium(II); Thiocyanate; Complexation; Formation constants; Spectrophotometry

1. Introduction

Hydrometallurgical processes play an important role in the processing, refining, and recycling of the platinum group metals and are typically divided into three general areas, leaching, solution purification, and metal recovery. Subsequent to leaching, the leach liquor has to undergo concentration of the metal ions that are to be recovered. As some undesirable metals may have also been taken into solution during the leaching process, the solution is often purified to eliminate these undesirable components. The two most common purification techniques employed are solvent extraction and ion exchange. With solvent extraction, a mixture of an extractant in a diluent is used to extract a metal from one phase to another and with ion exchange chelating agents, natural zeolite, activated carbon, resins, and liquid organics impregnated with chelating agents are all employed to exchange cations or anions within the solution [1–4]. A crucial foundation for all of the above-mentioned processes towards the development of any hydrometallurgical process is speciation, i.e. knowledge of the identity and distribution of specific metallic species in the solution. This would involve, in part, the construction of E_h–pH diagrams by which the stability regions of different metal complexes can be determined. To that regard, information on the formation constants of both noble metals and base metals is imperative for the development of effective separation processes. Information on the formation constants of the platinum group metal complexes in solution is not readily available. The United States' National Institute of Standards and Technology database of critically selected stability constants for metal complexes, as well as the IUPAC stability constants database, lists extremely limited data with regard to PGM complexes [5–7].

The palladium thiocyanate system is one such system for which the stability constants are extremely limited. Only a few papers are available and they only report values for $\log\beta_2$ and $\log\beta_4$. Apart from the data being limited, these values differ considerably. For $\log\beta_2$, only one reported value of 16.20 [8] is available, whereas reported values for $\log\beta_4$ are 19.46 [9], 25.6 [8], 27.20 [10], 27.60 [11], 28.22 [12], and 28.67 [13].

The determination of $\log\beta_2$ by Joshi *et al.* [8] entailed the preparation of a solution of palladium(II) with a known quantity of chloride as a starting material. The complexation of Pd(II) with SCN^- was expressed as mixed complexes (equation (1)).

$$PdCl_m + nSCN^- \rightleftharpoons Pd(SCN)_nCl_{m-n} + nCl^- \quad (1)$$

The nature of the complexes was determined employing both Job's continuous variation method and the slope ratio method using different individual solutions that contained specific ratios of Pd(II) and SCN^- with an excess of Cl^-. For the latter method, palladium

chloride was used as a source of palladium and the chloride concentration was kept constant while the solution was titrated with thiocyanate. These methods enabled the authors to spectrophotometrically calculate both $\log\beta_2$ and $\log\beta_4$ for the complexation of palladium with thiocyanate [8].

Other experimental methods employed mainly consisted of competition reactions between ligands having known stability constants with Pd(II) and thiocyanate [11–13]. This method limited the authors to calculate only one of the $\log\beta$ values due to the nature of the technique. The most recent literature on the complexation of palladium thiocyanate communicated a $\log\beta_4$ value of 27.20 [10]. The authors employed a rather complex competition reaction method where a solution of $[Pd(SCN)_4]^{2-}$ and 2,2,2-tet was prepared at pH 2 and then titrated with a base until a transition pH was reached. The 2,2,2-tet complex was deprotonated and the red $[Pd(SCN)_4]^{2-}$ ion was broken down to give the colorless [Pd (2,2,2-tet)]$^{2+}$ complex, which was used to calculate $\log\beta_4$ for the $[Pd(SCN)_4]^{2-}$ complex (equations (2) and (3)).

$$[Pd(SCN)_4]^{2-} + 2,2,2\text{-tet} + H^+ \rightleftharpoons [Pd(2,2,2\text{-tetH})SCN]^{2+} + 3SCN^- \quad (2)$$

$$[Pd(2,2,2\text{-tetH})SCN]^{2+} \rightleftharpoons [Pd(SCN)_4]^{2+} + SCN^- + H^+ \quad (3)$$

As yet no values for $\log\beta_1$ and $\log\beta_3$ have been reported.

In this study, the aim was to use the palladium tetra–aqua complex $[Pd(H_2O)_4]^{2+}$ as the starting material and titrate it with different volumes of a specifically prepared NaSCN solution to calculate the formation constants for the $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) system. The expected reaction scheme is shown below (equation (4)).

$$[Pd(H_2O)_4]^{2+} + nSCN^- \rightleftharpoons [Pd(SCN)_n(H_2O)_{4-n}]^{2-n} \quad (n = 0-4) \quad (4)$$

The same procedure was employed as in our earlier determination of the formation constants for $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) and $[PdCl_p(OH)_q]^{2-}$ ($p = 3$–0 and $q = 1$–4) [14].

2. Experimental

All reagents (Sigma Aldrich) were of analytical grade and solutions were prepared with water obtained from a Millipore Milli-Q system. Perchloric acid was standardized indirectly against potassium hydrogen phthalate by titration with sodium hydroxide.

Palladium sponge was dissolved in a mixture of concentrated perchloric acid ($HClO_4$) and fuming nitric acid (HNO_3). The nitric acid was driven-off by careful heating and the procedure was repeated until all the palladium was dissolved with the palladium subsequently being oxidized to palladium(II). A stock solution of palladium(II) with a concentration of 3×10^{-3} M (confirmed by ICP analyses) and 1.0 M with regard to perchloric acid was prepared. From this solution, an 8.0×10^{-5} M palladium solution was prepared which was 0.974 M with regard to $NaClO_4$ and 0.026 M with regard to $HClO_4$. A sodium thiocyanate (NaSCN) stock solution of 5.0×10^{-4} M was prepared that was also 0.974 M with regard to $NaClO_4$ and 0.026 M with regard to $HClO_4$, thereby ensuring constant pH and constant ionic strength (1.0 M) within the reaction vessel when palladium(II) and thiocyanate were titrated employing these two solutions.

Initial efforts to conduct the titration in a reaction vessel coupled to a 'sipper system,' which pumped the solution by means of a small peristaltic pump through a flow-through cuvette, failed due to the fact that early precipitation was initiated as a result of stirring and pumping. As a result of this, due to the low solubility of $[Pd(SCN)_2(H_2O)_2]$ (log $K_{sp} = -17.8$ [16]), a batch titration method was subsequently employed. A Metrohm 809.1 double burette auto-titrator was used to prepare 69 individual solutions containing 20 mL 8.0×10^{-5} M palladium solution and different volumes of the thiocyanate solution. This resulted in the thiocyanate concentration varying from 4.95×10^{-6} to 2.80×10^{-4} M and the palladium concentration varying from 7.92×10^{-5} to 3.52×10^{-5} M as a result of dilution. This small change in the concentration was accounted for when the different models were built and the formation constants were calculated using HypSpec [15]. Absorption spectra were recorded immediately thereafter within the wavelength range of 200–500 nm against water as reference at 25 °C. An Analytic Jena SPECORD® S600 UV–vis diode-array spectrophotometer, equipped with a quartz cuvette with a path length of 10 mm, was used for the absorption measurements. Equilibrium was reached instantaneously as no further change in the spectra of the solutions were observed over time and the precipitation of $[Pd(SCN)_2(H_2O)_2]$ only occurred after a few minutes. The end result of this method is the same as a normal titration and to that regard the absorption data, within HypSpec, is handled the same way as with a normal titration.

Three initial titrations, with larger concentration change increments, were carried out to determine the concentration range and repeatability. This information was then used to subsequently conduct further two titrations having smaller changes in the consecutive thiocyanate concentrations. A slight difference in the sigma value for the last two titrations was observed (8.94×10^{-3} and 8.23×10^{-3}, respectively) and the best-fitted data (lowest Sigma value) was used for the determination of the different stability constants with the standard deviations (from the HypSpec analysis) only calculated for the final titration data-set.

Competition of H^+ for SCN^- and the subsequent formation of HSCN are negligible in that the pK_a of HSCN is –1.85 [16]. A high free thiocyanate concentration at the desired perchlorate concentration is therefore ensured.

3. Results and discussion

The two main difficulties that had to be overcome employing this approach were (i) the low solubility of $[Pd(SCN)_2(H_2O)_2]$ and (ii) obtaining reasonable absorbances to calculate the corresponding log β values. To prevent the influence of precipitation having an effect on the calculation of the model, individual samples were prepared simulating a titration (as explained above). The palladium concentration was kept below 8.0×10^{-5} M and the possibility of the formation of polynuclear palladium species is highly unlikely. Polynuclear species exhibit weak d-d bands in the UV–near–visible spectral region [17] and the fact that no change in the absorption spectra was observed within this region confirms that no polynuclear species were formed. The change in absorption spectra with increasing thiocyanate concentration is shown in figure 1. A number of observable changes in the absorption spectra together with the absence of an isosbestic point allude to the existence of three or more species.

Similar to Harrington *et al.* [10] reporting that the four-coordinated $[Pd(SCN)_4]^{2-}$ exhibits a maximum absorption at 308 nm, we observed a major peak at 309 nm and therefore

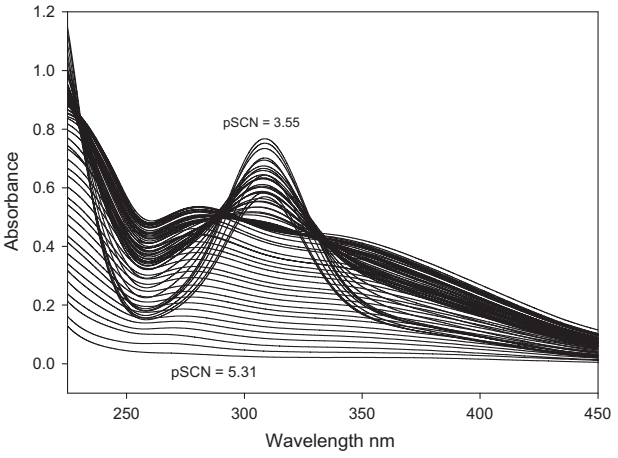

Figure 1. Change in absorption spectra with change in thiocyanate concentration.

focused our attention around this region. No recorded UV spectra or any molar absorbance spectra have been reported for the palladium thiocyanate system. Absorption data at every wavelength (every 0.5 nm) in the range 230–450 nm were treated with the program HypSpec 2009 to calculate equilibrium constants and absorption spectra for the initial complexes $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4). The molar absorption spectra for thiocyanate as well as for the aqua complex $[Pd(H_2O)_4]^{2+}$ were calculated independently under the same conditions (ionic strength and temperature) and were supplied as known spectra to HypSpec.

A measure of the overall quality of data refinement is indicated by the sigma (σ) value, derived from the squared residual r (equation (5)), where m is the number of data points, n the number of parameters, and w the weight as part of a least-squared calculation. The weighting scheme accounts for error in absorbance measurements and is specific to each spectrophotometer.

$$\sigma = \sqrt{\frac{\sum_i w_i r_i^2}{m - n}} \tag{5}$$

With a correct weighting scheme, the value of the scaled sum of squares (σ) has an expected value of unity. An absolute weighting scheme with a linear weighting function (chosen within HypSpec) was employed as part of this study, which is appropriate for the Analytic Jena SPECORD® S600 UV–vis diode-array spectrophotometer. A refinement is good if the calculated values agree with the observations within the limits of experimental error. Subsequent to the repeated experimentation, it was found that the model that fitted the data the best, judged by the lowest sigma value, includes the five coordinate $[Pd(SCN)_5]^{3-}$. Good correlation between the actual and calculated titration curves at 240, 260, 280, and 309 nm, where major changes in the spectra are observed, highlights the legitimacy of this five-coordinate model (figure 2). Formation constants for models consisting of any number of complexes less than five could not be obtained as these models did not refine.

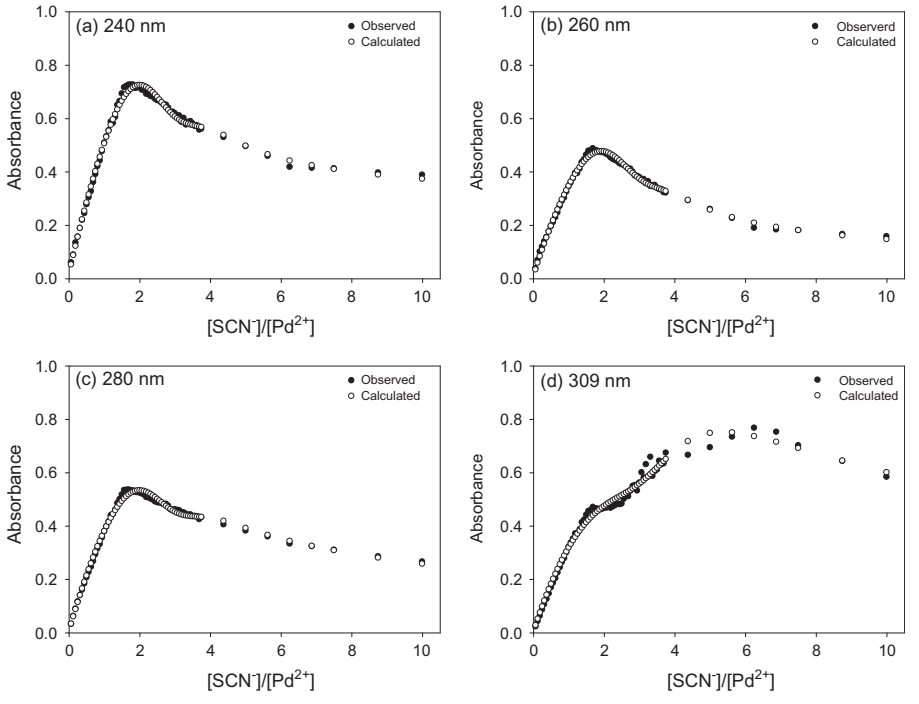

Figure 2. Actual/observed *vs.* calculated titration curves at specific wavelengths.

The values of the cumulative formation constants for the complexes $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) and $[Pd(SCN)_5]^{3-}$ are $\log\beta_1 = 8.14$, $\log\beta_2 = 15.46$, $\log\beta_3 = 21.94$, $\log\beta_4 = 27.42$, and $\log\beta_5 = 31.94$. The $\log\beta_2$ and $\log\beta_4$ values, calculated by us as part of the overall model, correspond well with those values obtained from the literature and are therefore a very good indication of the reliability of the other overall model and formation constants, i.e. for $[PdSCN(H_2O)_3]^+$, $[Pd(SCN)_3H_2O]^-$, and $[Pd(SCN)_5]^{3-}$, and for the existence of these complexes under the experimental conditions, which is now reported for the first time. A summary of the different formation constants is presented in table 1 together with the corresponding literature values. It is clear that a fair correlation exists between our value for $\log\beta_2$ (15.55) and the only published value of 16.20 [8]. Furthermore, of the six values reported for $\log\beta_4$, our value of 27.42 correlates well with two values reported, i.e. 27.20 [10] and 27.60 [11]. This provides further confirmation to the legitimacy of our model.

Table 1. Formation constants for $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 1$–4) and $[Pd(SCN)_5]^{3-}$ at 1.0 M ionic strength and 25 °C (N/A = not available, $\sigma = 8.23 \times 10^{-3}$).

n	Complex	Literature	$\log\beta_n$
1	$[PdSCN(H_2O)_3]^+$	N/A	8.14 ± 0.026
2	$[Pd(SCN)_2(H_2O)_2]$	16.20 [8]	15.46 ± 0.024
3	$[Pd(SCN)_3(H_2O)]^-$	N/A	21.94 ± 0.096
4	$[Pd(SCN)_4]^{2-}$	19.46 [9], 25.60 [8], 27.20 [10] 27.60 [11], 28.22 [12], 28.67 [13]	27.42 ± 0.274
5	$[Pd(SCN)_5]^{3-}$	N/A	31.94 ± 0.277

From the equilibrium constants, a distribution curve was constructed showing the complete speciation of the $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) system and $[Pd(SCN)_5]^{3-}$ employing a total Pd concentration of 1 M as an example (figure 3). At the maximum thiocyanate concentration for this investigation, i.e. at 2.80×10^{-4} M and at a palladium concentration of 3.52×10^{-5} M, more than 90% of the palladium is in the form of the pentathiocyanate complex $[Pd(SCN)_5]^{3-}$.

In most cases palladium(II) complexes are square planar [18–20], but some authors have suggested the possibility of palladium forming a five-coordinate trigonal–bipyramidal complex [21]. Desmarais *et al.* [22] have obtained a new class of palladium(II) olefin complex, which is five coordinate, using a specific nitrogen bidentate ligand. Similar work has been conducted by Albano *et al.* [23] who produced five-coordinate olefin complexes of palladium(II). In addition, Lopez-Torres *et al.* [24] investigated the reaction of cyclometalated halide-bridged palladium(II) complexes with a tertiary triphosphine ligand to produce a complex with a five-coordinate palladium as confirmed by spectroscopic and analytic data. We modeled the five-coordinate $[Pd(SCN)_5]^{3-}$ complex, employing Accelrys Materials Studio 5.5, starting out with the trigonal–bipyramidal structure and allowing it to stabilize. The structure changed from the trigonal–bipyramidal structure to a square pyramidal configuration (figure 4) in both cases where the ligand binds to the metal through either nitrogen or sulfur. This was confirmed by modeling in Avogadro [25, 26] in that the trigonal–bipyramidal structure also stabilized in the square pyramidal configuration (figure 5).

The molar absorption spectra for all complexes are shown in figure 6. $[Pd(SCN)_5]^{3-}$ has the strongest charge transfer band at 309 nm. In the case of the $[PdCl_n(H_2O)_{4-n}]^{2-n}$ system the charge transfer bands shifted to shorter wavelengths (higher energies) when chloride was substituted by water [14]. It is therefore expected that the charge transfer bands in the case of the $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) system, as well as for $[Pd(SCN)_5]^{3-}$, will also shift towards shorter wavelengths with substitution of thiocyanate by water; in the present

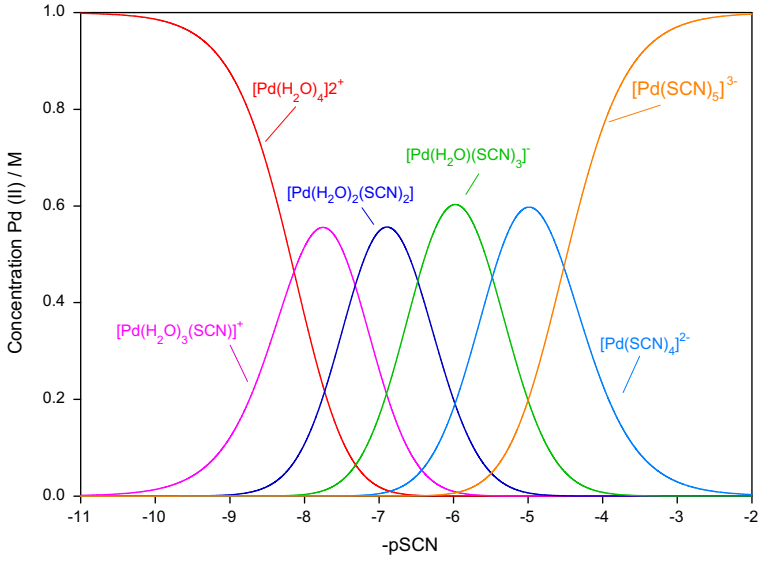

Figure 3. Distribution of $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) and $[Pd(SCN)_5]^{3-}$ species as a function of –pSCN.

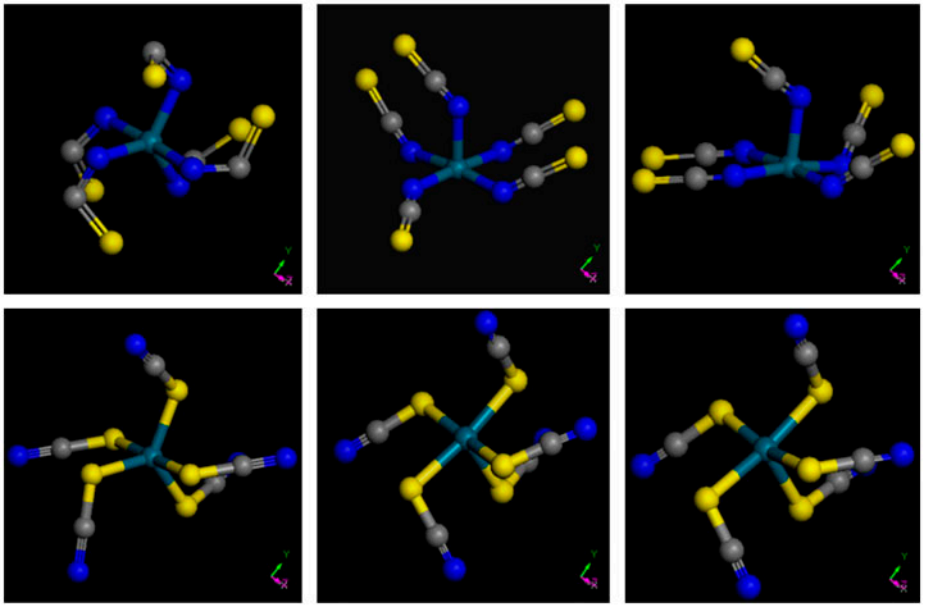

Figure 4. Modeled configurations of the five-coordinate $[Pd(SCN)_5]^{3-}$ complex showing the change from trigonal-bipyramidal (at the left) to square pyramidal (to the right).

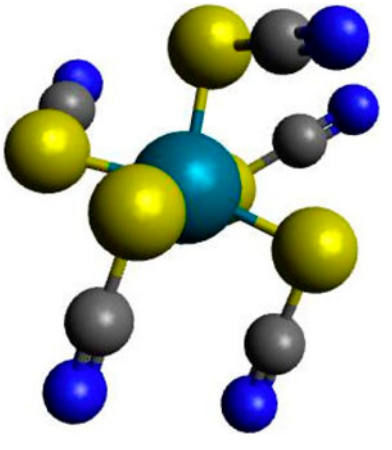

Figure 5. The stabilized five-coordinate $[Pd(SCN)_5]^{3-}$ complex as modeled by Avogadro [25, 26].

case even more so. Due to the pi-bonds present within the thiocyanate ligand, one would expect it to be the main chromophore in the different complexes. This also explains why there is a similarity between the absorbance spectra of some of the complexes. The highest absorbance is for the most substituted complex, $[Pd(SCN)_5]^{3-}$ (figure 6), which fits well with the statement of SCN^- being the main chromophore.

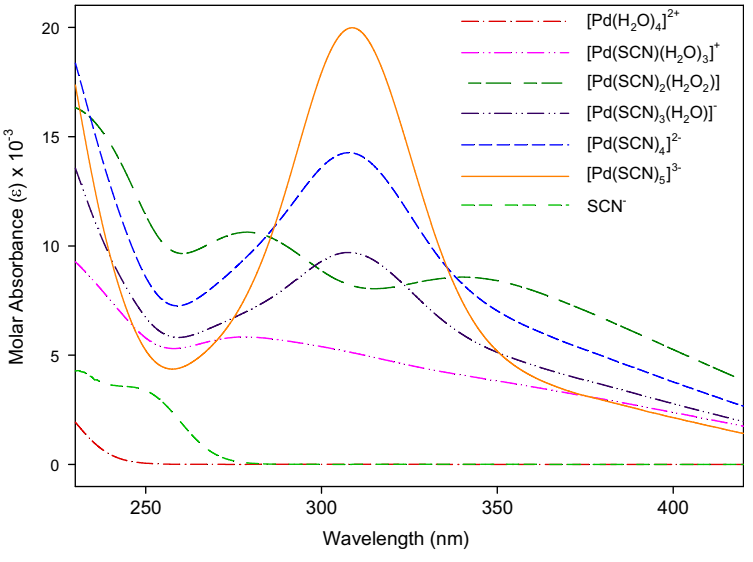

Figure 6. Calculated molar absorption spectra of $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) and $[Pd(SCN)_5]^{3-}$.

4. Conclusion

A successful spectrophotometric investigation into the complexation of palladium(II) with thiocyanate, i.e. obtaining a relevant and true sequential series of absorption spectra, modeling and proper data fitting, depended on preventing the precipitation of $[Pd(H_2O)(SCN)_2]$. This could not be accomplished by automated titration into a reaction vessel followed by circulation of the solution by means of a peristaltic pump through a flow-through cuvette as it was ascertained that mechanical stirring and pumping accelerated precipitation. This could be circumvented by making up individual solutions, also employing automated titration, and capturing the absorption spectrum immediately after proper mixing for each solution. The only model that fit the data involves the formation of five sequential complexes. Values for the formation constants of the five palladium(II) thiocyanate complexes, i.e. $[Pd(SCN)(H_2O)_3]^+$, $[Pd(SCN)_2(H_2O)_2]$, $[Pd(SCN)_3(H_2O)]^-$, $[Pd(SCN)_4]^{2-}$, and $[Pd(SCN)_5]^{3-}$, have been determined at an ionic strength of 1.0 M and a temperature of 25 °C. The formation constants are $\log \beta_1 = 8.14$, $\log \beta_2 = 15.46$, $\log \beta_3 = 21.94$, $\log \beta_4 = 27.42$, and $\log \beta_5 = 31.94$, with formation constants for the one-, three-, and five-coordinated complexes being reported here for the first time. Within this five-coordinate model, our values of $\log \beta_2$ (15.46) and $\log \beta_4$ (27.42) are in good agreement with the reported values, i.e. 16.20 [8] for the two-coordinate complex and 27.20 [10] and 27.60 [11] for the four-coordinate complex. This supports the legitimacy of this five-coordinate model. Molecular modeling furthermore postulates that the five-coordinate $[Pd(SCN)_5]^{3-}$ complex is square pyramidal.

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A detailed spectrophotometric investigation of the complexation of palladium(II) with chloride and bromide

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ABSTRACT

As the speciation of metal species, especially the noble metals, are crucial for recovery and separation purposes, the complex formation of Pd(II), with chloride and bromide respectively, has been investigated employing spectrophotometry at 25 °C and an ionic strength of 1.0 M Hyperquad Simulation and Speciation (HySS) was employed to determine the ideal titration conditions and an autotitrator (equipped with a flow-through cell) was used to accurately vary the chloride and bromide concentrations over an increased number of intervals, i.e. 128 and 300 respectively. All of these data points were used to calculate the formation constants of both palladium systems employing HypSpec (software specifically developed for the determination of equilibrium constants from spectrophotometric data). The formation constants, β_n, for the palladium(II)-chloride and -bromide complexes, have been determined. For $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4), the log β values are: log $\beta_1 = 4.49$, log $\beta_2 = 7.80$, log $\beta_3 = 10.18$ and log $\beta_4 = 11.54$, while the log β values for $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4), are: log $\beta_1 = 5.04$, log $\beta_2 = 9.12$, log $\beta_3 = 12.38$ and log $\beta_4 = 14.55$. The formation constants for the palladium-chloride complexes agree well with the published data, while the formation constants for the bromide complexes differ from somewhat from published data suggesting a different, but more accurate speciation. Molar absorption spectra for all the complexes in question have been obtained. Pourbaix diagrams were constructed from the new speciation data showing the predominant species for each system.

1. Introduction

Due to the excellent catalytic properties of the platinum group metals (PGMs), especially platinum, palladium and ruthenium, they are ideally suited for various applications that include fuel cell technology, industrial catalysts and catalytic converters, with the added benefit that they can be recycled (Faur Ghenciu, 2002; Úbeda et al., 2016; Jimenez de Aberasturi et al., 2011; Schäfer and Puchelt, 1998). Hydrometallurgical processes play a significant part in the processing, refining and recycling of the PGMs and are generally divided into three key areas, i.e. leaching, solution purification and metal recovery. During the process of leaching, which involves the use of aqueous lixiviant solutions to extract metal from metal bearing materials, some unwanted metals may have also been taken into solution and the solution is subsequently purified to eliminate these undesirable components. The two most common purification techniques that are currently used are solvent extraction and ion exchange. In the case of solvent extraction, a mixture of an extractant and a diluent is employed to extract a metal species/complex from one phase to another, while in the case of ion exchange natural zeolite, chelating agents, resins, activated carbon, and liquid organics impregnated with chelating agents are all employed to exchange cations or anions within the solution (Duclos et al., 2016; Fernandes et al., 2016; Kaya, 2016; Nguyen et al., 2016; Torres and Lapidus, 2016; Mpinga et al., 2015; Nikoloski et al., 2015; Rajiv Gandhi et al., 2015; Suoranta et al., 2015; Brits and Deglon, 2007; Swain et al., 2010; Viñals et al., 2006). In many instances, chloride (Duclos et al., 2016; Fernandes et al., 2016; Torres and Lapidus, 2016; Mpinga et al., 2015; Viñals et al., 2006; Shen et al., 2011) and in some cases bromide (Duclos et al., 2016; Kaya, 2016; Torres and Lapidus, 2016; Mpinga et al., 2015), is used as a complexing agent. A vital basis for all of the above-mentioned processes, towards the development of any hydrometallurgical process, is speciation, i.e. knowledge of the identity and distribution of specific metallic species/complexes in solution. This would include, in part, the construction of distribution- and E_h pH-diagrams by which the stability regions of different metal complexes can be determined.

The complexation equilibria of palladium(II) with chloride and bromide have been investigated by various authors and values for the formation constants have been determined. These complexes are assumed to be square planar and can be represented by the general formula $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) and $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) respectively. Information on the formation constants of the platinum group metal complexes in solution is not readily available, with the

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Table 1
Published stepwise formation constants for the complexation of palladium(II) with chloride.

Log β_1	Log β_2	Log β_3	Log β_4	Reference
4.47	7.76	10.17	11.54	Elding (1972)
4.40	7.74	10.08	11.46	Weed (1964)
4.47	7.80	10.18	11.53	Cruywagen and Kriek (2007)

United States' NIST (National Institute of Standards and Technology) database of critically selected stability constants for metal complexes, as well as the IUPAC stability constants database, listing extremely limited data. This is true for palladium(II)-chloride and more so for palladium(II)-bromide.

From the published data, it is evident that different methods were used to prepare the palladium(II) 'starting' solution, where the most common method of preparation has been the precipitation of palladium hydroxide from chloride or nitrate followed by the dissolution of the washed hydroxide in perchloric acid (Shchukarev et al., 1964; Biryukov et al., 1966; Shlenskaya et al., 1966; Shlenskaya and Biryukov, 1964; Boily and Seward, 2005; Van Middlesworth and Wood, 1999; Boily et al., 2007; Tait et al., 1991). So as to ensure the absence of any polynuclear hydrolysis products as well as colloidal species in the palladium(II) 'starting' solution palladium sponge was dissolved in hot fuming nitric acid with the nitric acid having been removed subsequently by several evaporations employing concentrated perchloric acid. This include our own work (Cruywagen and Kriek, 2007; Le Roux et al., 2014) and that of Elding (1972), which resulted in more satisfactory results.

Various authors have presented values for formation constants for the complexation of palladium(II) with chloride (Shchukarev et al., 1964; Biryukov et al., 1966; Shlenskaya et al., 1966; Shlenskaya and Biryukov, 1964; Boily and Seward, 2005; Van Middlesworth and Wood, 1999; Boily et al., 2007; Tait et al., 1991; Cruywagen and Kriek, 2007; Elding, 1972; Gulko and Schmuckler, 1973; Popovicheva and Shlenskaya, 1964; Weed, 1964). The majority of these values vary considerably with the best agreement having been obtained for formation constants determined more than 40 years ago by Elding (1972) and Weed (1964), and more recently (2006) by Cruywagen and Kriek (2007) (see Table 1).

All of the above-mentioned authors made use of a batch type experimental procedure whereby individual samples were prepared. The values presented by Weed (1964) in his PhD thesis raises some concerns as the wavelength range of recorded UV spectra, from which the stability constants were calculated, varied between 320 nm and 600 nm, which is out of the range of 'normal' investigations. All other published values where obtained from UV spectra with wavelengths ranging between 200 nm and 350 nm. Although good agreement has been obtained for the values calculated by Cruywagen and Kriek (2007)) and Elding (1972)), some uncertainty does exist as to the accuracy of the calculation of the formation constants as only a limited number of concentration variations were employed. In the publication by Cruywagen and Kriek a series of only 24 *individual* solutions was prepared of which the chloride concentration was varied from 6×10^{-5} to 0.69 M by adding calculated amounts of a standardised hydrochloric acid stock solution. The palladium(II) concentration (3×10^{-5} M), ionic strength, temperature and acid concentration was kept constant for all solutions. A GBC 920 UV–Vis double beam spectrophotometer equipped with a Peltier thermos cell with a 1 cm path length was used for the absorption measurements. Absorbance data were treated with the program HYPERQUAD 2000 (Gans et al., 1996) to calculate equilibrium constants and absorption spectra for the complexes $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4). In contrast, Elding also prepared a series of *individual* solutions (189 in total) for which both the palladium(II) and chloride concentrations were varied. From this set of solutions, however, only 30 solutions were employed to calculate the formation constants. The stability constants were calculated using the spectrophotometric version of Sillen's least squares programme Letagrop.

Table 2
Known stability constants for palladium (II) bromide.

Log β_1/K1	Log β_2	Log β_3	K4	Log β_4	Reference
5.17	9.42	12.7	2.20	14.9	Elding (1972)
			2.23		Gulko and Schmuckler (1973)
				13.05	Biryukov et al. (1966)
			2.16		Shlenskaya et al. (1966)
			2.20		Shlenskaya and Biryukov (1964)
4.37			3.50		Shchukarev et al. (1964)

In comparison to the chloride complexes the formation constants for the palladium(II)-bromide complexes are even more limited with Elding (1972) being the only author that have reported four consecutive stepwise formation constants for the $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) system. Other authors presented K values with some of them varying considerably. All available formation constants at the time of writing this paper are listed in Table 2.

The study by Elding (1972) obviously proves to be the most complete speciation study to date presenting values for all four stability constants. The author prepared a total of 207 *individual* solutions by adding a constant volume of palladium(II) stock solution and varying amounts of the bromide stock solution prepared from hydrobromic and perchloric acid. The ionic strength was kept constant at 1 M with perchloric acid as supporting electrolyte with the temperature kept constant at 25 °C. However, from the 207 *individual* solutions only 39 solutions, incorporating three different palladium concentrations, i.e. 4.76×10^{-5} M, 4.70×10^{-5} M and 4.70×10^{-3} M with varying bromide concentration, were employed to record the UV spectra. The stability constants were calculated using the same method as for the chloride system.

It is clear from the above that in all instances a batch experimental method, i.e. the making up of *individual* solutions, was employed to determine the formation constants with only a limited number of solutions (or data points) having been used. The aim of this study was to employ a more detailed and accurate experimental method that can produce and employ substantially more usable concentration variations within the desired ligand concentration range. This revised technique was first applied to the better known palladium(II)-chloride system so as to validate the technique against the published formation constants. Subsequently, this method was adjusted to accurately determine the various palladium(II)-bromide stability constants, employing HypSpec

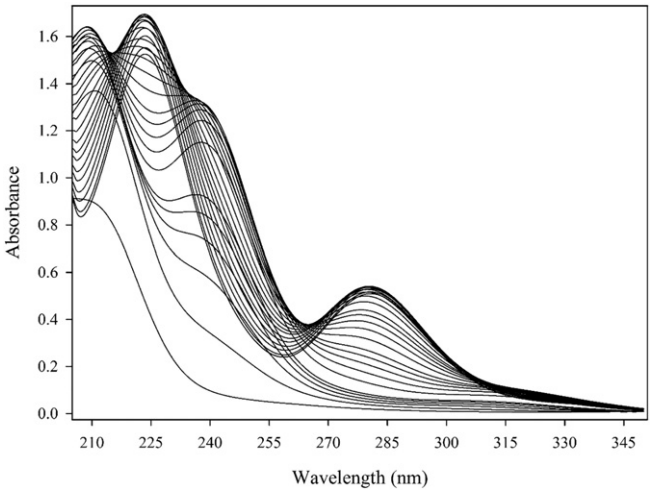

Fig. 1. Change in absorption spectra with change in chloride concentration (every 5th absorption spectrum shown for improved visualisation).

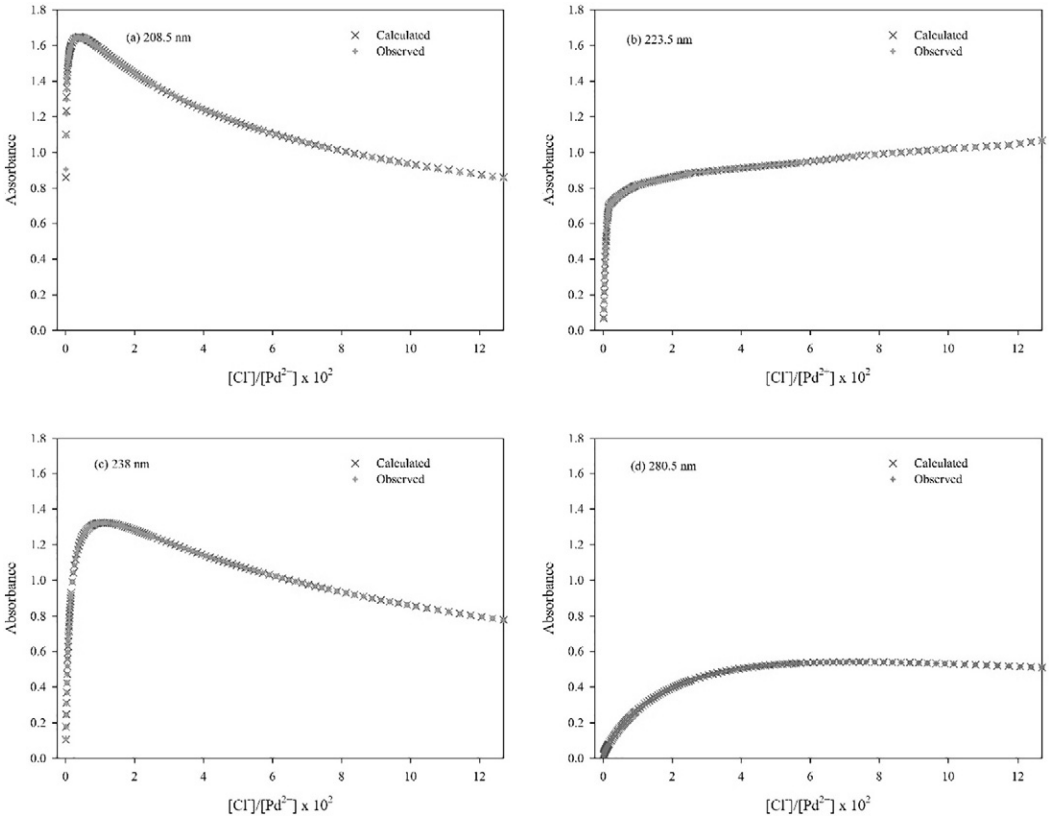

Fig. 2. Actual/observed vs calculated absorbance at specific wavelengths for $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4).

(Gans et al., 1996) (specifically designed for calculating stability constants). This program is part of the Hyperquad suite and shares some features with other programs within the suite and can be used to derive equilibrium constants from spectrophotometric data. The data may be in the form of one or more titration data sets, or single data points (batch data). The program combines the functionality of Hyperquad (Gans et al., 1996) and pHab (Gans et al., 1999), but with some simplifications.

2. Experimental

All reagents (Sigma Aldrich) were of analytical grade and solutions were prepared with water obtained from a Millipore Milli-Q system.

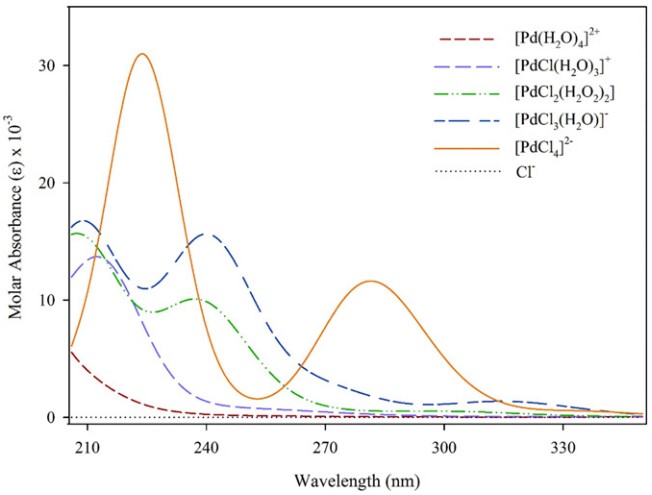

Fig. 3. Calculated molar absorption spectra of $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4).

Perchloric acid was standardised indirectly against potassium hydrogen phthalate by titration with sodium hydroxide. Hyperquad Simulation and Speciation (HySS) (Alderighi et al., 1999) software was used to determine the ideal titration conditions with a model having been specified by defining a set of equilibrium constants (Eq. (1)).

$$\beta_{bq\cdots} = \frac{[A_pB_q\ldots]}{([A]^p[B]^q\ldots)} \quad (1)$$

The titration was subsequently simulated by specifying a set of titration conditions and calculating the concentrations of each complex species as the titration proceeds. The optimised titration conditions obtained is then used to calculate the ideal concentrations for the different solutions.

Palladium sponge was dissolved in a mixture of concentrated perchloric acid ($HClO_4$) and fuming nitric acid (HNO_3). The nitric acid was driven off and the procedure repeated until all the palladium was dissolved and oxidized to palladium(II). A stock solution of palladium(II) with a concentration of 3.0×10^{-3} M (confirmed by ICP analyses) and 1.0 M with regard to perchloric acid was prepared. From this solution a 1.05×10^{-4} M and a 1.02×10^{-4} M palladium solution was prepared, which was 0.966 M with regard to $NaClO_4$ and 0.034 M with regard to $HClO_4$.

Table 3
Formation constants for $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 1$–4) at 1.0 M ionic strength and 25 °C.

n	Log β_n (Titration 1)	Log β_n (Titration 2)	Log β_n (Titration 3)	Log β_n (Average)
1	4.460 ± 0.001	4.499 ± 0.0013	4.497 ± 0.002	4.485 ± 0.001
2	7.817 ± 0.002	7.758 ± 0.002	7.817 ± 0.003	7.797 ± 0.002
3	10.187 ± 0.003	10.170 ± 0.004	10.187 ± 0.005	10.181 ± 0.004
4	11.541 ± 0.003	11.524 ± 0.004	11.535 ± 0.005	11.535 ± 0.004
σ	1.928×10^{-3}	2.228×10^{-3}	3.015×10^{-3}	2.390×10^{-3}

Table 4
Comparative stepwise formation constants for the complexation of palladium(II) with chloride.

Log β_1	Log β_2	Log β_3	Log β_4	Reference
4.47 ± 0.01	7.76 ± 0.04	10.17 ± 0.07	11.54 ± 0.09	Elding (1972)
4.47 ± 0.07	7.80 ± 0.11	10.18 ± 0.14	11.53 ± 0.15	Cruywagen and Kriek (2007)
4.485 ± 0.001	7.797 ± 0.002	10.181 ± 0.004	11.535 ± 0.004	This work

Sodium chloride (NaCl) and sodium bromide (NaBr) stock solutions of 0.02 M were prepared in a solution of $NaClO_4$ and $HClO_4$, which was 0.946 M with regard to $NaClO_4$ and 0.034 M with regard to $HClO_4$ thereby ensuring a constant pH and ionic strength of 1.0 M throughout all solutions.

For palladium(II)-chloride speciation 300 mL of the palladium stock solution (0.0315 mM) was added to a jacketed reaction flask that was thermostatically controlled at a fixed temperature of 25 °C employing a Julabo F12-ED refrigerated/heating circulator. A Metrohm 809.1 double burette auto-titrator was used to vary the chloride concentration over 128 intervals from 6.66×10^{-5} M to 8.00×10^{-2} M by adding precalculated volumes of the chloride containing solution. Although the palladium concentration slightly varied from 1.05×10^{-4} M to 6.30×10^{-5} M as a result of dilution, this is taken into account by HypSpec (Gans et al., 1996). For palladium(II)-bromide speciation 200 mL of the palladium stock solution (0.0204 mM) was added to the temperature controlled reaction flask and the bromide concentration was varied over 300 intervals from 9.995×10^{-6} M to 1.204×10^{-2} M. Again, the palladium concentration slightly varied from 1.020×10^{-4} M to 4.06×10^{-5} M, which was accounted for by HypSpec (Gans et al., 1996).

An Analytic Jena SPECORD® S600 UV–Vis diode-array spectrophotometer, equipped with a quartz flow-through cuvette (10 mm path length), was used for the absorption measurements. This ensured uniform and constant intervals between successive ligand additions and the recording of the individual UV spectra. The solution inside the temperature controlled reaction cell was constantly circulated through the flow-through cuvette by means of a peristaltic pump ensuring effective mixing and temperature control of the solution after every addition. Equilibrium is reached instantaneously as no further changes in the spectra of the solutions were observed over time. Spectra were recorded every 200 s in the wavelength range 200–500 nm against water as reference. The process of titration, mixing, flow-through and UV-spectra recording was fully automated employing a software program, Auto Mouse Clicker (with built-in timer).

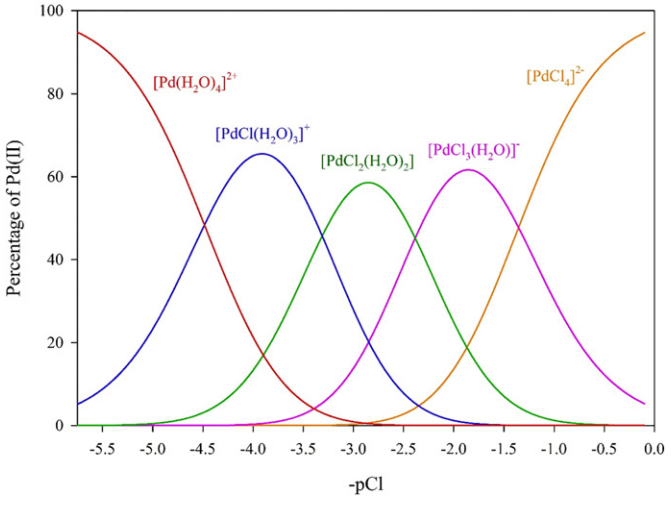

Fig. 4. Distribution of $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) species as a function of -pCl.

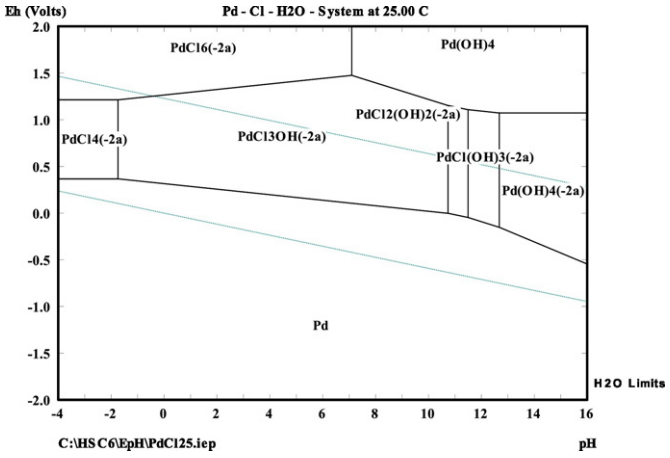

Fig. 5. E_h pH-diagram for the Pd-Cl-H_2O system, ($[Pd^{2+}] = 1$ mmol/kg H_2O; $[Cl^-] = 10$ mol/kg H_2O).

Competition of H^+ for Cl^- and Br^-, with the subsequent formation of HCl and HBr, are negligible in that the pK_a of HCl and HBr is −9.0 and −11.0 respectively (Haynes and Lide, 2011). A high free chloride and bromide concentration at the desired ligand concentration is therefore ensured.

3. Results and discussion

3.1. Palladium(II)-chloride complexation

The change in absorption spectra with increasing chloride concentration is shown in Fig. 1. Absorption data at every wavelength (every 0.5 nm) in the range 206 nm to 350 nm were treated with the program HypSpec (Gans et al., 1996) to calculate equilibrium constants and molar absorption spectra for the complexes $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4). The molar absorption spectra for chloride as well as for the aqua complex $[Pd(H_2O)_4]^{2+}$ were determined independently at the same and constant ionic strength and temperature and supplied as known spectra to HypSpec (Gans et al., 1996). By supplying these spectra, the calculation becomes less complex resulting in a more accurate result. After the different spectra were carefully examined the absorbance measurements below 206 nm were excluded from the calculations due to the high absorbance of chloride in this region.

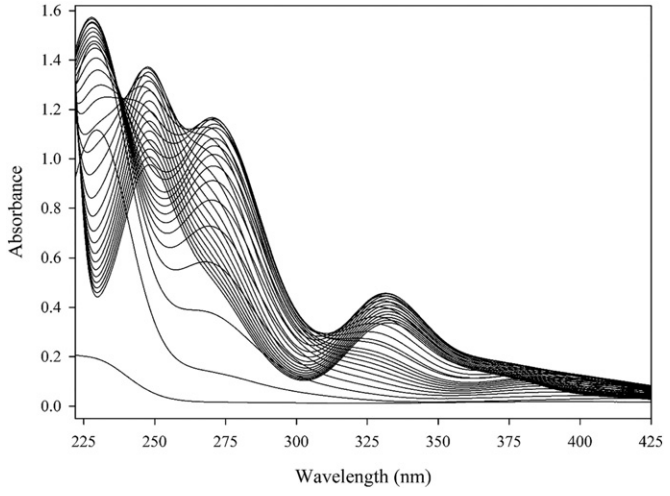

Fig. 6. Change in absorption spectra with change in bromide concentration (every 10th absorption spectrum shown for improved visualisation).

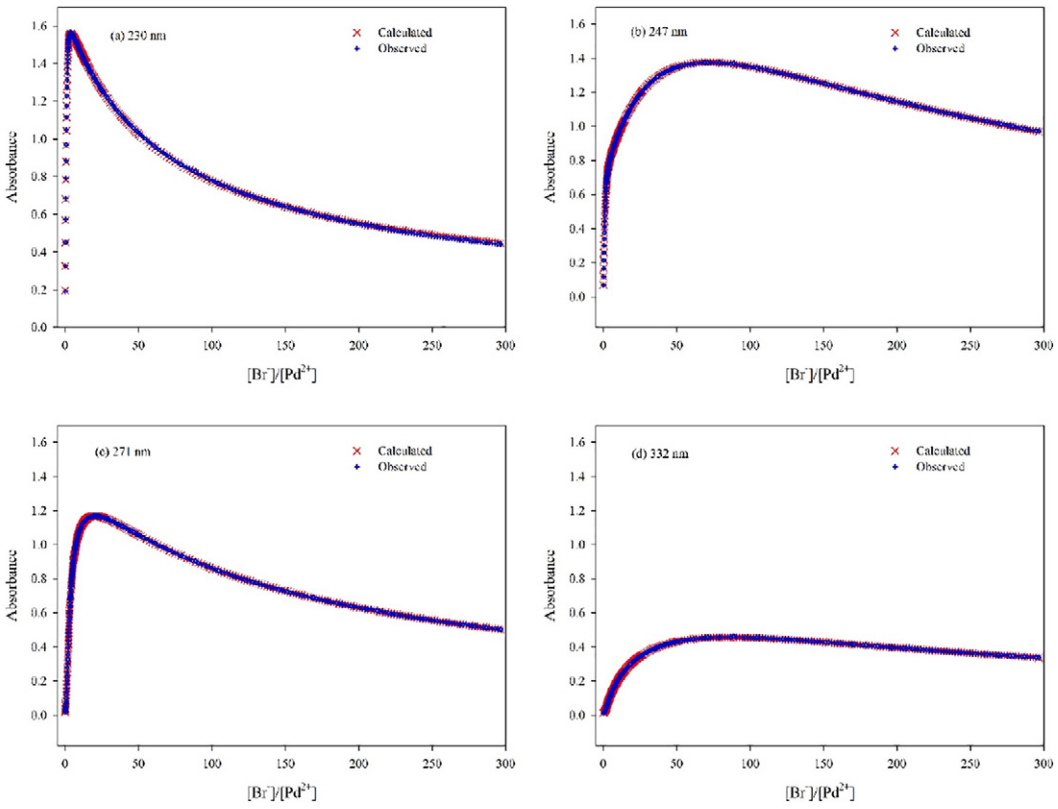

Fig. 7. Actual/observed vs calculated absorbance at specific wavelengths for $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4).

A measure of the overall quality of data refinement is indicated by the sigma (σ) value, derived from the squared residual r (Eq. (2)), where m is the number of data points, n the number of parameters, and w the weight as part of a least squared calculation. The weighting scheme accounts for the error in absorbance measurements and is specific to each spectrophotometer.

$$\sigma = \sqrt{\frac{\sum_i w_i r_i^2}{m-n}} \tag{2}$$

With a correct weighting scheme, the value of the scaled sum of squares (σ) has an expected value of unity. An absolute weighting scheme with a linear weighting function (chosen within HypSpec) was employed as part of this study, which is appropriate for the Analytic Jena SPECORD® S600 UV–Vis diode-array spectrophotometer. A refinement is considered accurate if the calculated values agree with the observations within the limits of experimental error.

Changes in the absorbance data can be observed at 208.5 nm, 223.5 nm, 238 nm and 280.5 nm. The calculated absorbance values and the observed absorbance values at these specific wavelengths are compared in Fig. 2, highlighting the high accuracy of the experimental data and the excellent correlation between the experimental and calculated data. The molar absorption spectra are shown in Fig. 3. Similar to Elding (1972) and Cruywagen and Kriek (2007) the $[PdCl_4]^{2-}$ complex has the highest absorption band with a maximum absorbance at 224 nm and a lower absorption band at 282 nm. These charge transfer bands, caused by the transition of electrons from the chloride ligands to molecular orbitals localized primarily on palladium, are shifted towards shorter wavelengths with higher energies when chloride is substituted by water in the complexes. The characteristics of these bands have been investigated and discussed previously (Elding, 1972).

The calculated values of the cumulative formation constants (see Table 3) are in good agreement with the values reported by Elding (1972) and more recently, Cruywagen and Kriek (2007). In contrast to the studies of these authors, the current investigation employed an additional fifteen data points at the lower end of the chloride concentration range, which together with the increased number of data points distributed over the rest of the chloride concentration range increased the accuracy in calculating the associated model.

For comparative purposes our newly calculated formation constant are compared to that of the already published data (see Table 4) and it is evident that the data correlate well, which supports our methodological approach, although we would add more value to the current data due to the increased number of titration points (an increase of more than a factor of four). The distribution of the complexes as a function of $\log[Cl^-]$ is shown in Fig. 4. In this study the chloride concentration was varied over 128 different concentration intervals from 6.30×10^{-5} M to

Table 5
Formation constants for $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 1$–4) at 1.0 M ionic strength and 25 °C.

n	Log β_n (Elding, 1972)	Log β_n (Titration 1)	Log β_n (Titration 2)	Log β_n (Titration 3)	Log β_n (Average)
1	5.17 ± 0.02	5.040 ± 0.002	5.031 ± 0.002	5.041 ± 0.002	5.037 ± 0.002
2	9.42 ± 0.03	9.118 ± 0.004	9.120 ± 0.004	9.120 ± 0.003	9.119 ± 0.004
3	12.72 ± 0.06	12.369 ± 0.005	12.380 ± 0.004	12.381 ± 0.004	12.375 ± 0.004
4	14.94 ± 0.08	14.540 ± 0.004	14.544 ± 0.004	14.552 ± 0.005	14.545 ± 0.004
σ	N/A	1.829×10^{-3}	1.811×10^{-3}	1.829×10^{-3}	1.828×10^{-3}

0.08 M. The first data point (at 6.30×10^{-5} M Cl^-) coincides with 53% of the Pd(II) being in the form of the monochloride complex $[PdCl(H_2O)_3]^+$, while the last data point (at 0.08 M Cl^-) coincides with 70% of the Pd(II) being in the form of the tetrachloride complex $[PdCl_4]^{2-}$, which attests to a representative range of chloride concentrations over which the solutions were made up and the model built.

HSC Chemistry® 6.0 from Outotec, a chemical reaction and equilibrium software package with an extensive thermochemical database, was used to construct a Pourbaix (E_hpH) diagram from the speciation data (Fig. 5). Our newly determined stability/formation constants for the $[PdCl_n(H_2O)_{4-n}]^{2-n}$ system ($n = 0$–4), together with the stability/formation constants of the mixed palladium(II) chloro-hydroxo complexes that were determined earlier (Cruywagen and Kriek, 2007), were employed to calculate the Gibbs free energies of formation for each complex and incorporated into the HSC Chemistry® 6.0 database.

3.2. Palladium(II)-bromide complexation

Major peak changes occurred at 229.5 nm, 247 nm, 271 nm and 332 nm (Fig. 6). Elding (1972) focused on three corresponding wavelengths, i.e. 247 nm, 265 nm and 332 nm. As already mentioned only a limited number of recorded UV spectra and molar absorbance spectra have been reported for the palladium bromide system at present (Elding, 1972). Initially the same number of concentration variations were employed (128 in total, similar to the palladium chloride investigation), however, satisfactory refinement of the model could not be obtained. Only after the number of concentration intervals were increased and varied over 300 intervals an accurate distinction between the transitions of the different species were obtained. This represents an increase of more than a factor of seven compared to the number of solutions employed by Elding (1972). Absorption data at every wavelength (every 0.5 nm) in the range 229.5 nm to 450 nm were treated with the program HypSpec (Gans et al., 1996) to calculate formation constants and absorption spectra for the complexes $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4). As in the case of chloride the molar absorption spectrum for bromide was determined and supplied to HypSpec (Gans et al., 1996) as a known spectrum together with the already determined spectrum for the aqua complex $[Pd(H_2O)_4]^{2+}$. Similar to the chloride investigation the absorbance measurements below 229.5 nm were excluded from the calculations due to the high absorbance of bromide in this region. Again, the calculated absorbance values and the observed absorbance values at these specific wavelengths are compared in Fig. 7, highlighting the high accuracy of the experimental data and the excellent correlation between the experimental and calculated data. The titration was repeated three times under the same conditions and the values of the cumulative formation constants for the complexes $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) are shown in Table 5 for the three individual titrations. The fact that we employed substantially more titration points, compared to Elding's (1972) limited number of individual solutions, is evident in that our calculated formation constants differ from that of Elding. The molar absorption spectra for all complexes are shown in Fig. 8 with $[PdBr_4]^{2-}$ having the strongest charge transfer band at 248.5 nm with a secondary peak at 332 nm.

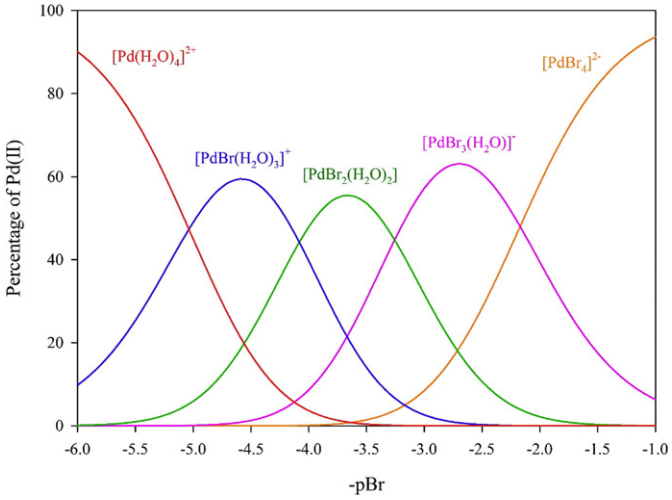

Fig. 9. Distribution of $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) species as a function of -pBr.

In the case of the $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) system the charge transfer bands were shifted towards shorter wavelengths (higher energies) when chloride was substituted by water (Weed, 1964). It is therefore expected that the charge transfer bands in the case of the $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4), will also shift towards shorter wavelengths with the substitution of bromide by water; in the present case, even more so. This is only the second proposed set of stepwise formation constants for $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 1$–4) at 1.0 M ionic strength and 25 °C. From the formation constants, a distribution diagram was constructed showing the complete speciation of the $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) system as a function of percentage palladium(II) (Fig. 9. At the maximum bromide concentration for this investigation, i.e. at 1.204×10^{-2} M, and at a palladium concentration of 4.06×10^{-5} M, in excess of 80% of the palladium is in the form of the tetra bromide complex $[PdBr_4]^{2-}$. At the lowest concentration 48% of the Pd(II) is in the form of the mono bromide complex $[PdBr(H_2O)_3]^+$.

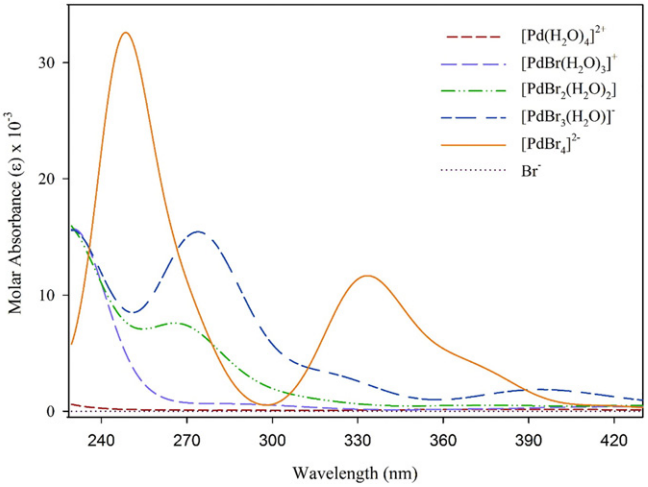

Fig. 8. Calculated molar absorption spectra of $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4).

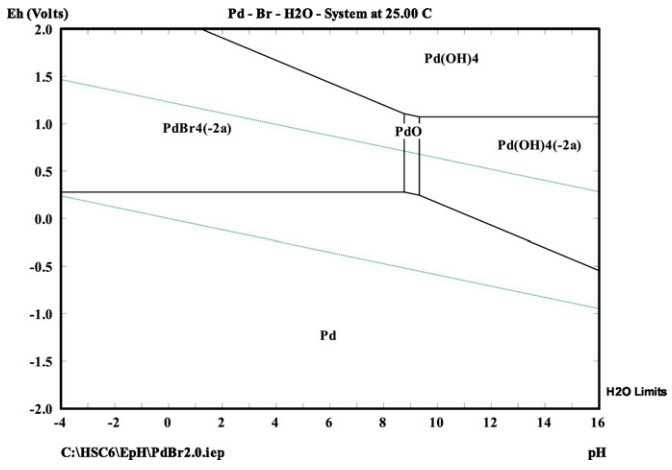

Fig. 10. E_h pH-diagram for the Pd-Br-H_2O system, ($[Pd^{2+}] = 1$ mmol/kg H_2O; $[Br^-] =$ 10 mol/kg H_2O).

Table 6
Comparison of experimental conditions employed.

	$[PdCl_n(H_2O)_{4-n}]^{2-n}$				$[PdBr_n(H_2O)_{4-n}]^{2-n}$	
	Elding (1972)	Cruywagen and Kriek (2007)	Weed (1964)	This work	Elding (1972)	This work
Wavelength range (nm)	210–300 305–605	203–325	320–600	206–350	210–300 305–605	229.5–450
Wavelengths	45 60	40	40	288	45 60	441
Wavelength interval (nm)	2.5 5	3	7	0.5	2.5 5	0.5
Concentration changes	30	24	40	128	39	300

Similar to the palladium(II) chloride speciation a Pourbaix diagram was constructed employing the newly determined formation constants (Fig. 10). To date, however, no speciation data exist for mixed palladium(II) bromo-hydroxo complexes (an investigation that we are currently busy with) as in the case of palladium(II) chloride. The lack of more complete speciation data for the Pd-Br-H_2O system is evident when the Pourbaix diagrams of the palladium(II) chloride and palladium(II) bromide systems are compared.

Comparing the log β values (formation/stability constants) of the palladium(II) chloride and -bromide systems, it is evident that the log β values of the bromide system are larger than those of the chloride system. This points towards the fact that the formation of the different species of the palladium(II) bromide system takes place at lower ligand concentrations compared to the chloride system. This is in line with the data of the palladium(II) thiocyanate system (Le Roux et al., 2014) for which the log β values are almost double. The strength of interaction between the central palladium(II) ion and the bound ligands therefore increases in the order $Cl^- < Br^- < SCN^-$.

For this work, in contrast to the already published data, the experimental conditions employed, to determine the best fit for the data and calculate the formation constants and molar absorbances for the different complexes, were significantly more extensive as can be seen from Table 6. This includes a vast increase in the number of wavelengths employed, i.e. smaller wavelength intervals, as well as a substantial increase in the number of concentrations that were employed. This was made possible by not making up individual solutions, but by conducting a single batch titration over the whole concentration range, which allowed for an improved fit of the data.

In support of the above-mentioned models and associated formation constants the potential influence of any kinetic effects during the formation of the different complexes were considered. Consistent with our experimental approach a single batch titration was initiated and stopped at pCl = 4.50. At this point scans were taken at every minute for 60 min, followed by a scan every hour for 23 h. Subsequent to this 'stationary' event the titration was continued to pCl = 3.25 and the afore-mentioned sequence of scans was repeated. This was repeated for pCl = 2.40 and pCl = 1.40. From Fig. 11 it is clear that overlays of all these scans do not show the existence of any kinetic effects. This was repeated for bromide (see Fig. 12). It is evident that all scans, for chloride and bromide, overlay perfectly indicating that there is no change in the spectra over a 24-h period, ruling out any kinetic effect during bond formation between palladium(II) and chloride and bromide respectively.

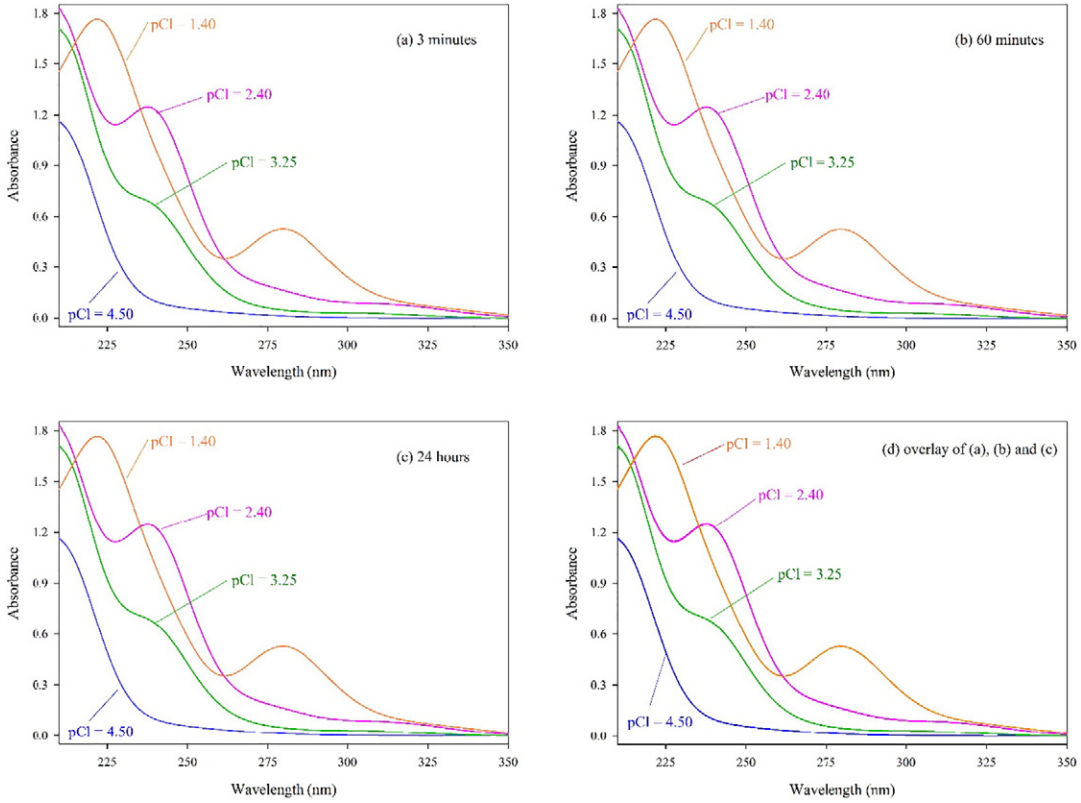

Fig. 11. Change in UV Spectra at selected pCl-values after (a) 3 min, (b) 60 min, (c) 24 h, with (d) being an overlay of (a), (b) and (c).

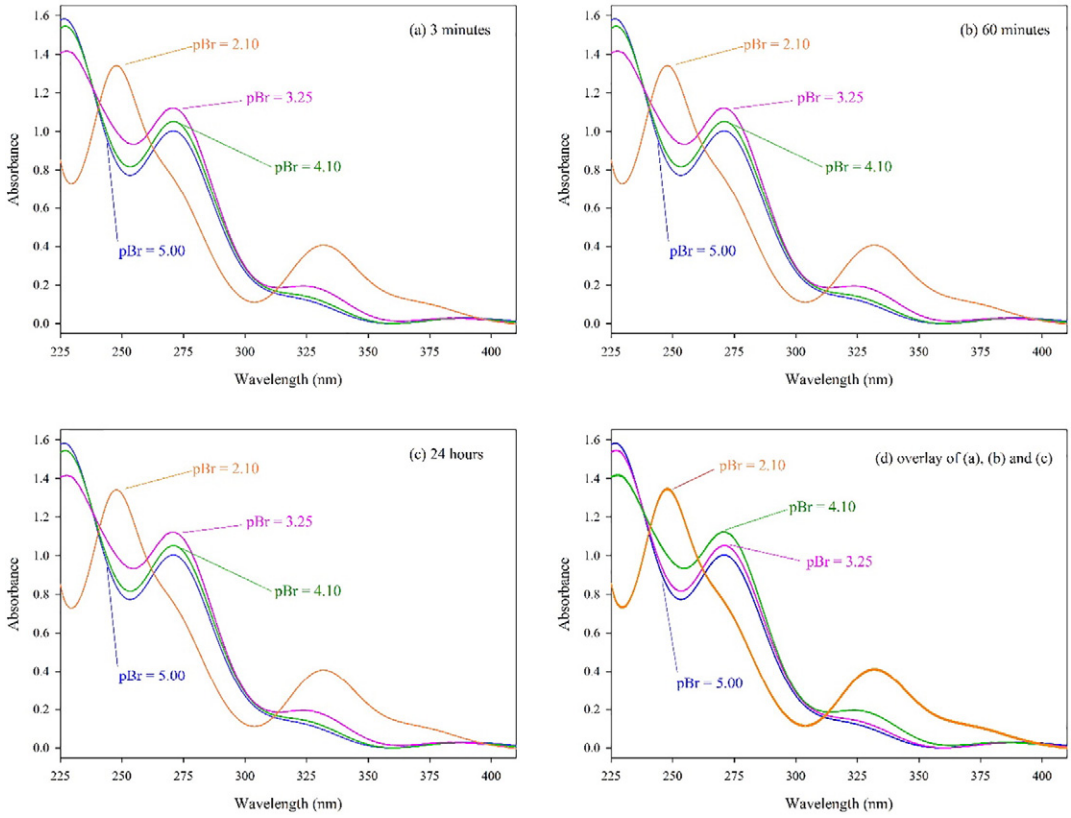

Fig. 12. Change in UV Spectra at selected pBr-values after (a) 3 min, (b) 60 min, (c) 24 h, with (d) being an overlay of (a), (b) and (c).

4. Conclusions

Hydrometallurgical processing of the PGMs, such as leaching, solvent extraction and ion exchange, require exact knowledge of the speciation of the specific metals involved. To this regard refined values for the stepwise formation constants of the palladium(II)-chloride system, i.e. $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4), have been determined spectrophotometrically at an ionic strength of 1.0 M and a temperature of 25 °C. Formation constants communicated for these two systems were based on a limited number of concentration variations, which entailed the making up of individual solutions that ranged between 24 and 30 solutions in total. The stepwise formation constants for the chloride system are: $\log \beta_1 = 4.485$, $\log \beta_2 = 7.797$, $\log \beta_3 = 10.181$ and $\log \beta_4 = 11.535$. The values obtained are still in good agreement with values published by both Elding (1972) and Cruywagen and Kriek (2007). After the titration method was successfully applied to the chloride system, it was customised and applied to the bromide system, $[PdBr_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4), for which the formation constants are: $\log \beta_1 = 5.037$, $\log \beta_2 = 9.119$, $\log \beta_3 = 12.375$ and $\log \beta_4 = 14.546$. These values differ from those published by Elding (1972) and provides a new model for palladium(II)-bromide speciation. When the different methods to generate the absorbance data and consequently the formation constants are compared, it is evident that the increased number of data points, titration method, repeatable results and customised calculation software, without a doubt increased the legitimacy and accuracy of the calculated formation constants for both the chloride and bromide systems.

Acknowledgement

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A detailed spectrophotometric investigation of the stability constants of $[PdCl_n(OH)_{4-n}]^{2-}$ and $[PdBr_n(OH)_{4-n}]^{2-}$ (n = 0 – 4)

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Abstract

Complex formation of mixed palladium(II) chloro-hydroxo and palladium(II) bromo-hydroxo complexes have been investigated employing spectrophotometry at 25 °C and an ionic strength of 1.0 M. Hyperquad Simulation and Speciation (HySS) was employed to determine the ideal titration conditions and an autotitrator (equipped with a flowthrough cell) was used to accurately vary the pH over 80 and 90 intervals respectively. The stability constants (log β_n) for the mixed chloro-hydroxo complexes $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), are: log β_1 = 18.36, log β_2 = 23.21, log β_3 = 26.91 and log β_4 = 29.68. These newly obtained values represent an improved speciation of the mixed palladium(II) chloro-hydroxo complexes. The same experimental procedure was employed to calculate, for the first time, the stepwise stability constants of the palladium(II) bromo-hydroxo system, $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), i.e. log β_1 = 18.73, log β_2 = 22.25, log β_3 = 25.58 and log β_4 = 28.47. Molar absorption spectra for all the complexes in question have been obtained. For both systems, complete Pourbaix diagrams were constructed from the new speciation data showing the predominant species for each system.

Keywords: palladium(II), bromide, chloride, hydroxide, stability constants, spectrophotometry

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1 Introduction

Hydrometallurgical processing of platinum group metals (PGMs) require exact knowledge of the speciation of the specific metals involved. Both chloride [1-6] and bromide [1, 4, 6, 7] anions are investigated for their application in hydrometallurgical processes as complexing agents. As mentioned previously [8, 9] the speciation of a specific system, i.e. the identity and distribution of specific metallic species/complexes in solution as characterised by the stability constants (also known as formation constants), is essential in developing, improving and understanding dedicated hydrometallurgical processes. The stability constants convert into Gibbs free energies that, when different, result in a shift of the stability regions of different complexes which is illustrated by a Pourbaix diagram. For example, an investigation into the rapid liquid-liquid extraction of palladium(II) employing hexadecylpyridinium

bromide (HDPB), the extraction was studied as a function of several parameters, which included pH [10]. The extraction efficiency of palladium(II) was carried out over the pH range 1 – 10 and it was possible to successfully extract palladium(II) at pH values as high as 5, while extraction decreased significantly at higher pH values. In addition, an investigation into the sorption-based recovery of palladium(II), employing the commercial basic anion exchanger Lewatit MonoPlus SR-7, the importance of knowing the speciation of palladium(II) in solution has been deemed crucial to determine the affinity of palladium(II) for binding sites [11]. Although platinum group metal (PGM) recovery is generally carried out in strong acidic media, the exact knowledge of platinum group metal ion speciation in more basic solutions facilitates the possibility to develop hydrometallurgical extraction processes in a wider pH range. This was illustrated in a leaching study conducted on the recovery of PGMs from gasoline and diesel fuel catalysts at eight predefined pH-static set points (pH = 2 - 9) [12]. Knowledge of the speciation of metal ions in solution is largely dependent on pH, metal concentration and the presence of ligands [13]. It therefore follows that a change in the pH of a solution can have a dual interaction effect on sorption performance due to the influence of the acidity/basicity together with the presence of halide ions.

The complexation equilibria of palladium(II) with only chloride and bromide, at low pH values, have been investigated by a number of authors and values for the formation constants have been determined [9, 14-23]. These complexes can be represented by the general formula $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) and $[PdBr_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) respectively. In contrast, at higher pH values, published formation constant values for the hydrolysis of palladium(II) [24-28] are available, however, limited data exists for mixed chloro-hydroxo complexes [16, 24-28], $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), while no data exists for the bromo-hydroxo complexes, $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4).

Furthermore, a lot of uncertainty exists with regard to the current published formation constant values, with the most complete study in terms of the stepwise formation of mixed chloro-hydroxo complexes being that of Cruywagen and Kriek [16]. Other authors focussed on the stability and kinetics of selected mixed chloro-hydroxo complexes [15, 24] presenting selected values and corresponding molar absorbances. Various authors [24, 28] also presented values for the mixed complex $[PdCl_3(OH)]^{2-}$ derived from $[PdCl_4]^{2-}$ employing reaction 1:

$$[PdCl_4]^{2-} + H_2O \rightleftharpoons [PdCl_3(OH)]^{2-} + H^+ + Cl^- \quad (1)$$

The majority of the above-mentioned authors made use of a batch type experimental procedure whereby individual samples were prepared. Cruywagen and Kriek [16] employed a double burette titration ensuring both the palladium and chloride concentrations were kept constant. A solution containing a mixture of $[PdCl_3]^-$ and $[PdCl_4]^{2-}$ (obtained by dissolving $PdCl_2$) was used as starting solution and

titrated with sodium hydroxide. A similar blank titration was carried out to correct the spectra. Although this is the only complete stepwise formation study to date, some uncertainty does exist as to the accuracy of the calculation of the formation constants as only a limited number of concentration variations were employed.

As part of previous investigations an automated titration and data collection setup was employed with great success [8, 9]. This automated experimental method was appropriately customized to accurately determine the stepwise formation constants for both palladium(II) chloro-hydroxo and palladium(II) bromo-hydroxo mixed complexes. For this study a solution containing $[PdCl_4]^{2-}$ was prepared by adding chloride to a stock solution of palladium(II) so as to ensure that this was the only initial species present. The concentration of both palladium(II) and chloride were kept constant with the only change that of the hydroxide concentration. Similar to previous investigations [8, 9], the same software program, HypSpec [29], was used to derive equilibrium constants from spectrophotometric data. The same experimental method was customised to determine the stability constants for palladium(II) bromo-hydroxo mixed complexes. A full set of stability constants for the palladium(II) bromo-hydroxo mixed complexes is reported here for the first time.

2 Experimental

2.1 Experimental Design

For the first time two specialized analytical apparatus, a Metrohm 809.1 double burette auto-titrator and an Analytic Jena SPECORD® S600 UV-Vis diode-array spectrophotometer equipped with a quartz flow-through cuvette, were combined by means of a software program to work as a dedicated speciation apparatus. The jacketed reaction flask was thermostatically controlled at a fixed temperature of 25 °C employing a Julabo F12-ED refrigerated/heating circulator. It was now possible to automatically vary the ligand concentration over various intervals ensuring a very accurate and consistent set of absorbance data. A detailed schematic diagram is presented in Figure 1.

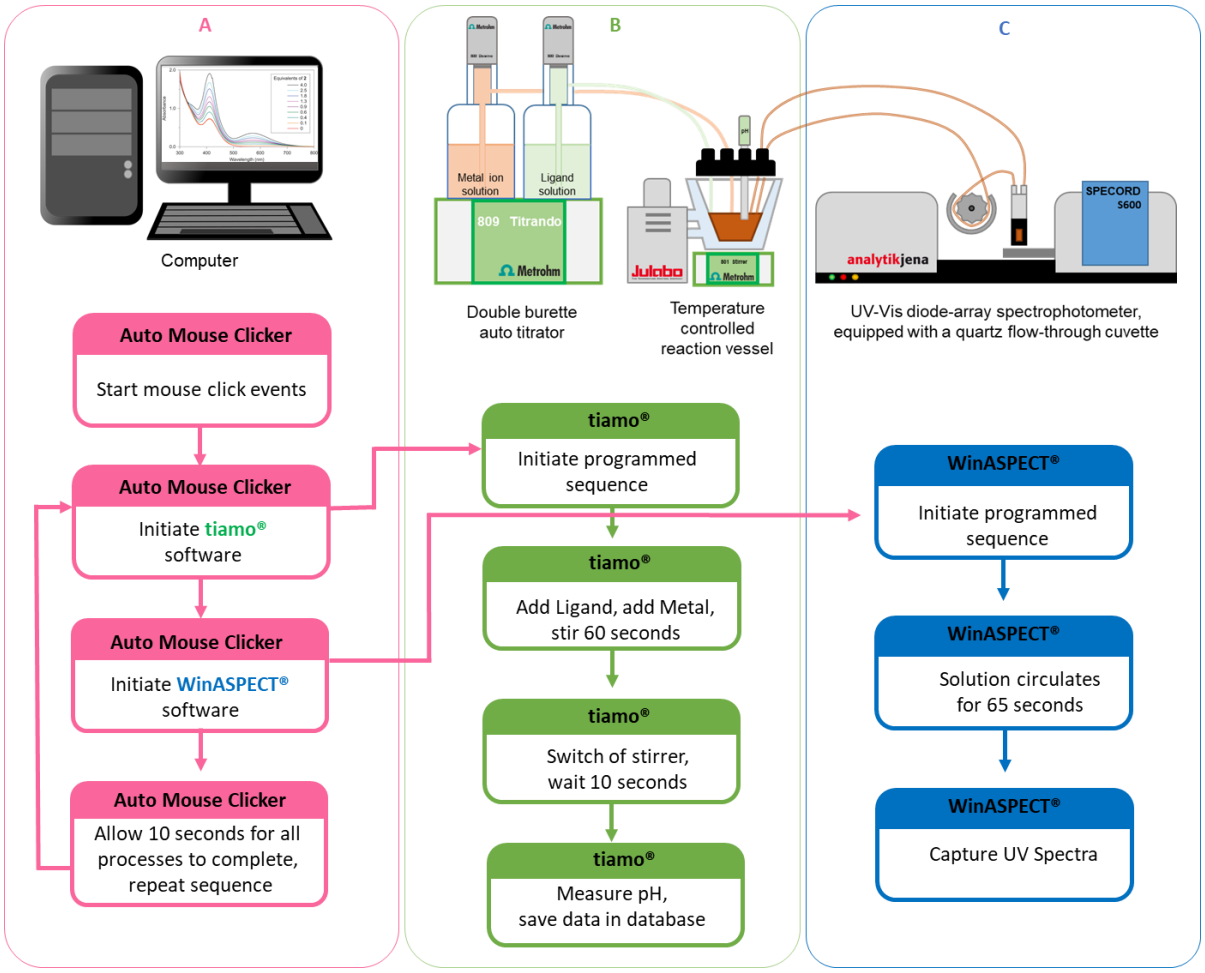

Figure 1: Detailed schematic diagram of the experimental procedure followed

The experimental procedure can be divided into three parts. Section A is represented by the computer and Auto Mouse Clicker software program. In section B the tiamo® software is in charge of controlling the Metrohm 809.1 double burette auto-titrator, which is responsible for the addition (dosing) of the

metal/ligand solutions, magnetic stirrer and the pH measurements. Finally, WinASPECT® controls the Analytic Jena SPECORD® S600 UV-Vis diode-array spectrophotometer as seen in C.

The Auto Mouse Clicker program (A) controls the other two software packages and once it is activated the procedure continues automatically. First, it will activate the tiamo software package (B), which will then continue executing the programmed sequence set. A short time interval of 5 seconds was set within the Auto Mouse Clicker program to ensure an adequate mixture of the solution inside the jacketed reaction flask before the WinASPECT® software is activated (C). The Analytic Jena SPECORD® S600 has a peristaltic pumping system (sipper) which circulates the solution from the reaction flask through the quartz flow-through cuvette. The time interval for the sipper system is controlled inside the WinASPECT® software and will execute before each UV measurement. The temperature of the reaction flask is controlled by setting a fixed temperature value on the Julabo F12-ED refrigerated/heating circulator.

The time intervals within all three software programs are set to ensure effective mixing in the reaction flask (B) and circulation of the solution through the flow-through cuvette (C). It also allows for the solution inside the reaction flask to settle for 10 seconds before the pH is measured (B). Once all the steps are completed, the procedure will be repeated as required.

The 809 Titrando high-end titrator has the option of connecting a large range of intelligent electrodes. In order to ensure accurate pH measurements, which is compulsory for determining the hydroxide concentration during the titration, the Metrohm Solitrode Pt 1000 electrode (6.0228.000) was employed. It was calibrated with standard pH buffers from Metrohm (4,7 and 9) before each titration. No special buffers or calibration was required as the pH range was between 4 and 13. Equilibrium is reached instantaneously as no further changes in the spectra of the solutions were observed over time. Spectra were recorded every 90 seconds in the wavelength range 200 – 500 nm for palladium(II) chloro-hydroxo mixed complexes and 240 – 550 nm for palladium(II) bromo-hydroxo mixed complexes against water as reference. For each speciation study a background titration that contained no palladium was done and the absorbance spectra was then subtracted from the original absorbance spectra. Competition of H^+ for Cl^- and Br^-, with the subsequent formation of HCl and HBr, are negligible in that the pK_a of HCl and HBr is -9.0 and -11.0 respectively [30].

For the $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) system absorption data at every wavelength (every 0.5 nm) from 220 nm to 320 nm (Table 1), within the pH range 4 – 12, were treated with the program HypSpec [29] to calculate the stability constants (β_n) and molar absorption spectra. As discussed and motivated earlier [9] the absorbance data below 220 nm were excluded from the calculations. For the $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) system absorption data at every wavelength (every 0.5 nm) between 240 nm and 425 nm (Table

1), coinciding with a pH range of 8 < pH < 12, were treated with the program HypSpec [29] to calculate stability constants and absorption spectra for the complexes. For the palladium(II) chloro-hydroxo speciation the number of datapoints (or concentration changes) increased to 71, compared to the earlier study that only investigated 17 concentration changes. For the palladium(II) bromo-hydroxo study a total of 80 concentration changes could be accommodated.

Table 1: Comparison of experimental conditions employed for $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) and $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4)

	$[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4)		$[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4)
	Cruywagen & Kriek [16]	This work	This work
Wavelength range (nm)	230 – 325	220 – 320	240 – 425
Wavelengths	32	220	370
Wavelength interval (nm)	3	0.5	0.5
Concentration changes	17	71	80
pH	4 < pH < 12	4 < pH < 12	8 < pH < 12

2.2 Solution preparation and titration

All reagents were of analytical grade and solutions were prepared with ultra-pure water obtained from a Millipore Milli-Q system. A stock solution of palladium(II), with a concentration of 3.0 x 10^{-3} M (confirmed by ICP analyses) in 1.0 M perchloric acid, was prepared [8]. From this stock solution, a palladium(II) chloride solution (6.0 x 10^{-5} M) was prepared by adding a suitable amount of NaCl (0.964 M total), while ensuring an ionic strength of 1.0 M. According to the stability constants previously published [9], palladium(II) chloride will be for all intents and purposes in the four-coordinated form, i.e. $[PdCl_4]^{2-}$. A 0.6 M sodium hydroxide solution, having an ionic strength of 1 M (by adding $NaClO_4$), was used to vary the pH for both chloride and bromide experiments.

An 80 mL sample of a palladium(II) chloride starting solution ($[Pd^{2+}]$ = 3 x10^{-5} M, $[Cl^-]$ = 0.482 M, I = 1.0 M) was added to the jacketed reaction flask that was thermostatically controlled at a fixed temperature of 25 °C (employing a Julabo F12-ED refrigerated/heating circulator). Equal amounts of the Palladium(II) chloride and sodium hydroxide solutions were dispensed from the double burette auto-titrator (see Figure 1), spread over 80 intervals, ensuring that both the palladium(II) and chloride concentration were constant throughout the titration. Initially, large amounts of both solutions (23 mL) had to be added to the palladium(II) chloride solution contained in the reaction vessel so as to ensure a significant change in the absorbance spectra. After this point was reached, small amounts (0.04 mL –

2.0 mL) were titrated simultaneously from both burettes in order to generate as many absorbance data as possible. A total of 2.40 mL of the 0.6 M NaOH solution was needed to vary the pH from 3.35 to 10.33 over 60 intervals and an additional 22 mL was spread over 20 intervals to obtain a maximum pH of 11.58.

For the palladium(II) bromo-hydroxo speciation 80 mL of a palladium(II) bromide starting solution ($[Pd^{2+}]$ = 3 x10^{-5} M, $[Br^{-}]$ = 0.482 M, I = 1.0 M) was added to the temperature-controlled reaction vessel. Once a noticeable change in the absorbance spectra was observed (26 mL) smaller amounts was titrated to again ensure the spread of a maximum number of data points over the desired pH range. A total of 1.6 mL of the 0.6 M NaOH solution was needed to vary the pH from 3.50 to 10.05, over 40 intervals, and an additional 32 mL was spread over 50 intervals to reach a maximum pH of 11.57.

2.3 Calculation of Stability Constants

The stability constants and molar absorbance spectra are determined from the spectrophotometric data by employing a software program HypSpec [29], which is specifically designed to derive equilibrium constants from spectrophotometric data and is part of the Hyperquad suit. The stability constants are calculated by a non-linear refinement process during which stability constant values are optimized. During the refinement three constraints are applied, i.e. the equations of mass-balance are always satisfied, the molar absorbance values are obtained by linear least-squares fitting of the absorbance values according to the Beer-lambert law: $A = l \Sigma \varepsilon c$, where c is a species concentration and the stability constants must have positive values. A measure of the overall quality of data refinement is indicated by the sigma (σ) value, which was explained as part of a previous publication [9].

In HypSpec a special convention is used for the hydroxide ion. Because of the self-ionization equilibrium ($H^+ + OH^- \rightleftharpoons H_2O$), HypSpec does not regard the hydroxide ion as a ligand, or competing species/reagent as is the case with the chloride ion (Cl^-). The amount of bound OH^- is determined from the pH-values, which points towards the free H^+ and free OH^- and are taken into consideration as per equations 2 – 4. For a general metal complex $[ML_n(OH)_{4-n}]$, where *M* is the metal, *L* the ligand and *n* the number of bonded ligands, we can write the following expression:

$$[ML_n(OH)_{4-n}] = \beta_{n,4-n}[M][L]^n[OH]^{4-n} \quad (2)$$

Since $[H^+][OH^-] = K_w$, and $[OH] = K_w[H]^{-1}$

$$[ML_n(OH)_{4-n}] = \beta_{n,4-n}[M][L]^n K_w^{4-n}[H]^{n-4} \quad (3)$$
$$= \beta_{n,4-n} K_w^{4-n} [M][L]^n [H]^{n-4}$$

$$= *\beta_{n,4-n}[M][L]^n[H]^{n-4} \quad (4)$$

The concentration of the hydroxide ion is now related to the concentration of the reagent H^+. Because of this convention the formation constants of hydrolysed species will appear to be on a different scale, which are reported in literature as log $*\beta$. For the two systems presented in this paper the relationship between log β (normally reported in literature) and log $*\beta$ are as follow:

$$\log *\beta_{n,\,4-n} = \log \beta_{n,4-n} + (4\text{-}n) \log K_w \quad (5)$$

Hyperquad Simulation and Speciation (HySS) software, which is also part of the Hyperquad suit, [31] was used to determine the ideal titration conditions with a model having been specified by defining a set of equilibrium constants (equation 2).

$$\beta_{pq}.. = [M_pL_q.] / ([M]^p[[L]^q..) \quad (6)$$

The titration was subsequently simulated by specifying a set of titration conditions and calculating the concentrations of each complex species as the titration proceeds. The optimised titration conditions obtained are then used to calculate the ideal concentrations for the different solutions.

In order to construct Pourbaix (E_h-pH) diagrams from the determined speciation data, HSC Chemistry® 6.0 (Outotec) was used. The enthalpy (H), entropy (S) and heat capacity (C_p) values of elements and compounds are stored in the database together with a variety of additional information. HSC Chemistry® also has the option to save additional species into its database to be used across all calculation modules.

3 Results and Discussion

3.1 Palladium(II) hydroxo-chloro complexation

The change in absorption spectra, with change in pH, is shown in Figure 2.

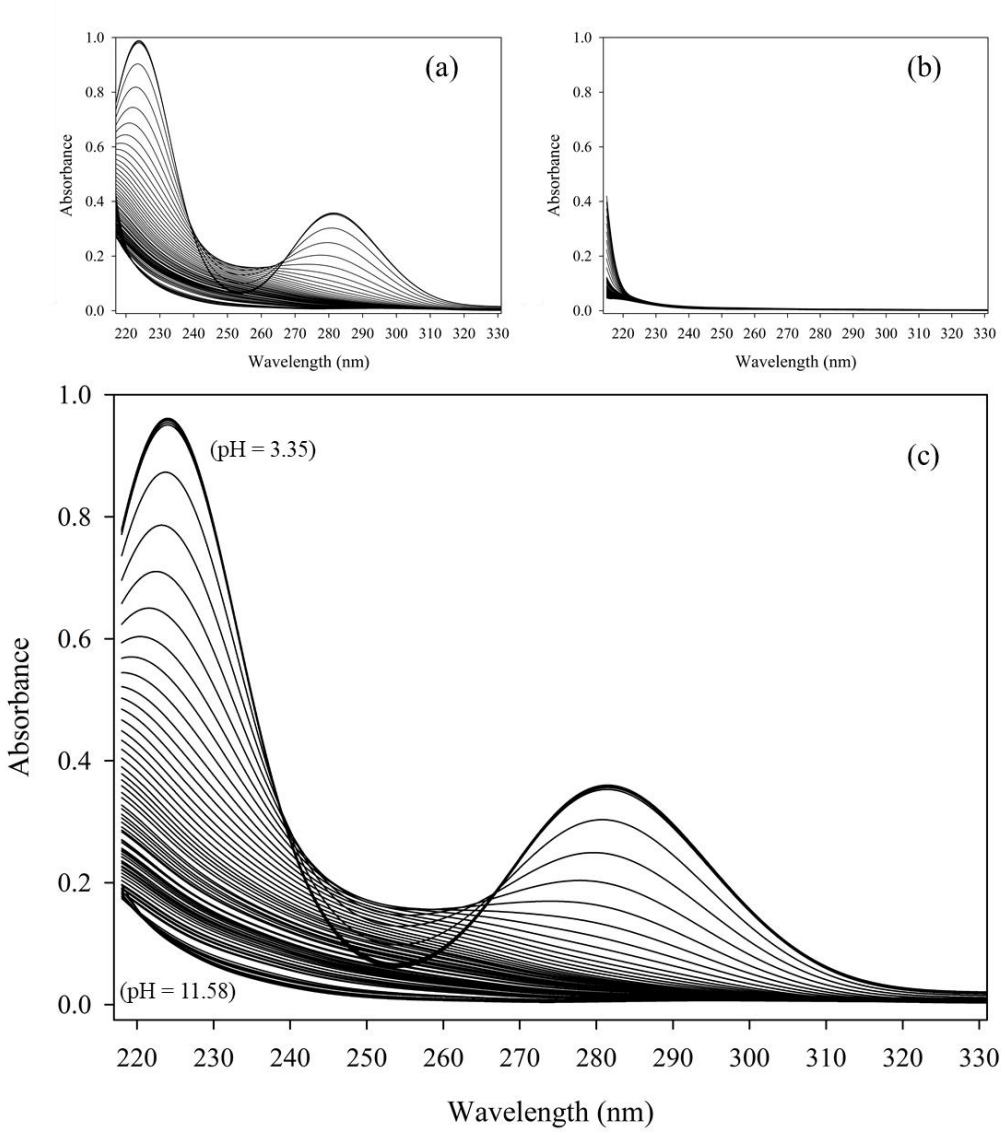

Figure 2: (a) Original absorption spectra, (b) background absorption spectra, and (c) final background subtracted absorption spectra with a change in pH for $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), ionic strength 1.0 M and 25 °C

Similar to results reported by Cruywagen and Kriek [16], noticeable changes in the absorbance spectra occurred at 224 nm and 282 nm. Employing the same model (as determined by Cruywagen and Kriek [16]) as initial input, together with the aid of HypSpec's factor analysis tool, as well as the fitting/correlation of the experimental and calculated data (Figure 3), it was ascertained that the same number of species were present. This also confirmed the dominance of the $[PdCl_4]^{2-}$ species at the start of the titration, and it was furthermore ascertained that the model did not change subsequent to including $[PdCl_3]^-$ as a known reagent, and it ($[PdCl_3]^-$) was subsequently excluded as a reagent from the final

model. Similar to previously published works [8, 9] the observed and calculated absorbance data, as a means of verifying the model, were compared at the above-mentioned wavelengths and excellent agreement was obtained (shown in Figure 3). This, in line with the small sigma (σ) value obtained, and the confirmation of the presence of four chloride complexes, supports the legitimacy of the proposed model.

Similar to previously published works [8, 9] the observed and calculated absorbance data, at the above-mentioned wavelengths, were compared. This excellent agreement, together with the small sigma (σ) value obtained, and the confirmation of the presence of four complexes, supports the legitimacy of the proposed model.

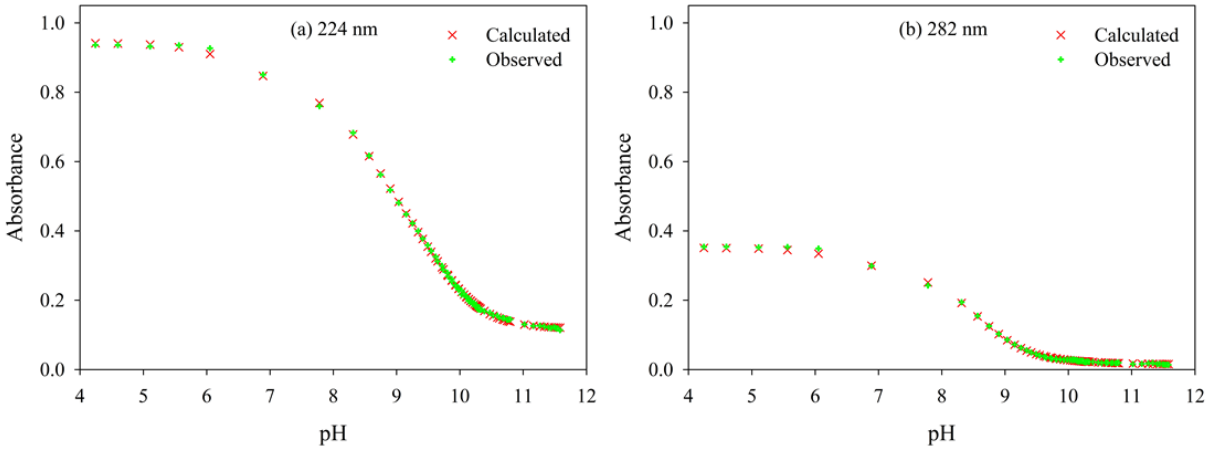

Figure 3: Observed vs calculated absorbance at specific wavelengths for $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4).

The calculated values of the cumulative stability constants for $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), as per the convention used by HypSpec, are displayed in Table 2. The titration was repeated three times and the average value converted as per equation 5 (pK_w = 13.74 for 1 M NaCl/$NaClO_4$ [32, 33]) to compare it to existing literature values (see discussion in Section 2.3).

Table 2: Stability constants for $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) at 1.0 M ionic strength and 25 °C

n	log $*\beta_n$ (Titration 1)	log $*\beta_n$ (Titration 2)	log $*\beta_n$ (Titration 3)	log $*\beta_n$ (Average)	log β_n ♦ (pK_w = 13.74)
0	-	-	-	-	11.54 ± 0.01 [9]
1	4.41 ± 0.01	4.67 ± 0.01	4.78 ± 0.02	4.62 ± 0.19	18.36 ± 0.19
2	-4.52 ± 0.01	-4.22 ± 0.01	-4.06 ± 0.02	-4.27 ± 0.74	23.21 ± 0.74
3	-14.72 ± 0.01	-14.17 ± 0.01	-14.04 ± 0.03	-14.31 ± 0.36	26.91 ± 0.36
4	-25.29 ± 0.02	-24.76 ± 0.07	-25.80 ± 0.13	-25.28 ± 0.52	29.68 ± 0.52
σ	3.13×10^{-3}	3.92×10^{-3}	7.31×10^{-3}	4.78×10^{-3}	4.78×10^{-3}

♦ **The data in the last column refer to Equation 2**

To date, the only other complete speciation study of mixed palladium(II) chloro-hydroxo complexes was that of Cruywagen and Kriek [16]. Van Middlesworth and Wood [24] determined the stability constants of various palladium(II) hydroxide and hydroxy-chloride complexes, typically present in seawater. They reported a stability constant (log β_1) for $[PdCl_3(OH)]^{2-}$ of = 18.36 at the same reaction conditions but by employing different solubility methods. When comparing the newly proposed values to that of Cruywagen and Kriek [16] one of the major differences is the value of log β_1 = 18.36 (this work) vs log β_1 = 16.48 [16]. Furthermore, the newly determined absorbance spectra (Figure 4) now includes data for the wavelength region 220 – 230 nm, which did not form part of the earlier investigation [16].

Similar to an earlier investigation on the complexation of palladium(II) with chloride and bromide [9], the experimental conditions employed for the present investigation were expressively more extensive so as to determine the best fit for the data and accurately calculate the formation constants and molar absorbances for the different mixed complexes (see Table 1). This includes a vast increase in the number of wavelengths employed, i.e. smaller wavelength intervals, as well as a substantial increase in the number of concentrations that were employed. This was made possible by accurately dispensing a minimum volume of 0.004 mL. A summary of the relevant calculated overall (β_n) formation constants is shown in Table 3. This investigation includes not only more absorbance spectra over the whole pH-range studied, but also more absorbance data at lower wavelengths (below 230nm). This results in a 2 – 3 order of magnitude difference in the newly determined overall formation constants (β_n) when compared to the previously determined values [16]. This is a direct result of an approximately two-order of magnitude difference in the first stepwise formation constant (K_1) for the formation of $[PdCl_3(OH)]^{2-}$ out of $[PdCl_4]^{2-}$ (Table 4). From Table 4 it is clear that the biggest difference is evident

for the first stepwise formation constant (K_1) as this work allowed for more data points in the low pH-value region where $[PdCl_3(OH)]^{2-}$ formed out of $[PdCl_4]^{2-}$. Although being slightly higher, subsequent stepwise formation constants (K_n), for n = 2 – 4, are in line with the earlier work. Our K_1-value is furthermore in line with the work of Van Middlesworth [24].

Table 3: Summary, and comparison with literature data, of overall stability constants (β_n) for mixed palladium(II) chloro-hydroxo complexes

Mixed Pd(II) chloro-hydroxo complexes				Literature	Experimental
$[PdCl_3(OH)]^{2-}$	$[PdCl_2(OH)_2]^{2-}$	$[PdCl(OH)_3]^{2-}$	$[Pd(OH)_4]^{2-}$	Reference	Conditions
16.12	-	-	26.4	[28]	25 °C, I = 0.75 M
18.23	-	-	-	[24]	25 °C, I = 1.0 M
-	-	-	26.4	[26]	17 °C, I = 0.1 M
16.48	20.63	24.02	26.23	[16]	25 °C, I = 1.0 M
18.36	23.12	26.91	29.68	This work	25 °C, I = 1.0 M

Table 4: Summary of stepwise formation constants (K_n) for mixed palladium(II) chloro-hydroxo complexes

Mixed Pd(II) chloro-hydroxo complexes					Literature
$[PdCl_4]^{2-}$	$[PdCl_3(OH)]^{2-}$	$[PdCl_2(OH)_2]^{2-}$	$[PdCl(OH)_3]^{2-}$	$[Pd(OH)_4]^{2-}$	Reference
11.54 [9]	6.69	-	-	-	[24]
11.54 [9]	4.94	4.15	3.39	2.21	[16]
11.54 [9]	6.82	4.76	3.79	2.77	This work

From Figure 4 it is evident that there is a considerable change in absorbance data values between 220 nm and 230 nm, as noticeable changes in the absorbance spectra occurred at 224 nm. In an effort to compare our data to that of Cruywagen and Kriek [16], absorbance data generated below 230 nm was excluded, which resulted in us not being able to obtain a refinement of the model or to conduct a manual fitting of the data. Although there was a slight difference in the stability constants of the three titrations, the trend was similar.

As chloride is substituted by hydroxide, with an associated increase in pH, a decrease in absorbance is evident due the shift in bands towards the shorter wavelengths

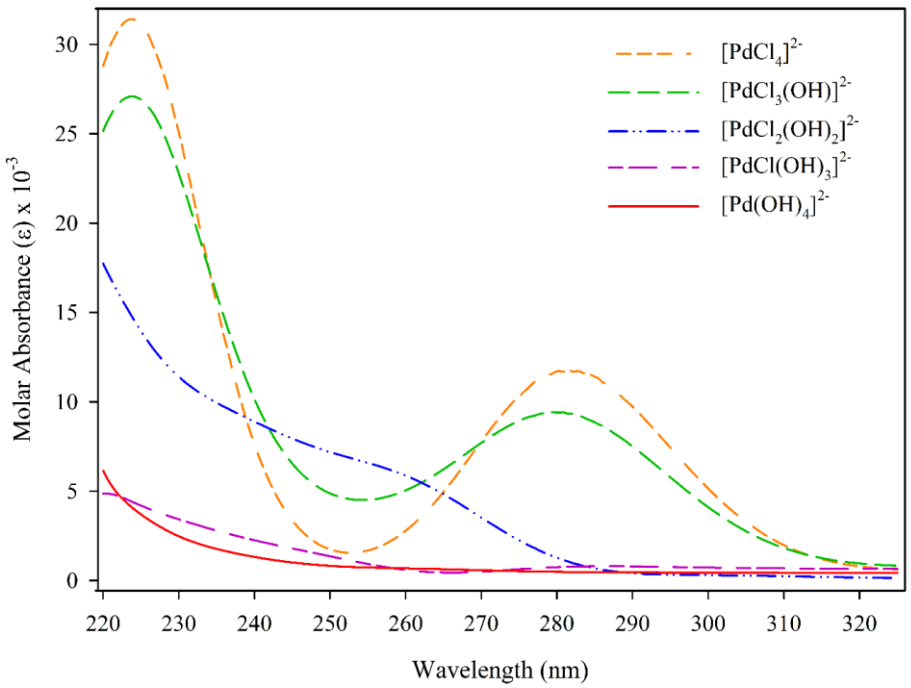

Figure 4: Calculated molar absorption spectra of $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4).

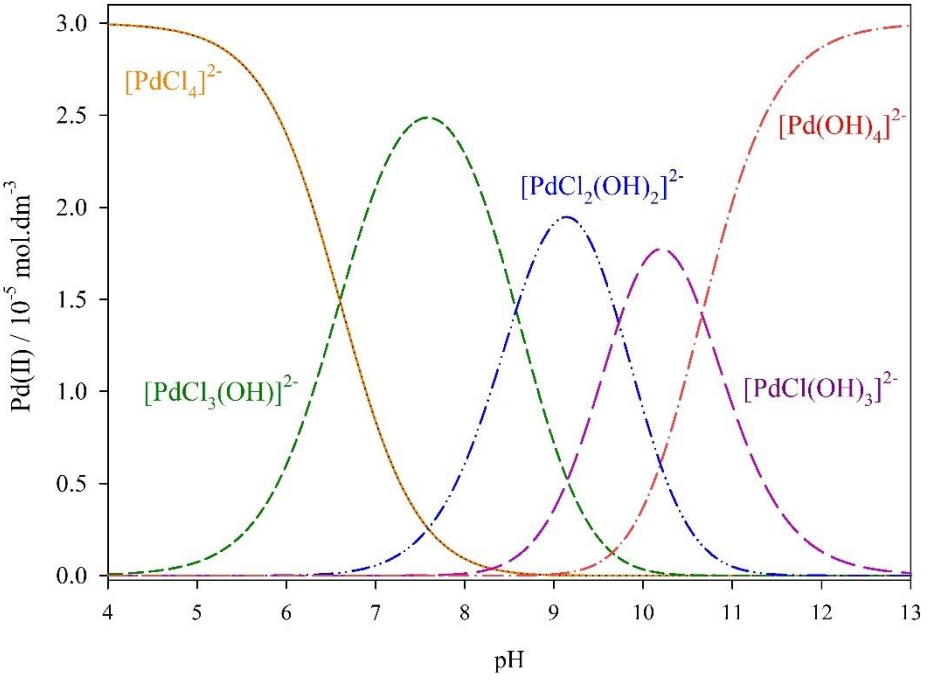

Figure 5: Distribution of $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) species as a function of pH at 25 °C. $[Pd^{2+}] = 3 \times 10^{-5}$ M, $[Cl^-] = 0.482$ M, ionic strength 1.0 M.

The software program HySS, which is part of the Hyperquad Suite, was used to calculate the distribution of the complexes from the newly determined formation constants (Table 3) as a function of pH and is shown in Figure 5. It is evident that $[PdCl_3(OH)]^{2-}$ is the most dominant mixed ligand complex at pH 6.5 – 8.5, which coincides with a study conducted by Van Middlesworth and Wood [24] on the stability of palladium(II) hydroxide and palladium(II) chloro-hydroxo complexes. This complex is present in the pH-range 5 – 10 and has its strongest presence at pH = 7.5. The other mixed complexes are dominant in the range 8 < pH < 11, after which palladium (II) hydroxide dominates at pH-values above 10.5.

Our newly determined stability constants for the mixed palladium(II) chloro-hydroxo complexes $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), together with the stability constants of the $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (n = 0 – 4) system that were determined earlier [9] were employed to calculate the Gibbs free energies of formation for each complex that was subsequently incorporated into the HSC Chemistry® 6.0 database and used to construct the Pourbaix diagram as shown in Figure 6.

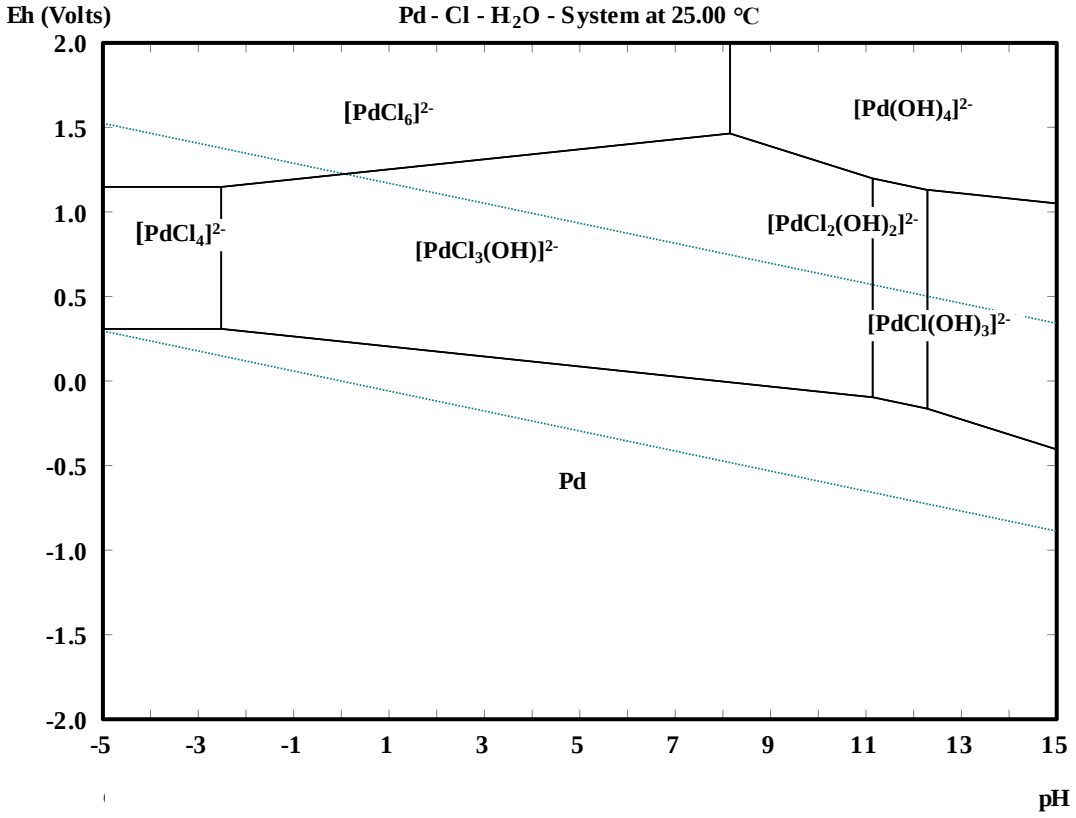

Figure 6: E_h-pH diagram for the Pd-Cl-H_2O system, ($[Pd^{2+}]$ = 1 mmol/ kg H_2O; $[Cl^-]$ = 1000 mol/kg H_2O), constructed employing new stability constants listed in Table 2 and reference [9]

3.2 Palladium(II) hydroxo-bromo complexation

The change in absorption spectra, with a change in pH, for mixed palladium(II) bromo-hydroxo complexes are shown in Figure 7. When the absorption spectra are compared to that of the palladium(II) chloro-hydroxo absorption spectra (Figure 2) it is evident that most of the changes in speciation took place in solutions of pH > 8. As a result, it was experimentally easier to obtain more data points as the majority of the changes in speciation took place after the neutralisation point of NaOH and $HClO_4$. Major peak changes occurred at 249 nm and 334 nm as the absorbance decreased with the substitution of bromide by hydroxide.

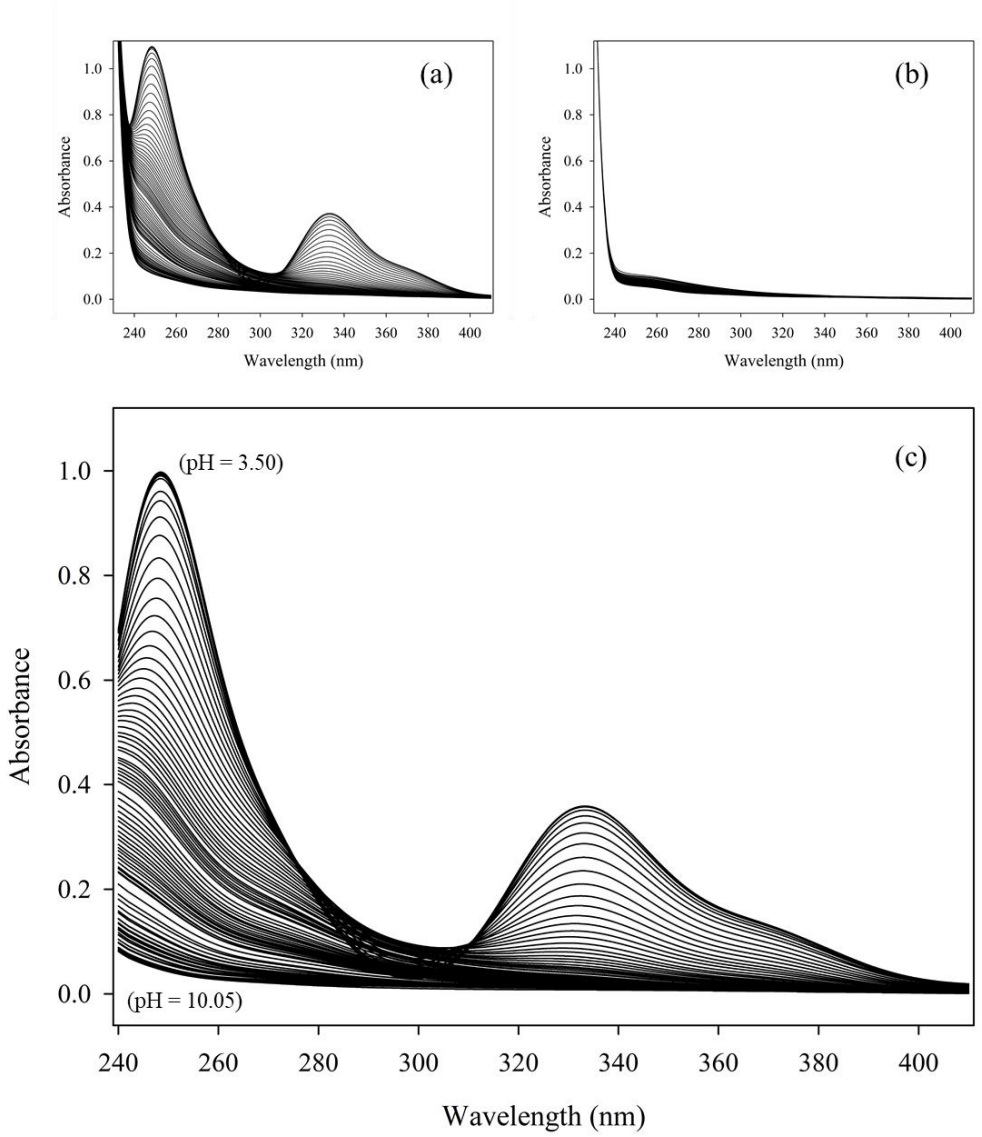

Figure 7: (a) Original absorption spectra, (b) background absorption spectra, and (c) final background subtracted absorption spectra with a change in pH for $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), ionic strength 1.0 M and 25 °C

Similar to the chloro-hydroxo investigation, the excellent agreement between the calculated and observed absorbances at these two wavelengths (Figure 8), together with the small sigma value after

successful refinement confirms the legitimacy of the proposed formation constants. The absorbance measurements below 240 nm were excluded from the calculations due to the high absorbance of bromide and hydroxide in this region [9, 17].

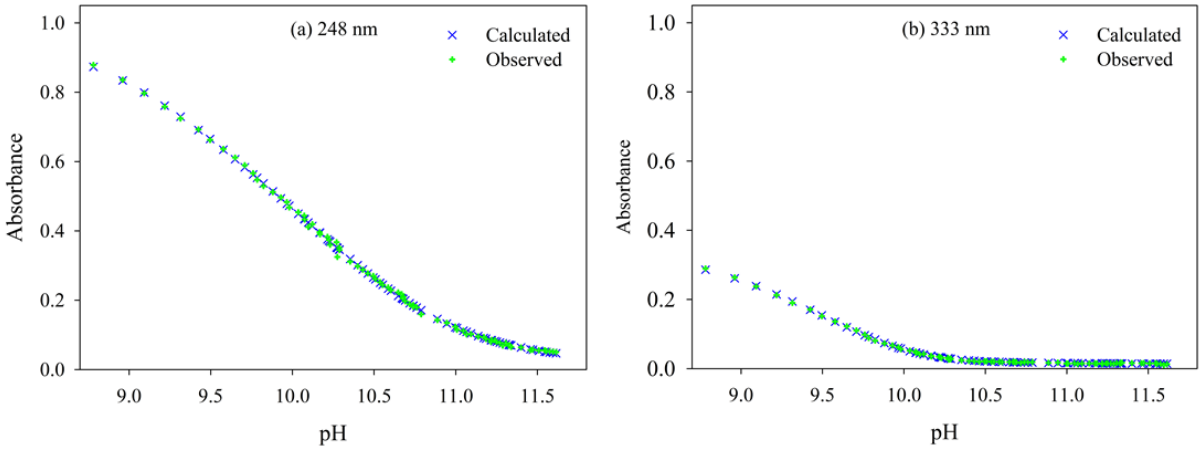

Figure 8: Observed vs calculated absorbance at specific wavelengths for $[Pd(OH)_{4-n}Br_n]^{2-}$ (n = 0 – 4)

The titration was repeated three times under the same conditions and the values of the cumulative formation constants for the complexes $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) are shown in Table 5 for the three individual titrations.

Table 5: Summary of overall stability constants for $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) at 1.0 M ionic strength and 25 ºC

n	log $*\beta_n$ (Titration 1)	log $*\beta_n$ (Titration 2)	log $*\beta_n$ (Titration 3)	log $*\beta_n$ (Average)	log β_n ♦ (pK_w = 13.745)
0	-	-	-	-	14.55± 0.01 [9]
1	5.01 ± 0.01	4.92 ± 0.01	5.01 ± 0.01	4.99 ± 0.05	18.73 ± 0.05
2	-5.20 ± 0.01	-5.37 ± 0.01	-5.20 ± 0.01	-5.24 ± 0.10	22.35 ± 0.10
3	-15.58 ± 0.02	-15.85 ± 0.02	-15.58 ± 0.02	-15.66 ± 0.16	25.58 ± 0.16
4	-26.39 ± 0.03	-26.76 ± 0.03	-26.37 ± 0.04	-26.51 ± 0.22	28.47 ± 0.22
σ	2.46 x 10^{-3}	2.46 x 10^{-3}	2.48 x 10^{-3}	2.47 x 10^{-3}	2.47 x 10^{-3}

♦ **The data in the last column refer to Equation 2**

This is, to date, the only available set of formation constants for $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4). The calculated molar absorbance spectra for the mixed palladium(II) bromo-hydroxo complexes are presented in Figure 9.

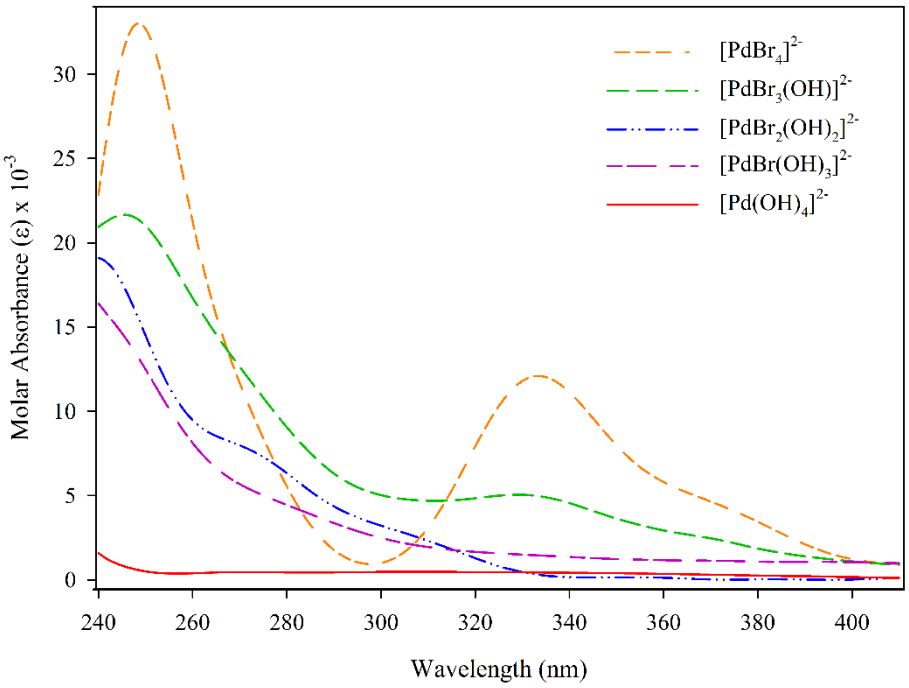

Figure 9: Calculated molar absorption spectra of $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4)

When the individual log β values of the palladium(II) chloro-hydroxo and the palladium(II) bromo-hydroxo are compared, it is evident that the log β values of the bromide system are slightly smaller than those of the chloride system. Bromide is a slightly stronger ligand than chloride [9] and as a result it will be more difficult for hydroxide to displace the bromide ion bonded in the palladium(II) complex. This is also the reason why most of the mixed palladium(II) bromo-hydroxo species only exist at higher pH values compared to that of the mixed palladium(II) chloro-hydroxo complexes.

From the formation constants, a distribution diagram was constructed showing the complete speciation of the $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) system as a function of concentration palladium(II) (Figure 10). From the distribution diagram, it is evident that $[PdBr_3(OH)]^{2-}$ is the dominant mixed palladium(II) bromo-hydroxo complex, similar to that of the palladium(II) chloro-hydroxo speciation.

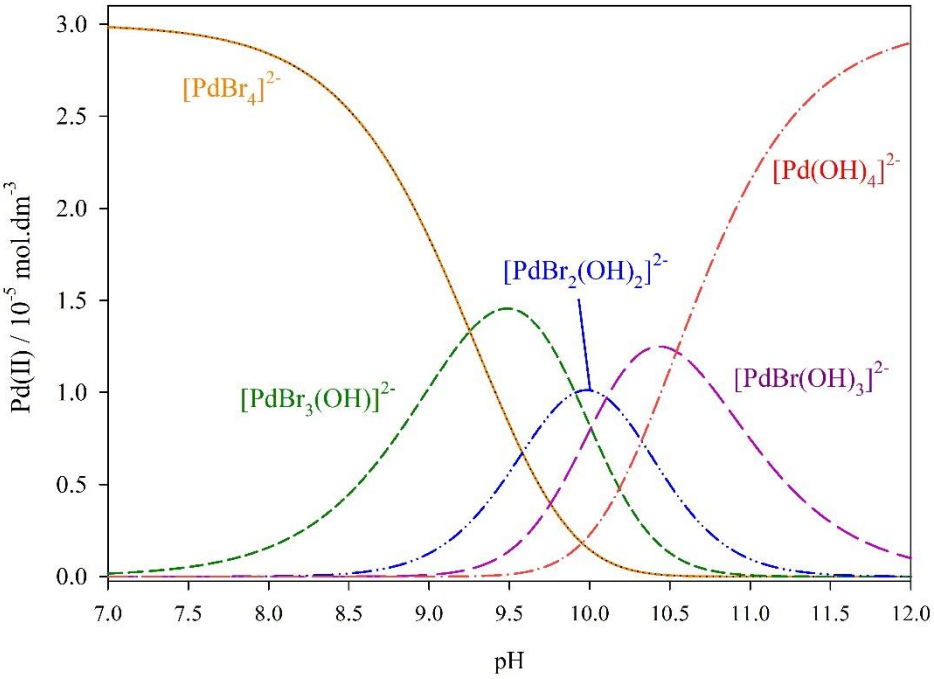

Figure 10: Distribution of $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) species as a function of pH at 25 °C. $[Pd^{2+}] = 3 \times 10^{-5}$ M, $[Br^-] = 0.482$ M, ionic strength 1.0 M

A Pourbaix diagram was also constructed for the Pd-Br-H_2O system (Figure 11) employing the newly determined stability constants. Previously, no speciation data existed for the mixed palladium(II) bromo-hydroxo complexes [10], however, with the introduction of the newly obtained stability constants one is now able to construct a more complete Pourbaix diagram including all of the mixed complexes. When the Pourbaix diagram of the palladium(II) bromo-hydroxo system is compared to that of the palladium(II) chloro-hydroxo system it is evident that $[PdBr_3(OH)]^{2-}$ has a smaller region of stability, while the mono bromide mixed complex, $[PdBr(OH)_3]^{2-}$ is more stable at higher pH values.

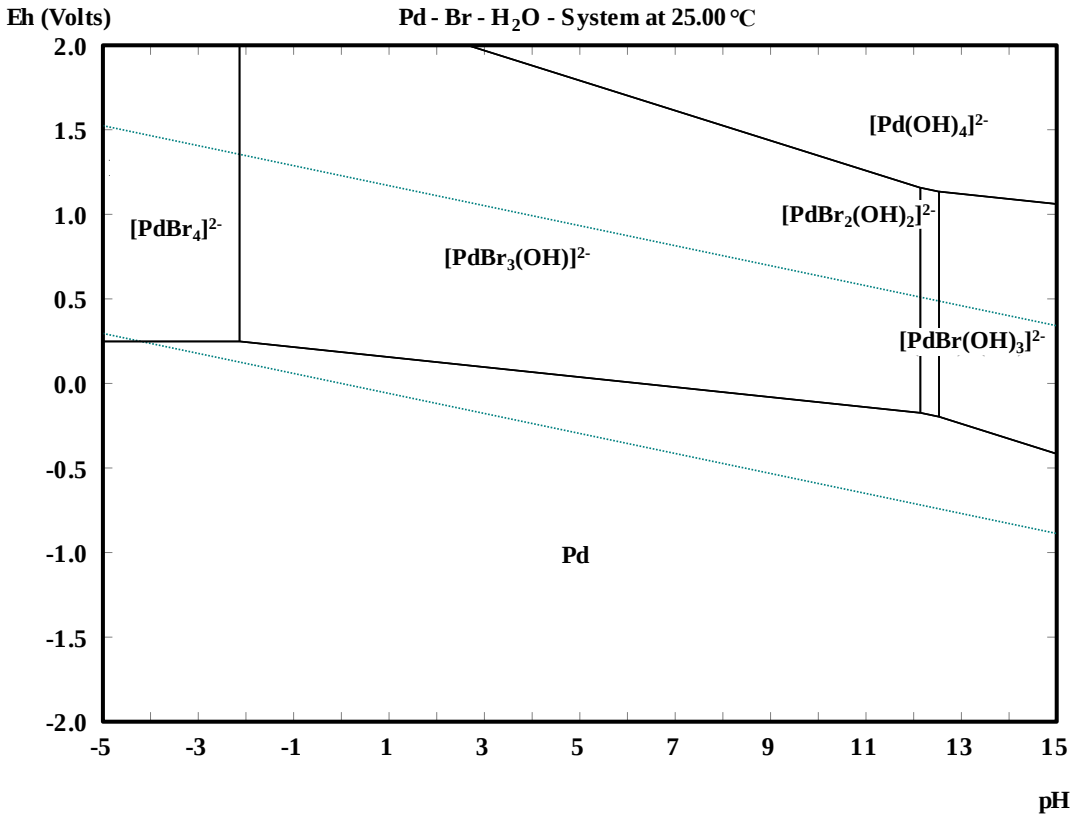

Figure 11: E_h-pH diagram for the Pd-Br-H_2O system, ([Pd^{2+}] = 1 mmol/ kg H_2O; [Br^-] = 10 mol/kg H_2O), constructed employing new stability constants listed in Table 4 and reference [9]

4 Conclusions

The average values determined for the stability constants, β_n, $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4), are: log β_1 = 18.36, log β_2 = 23.21, log β_3 = 26.91 and log β_4 = 29.68. These values differ somewhat from those published by Cruywagen and Kriek [16], but provides a refined model for the mixed palladium(II) chloro-hydroxo complexes. After the titration method was successfully applied to the palladium(II) chloro-hydroxo system, it was customised and applied to the palladium(II) bromo-hydroxo system, $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4). These stability constants are: log β_1 = 18.73, log β_2 = 22.25, log β_3 = 25.58 and log β_4 = 28.47, which represent the first known full set of stability constants for this system. Chloride is already used as a complexing agent for the leaching of the PGMs, and the refined stability constants for $[PdCl_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) provides a more precise model of this system. Should bromide be investigated as complexing agent for the leaching of the PGMs, a precise model for the $[PdBr_{4-n}(OH)_n]^{2-}$ (n = 0 – 4) is now available.

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