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Comparative geochemistries of Pd^{II} and Pt^{II}: Formation of mixed hydroxychloro and chlorocarbonato-complexes in seawater

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Abstract—Comparative observations of Pd^{II} and Pt^{II} hydrolysis in chloride solutions indicate that $[\text{PdCl}_3\text{OH}^{2-}]/[\text{PdCl}_4^{2-}]$ and $[\text{PtCl}_3\text{OH}^{2-}]/[\text{PtCl}_4^{2-}]$ concentration ratios in salinity 35 seawater ($S = 35$) are smaller than one at a typical surface ocean pH (~ 8.2), and are larger than one at pH = 8.2 when $S < 10$. The hydrolysis behaviors of PdCl_4^{2-} and PtCl_4^{2-} are very similar. In 0.5 M NaCl at 25°C the hydrolysis constant for both elements, written in the form $\beta_1^* = [\text{MCl}_3\text{OH}^{2-}][\text{Cl}^-][\text{H}^+][\text{MCl}_4^{2-}]^{-1}$, is $\log \beta_1^* = -8.97$. Between ionic strengths 0.3 M and 1.0 M for Pd^{II} and between 0.1 M and 1.0 M for Pt^{II}, $\log \beta_1^*$ is within approximately 0.1 units of the value appropriate to 0.5 M NaCl. This small dependence of PdCl_4^{2-} and PtCl_4^{2-} hydrolysis constants on ionic strength is consistent with predictions based on expected activity coefficient behavior.

Carbonate is observed to complex PdCl_4^{2-} significantly, but to a smaller extent than OH^- under conditions appropriate to seawater. Complexation of PtCl_4^{2-} by CO_3^{2-} was observed in this work but the rate of complexation was too slow to allow equilibrium observations. The principal dissimilarity between the chemistries of Pd^{II} and Pt^{II} in our investigation was the sharp contrast in observed Pd^{II} and Pt^{II} reaction rates. Differences in reaction kinetics may cause fractionation of Pd^{II} and Pt^{II} in the environment. The speciation of Pt^{II}, unlike Pd^{II}, is likely to be based on chemical environments experienced by Pt^{II} over a period of days, and perhaps weeks. Copyright © 2003 Elsevier Science Ltd

1. INTRODUCTION

The closely related solution chemistries of Pd^{II} and Pt^{II} make comparative investigations of these elements potentially useful for establishing relationships between fundamental chemical properties and geochemical behavior. The utility of comparative geochemical investigations using closely related elements is illustrated by the substantial body of work (e.g., Taylor and McLennan, 1988 and references therein; Byrne and Sholkovitz, 1996 and references therein) devoted to the rare earth elements (REEs), whose chemical properties vary subtly but systematically across a suite of fifteen elements. Although the use of Pd^{II} and Pt^{II} for comparative studies involves only two elements, the chemistries of these elements are quite distinct from the group chemistries of other elements used in comparative studies, hence these elements can also be expected to provide unique insights relating chemical properties and geochemical behavior.

The solution interactions of Pd^{II} and Pt^{II} are very strongly dominated by covalent bonding (Martell and Hancock, 1996; Cotton et al., 1999). Although associations of these elements with chloride are substantially weaker than their associations with many other electron donating ligands (Hancock et al., 1977), formation constants for PdCl_4^{2-} and PtCl_4^{2-} (Martell and Smith, 1982) indicate that the $[\text{Pd}^{2+}]/[\text{PdCl}_4^{2-}]$ concentration ratio in salinity 35 seawater ($S = 35$) is less than $10^{-10.5}$ and the $[\text{Pt}^{2+}]/[\text{PtCl}_4^{2-}]$ ratio is approximately 10^{-13} . As such, considering the subpicomolar concentrations of total Pd^{II} and Pt^{II} in seawater (Byrne, 2002), the concentrations of free Pd^{2+} and Pt^{2+} ions in seawater are no more than approximately $10^{-22.5}$ M and $10^{-25.6}$ M, respectively. The extent of compl-

exation of Pd^{II} and Pt^{II} in seawater is such that both elements are dominantly present with their maximum coordination number of four (e.g., PdCl_4^{2-} and PtCl_4^{2-}). In the presence of strongly covalent ligands with even greater covalent binding affinities than Cl^- (e.g., OH^- , HS^- , Br^- , I^-), potentially important species are expected to include mixed ligand complexes such as $\text{MCl}_3\text{OH}^{2-}$ (where M is Pd^{II} or Pt^{II}). While the importance of $\text{PdCl}_3\text{OH}^{2-}$ in seawater has been controversial (Kump and Byrne, 1989; Tait et al., 1991; Byrne and Kump, 1993; van Middlesworth and Wood, 1999), recent observations indicate that the $[\text{PdCl}_4^{2-}]/[\text{PdCl}_3\text{OH}^{2-}]$ concentration ratio in seawater ($S = 35$) is significantly larger than one (Byrne and Yao, 2000). This observation indicates that Pd^{II} speciation in seawater is comparatively simple because there is a relatively weak dependence on pH. Since the affinity of Pt^{II} for covalent ligands is generally greater than the affinity of Pd^{II} for such ligands (Hancock et al., 1977), and OH^- exhibits strong covalent bonding (Martell and Hancock, 1996), $\text{PtCl}_3\text{OH}^{2-}$ is potentially a more significant species than $\text{PdCl}_3\text{OH}^{2-}$ in seawater. The extent of $\text{PtCl}_3\text{OH}^{2-}$ formation in seawater has received less attention than the extent of $\text{PdCl}_3\text{OH}^{2-}$ formation and, therefore, is relatively poorly defined. Pd^{II} and Pt^{II} chemistries have not been directly compared under conditions relevant to seawater.

In the present work we provide, for the first time, direct comparative observations of the influence of ionic strength, chloride concentration, and pH on both Pd^{II} and Pt^{II} partitioning between MCl_4^{2-} and $\text{MCl}_3\text{OH}^{2-}$. As a second component of this work we have investigated the significance of carbonate as a ligand relevant to platinum group element (PGE) speciation. Our work is particularly pertinent to the behavior of Pd^{II} and Pt^{II} in estuaries. We note, in this context, that the distribution of Pd^{II} and Pt^{II} in the environment is undergoing a dramatic transformation. Whereas the PGEs are among the

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least abundant elements in the earth's crust (Cox, 1989), anthropogenic emissions have enriched roadside soils to an extent that recovery of PGEs in some locales is approaching economic viability (Ely et al., 2001). Estuaries and coastal environments can be anticipated to receive increasing PGE inputs in the future, and it should be expected that the strong affinity of PGEs for certain macroalgae (Yang, 1989) will be significantly influenced by solution speciation.

2. THEORY

The UV-visible absorbance of solutions containing Pd^{II} and Pt^{II} is a sum of contributions from chloride complexes and mixed complexes such as MCl₃X where X is, for example, either OH⁻ or CO₃²⁻. The absorbance contribution of each Pd or Pt solution complex can be written in the form

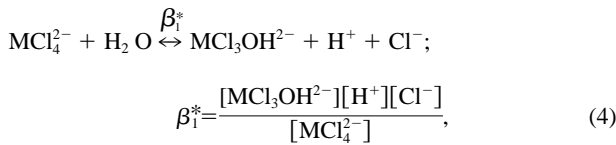
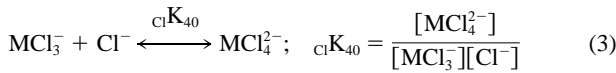
$$\lambda A_{ij} = \lambda \epsilon_{ij} [\text{MCl}_i \text{X}_j] \cdot \ell \quad (1)$$

where [MCl_iX_j] is the concentration of solution species MCl_iX_j, $\lambda \epsilon_{ij}$ is the molar absorptivity of solution species MCl_iX_j at wavelength λ , λA_{ij} is the absorbance of this species at wavelength λ , and ℓ represents optical path length. Under the conditions of this work, dominant solution species are MCl₃⁻, MCl₄²⁻, MCl₃OH²⁻ and MCl₃CO₃³⁻. Thus, at constant chloride concentration, the sum absorbance of all these species can be written as

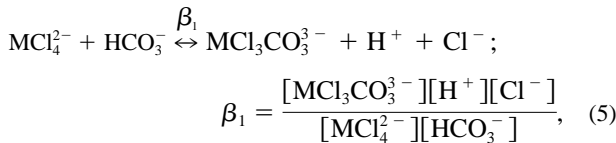
$$\lambda A = \sum \lambda A_{ij} = (\lambda \epsilon_{30} [\text{MCl}_3^-] + \lambda \epsilon_{40} [\text{MCl}_4^{2-}] + \lambda \epsilon_{31}^* [\text{MCl}_3\text{OH}^{2-}] + \lambda \epsilon_{31} [\text{MCl}_3\text{CO}_3^{3-}]) \cdot \ell \quad (2)$$

where $\lambda \epsilon_{40}$ is the molar absorptivity of MCl₄²⁻, $\lambda \epsilon_{30}$ is the molar absorptivity of MCl₃⁻, $\lambda \epsilon_{31}^*$ is the molar absorptivity of MCl₃OH²⁻ and $\lambda \epsilon_{31}$ is the molar absorptivity of MCl₃CO₃³⁻.

Using equilibrium constants for reactions involving MCl₄²⁻, MCl₃OH²⁻ and MCl₃CO₃³⁻:



and



total metal concentration in solution can be written as

$$M_T = [\text{MCl}_4^{2-}](1 + {}_{\text{Cl}}K_{40}^{-1}[\text{Cl}^-]^{-1} + \beta_1^*[\text{H}^+]^{-1}[\text{Cl}^-]^{-1} + \beta_1[\text{H}^+]^{-1}[\text{HCO}_3^-][\text{Cl}^-]^{-1}) \quad (6)$$

Similarly, using Eqn. 2 through 5, the absorbance of either Pd^{II} or Pt^{II} in solution can be written as

$$\begin{aligned} \lambda A = \ell \cdot [\text{MCl}_4^{2-}] & (\lambda \epsilon_{40} \\ & + \lambda \epsilon_{30} {}_{\text{Cl}}K_{40}^{-1}[\text{Cl}^-]^{-1} + \lambda \epsilon_{31}^* \beta_1^*[\text{H}^+]^{-1}[\text{Cl}^-]^{-1} \\ & + \lambda \epsilon_{31} \beta_1[\text{H}^+]^{-1}[\text{HCO}_3^-][\text{Cl}^-]^{-1}) \quad (7) \end{aligned}$$

Finally, combining Eqn. 6 and (7), λA is written as

$$\frac{\lambda A}{\ell \cdot M_T} = \frac{(\lambda \epsilon_{40} + \lambda \epsilon_{30} {}_{\text{Cl}}K_{40}^{-1}[\text{Cl}^-]^{-1} + \lambda \epsilon_{31}^* \beta_1^*[\text{H}^+]^{-1}[\text{Cl}^-]^{-1} + \lambda \epsilon_{31} \beta_1[\text{H}^+]^{-1}[\text{HCO}_3^-][\text{Cl}^-]^{-1})}{(1 + {}_{\text{Cl}}K_{40}^{-1}[\text{Cl}^-]^{-1} + \beta_1^*[\text{H}^+]^{-1}[\text{Cl}^-]^{-1} + \beta_1[\text{H}^+]^{-1}[\text{HCO}_3^-][\text{Cl}^-]^{-1})} \quad (8)$$

At sufficiently low pH the solution concentrations of MCl₃OH²⁻ and MCl₃CO₃³⁻ are negligible. Consequently the observed absorbance at low pH (λA^0) is given as

$$\frac{\lambda A^0}{\ell \cdot M_T} = \frac{\lambda \epsilon_{40} + \lambda \epsilon_{30} {}_{\text{Cl}}K_{40}^{-1}[\text{Cl}^-]^{-1}}{1 + {}_{\text{Cl}}K_{40}^{-1}[\text{Cl}^-]^{-1}} \quad (9)$$

Eqn. 8 and (9) can then be combined to yield the following equation

$$\frac{\lambda A^0}{\lambda A} = \frac{1 + B_1^*[\text{Cl}^-]^{-1}[\text{H}^+]^{-1} + B_1[\text{Cl}^-]^{-1}[\text{H}^+]^{-1}[\text{HCO}_3^-]}{1 + \lambda C_1^*[\text{Cl}^-]^{-1}[\text{H}^+]^{-1} + \lambda C_1[\text{Cl}^-]^{-1}[\text{H}^+]^{-1}[\text{HCO}_3^-]} \quad (10)$$

where

$$\lambda C_1^* = \lambda \epsilon_{31}^* \beta_1^* (\lambda \epsilon_{40} + \lambda \epsilon_{30} {}_{\text{Cl}}K_{40}^{-1}[\text{Cl}^-]^{-1})^{-1} \quad (11)$$

$$\lambda C_1 = \lambda \epsilon_{31} \beta_1 (\lambda \epsilon_{40} + \lambda \epsilon_{30} {}_{\text{Cl}}K_{40}^{-1}[\text{Cl}^-]^{-1})^{-1} \quad (12)$$

$$B_1^* = \beta_1^* (1 + {}_{\text{Cl}}K_{40}^{-1}[\text{Cl}^-]^{-1})^{-1} \quad (13)$$

and

$$B_1 = \beta_1 (1 + {}_{\text{Cl}}K_{40}^{-1}[\text{Cl}^-]^{-1})^{-1}. \quad (14)$$

Inspection of Eqn. 4, 5, 13 and 14 shows that the formation constants β_1^* and β_1 differ from B_1^* and B_1 in that the former directly provide ratios in the form [MCl₃OH²⁻]/[MCl₄²⁻] and [MCl₃CO₃³⁻]/[MCl₄²⁻] while the latter are expressed in terms of concentration ratios written as [MCl₃OH²⁻]/([MCl₄²⁻] + [MCl₃⁻]) and [MCl₃CO₃³⁻]/([MCl₄²⁻] + [MCl₃⁻]). Thus, the formation constants B_1^* and B_1 are smaller than β_1^* and β_1 (Eqn. 4 and 5) by the ratio [MCl₄²⁻]/([MCl₄²⁻] + [MCl₃⁻]). At high chloride concentrations [MCl₄²⁻] >> [MCl₃⁻] and $\beta_1^* \approx B_1^*$.

Bicarbonate concentrations were calculated from [H⁺] and total inorganic carbon (added as NaHCO₃) using the following relationship

$$[\text{HCO}_3^-] = \frac{C_T}{([\text{H}^+]/K_1' + 1 + K_2'/[\text{H}^+])} \quad (15)$$

where C_T is the sum concentration of all forms of inorganic carbon in the solution ($C_T = [\text{CO}_2] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$), and K_1' and K_2' are defined as

$$K_1' = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2] + [\text{H}_2\text{CO}_3]} \quad (16)$$

and

$$K'_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (17)$$

Equilibrium constants, K'_1 and K'_2 , appropriate to NaCl solutions in this work were taken from Dyrssen and Hansson (1972–1973).

Similar mathematical developments can be used to show that the ultraviolet absorbance of Pd^{II} at low pH can be described in terms of MCl_4^{2-} , MCl_3^- , and MCl_2^0 absorbance contributions with the following equation:

$$\lambda a = \frac{\lambda A}{\ell \cdot [Pd^{II}]_T} = \frac{\lambda \epsilon_{20} + \lambda \epsilon_{30}(c_1 K_{30}[Cl^-]) + \lambda \epsilon_{40}(c_1 K_{30})(c_1 K_{40}[Cl^-]^2)}{1 + (c_1 K_{30}[Cl^-]) + (c_1 K_{30})(c_1 K_{40}[Cl^-]^2)} \quad (18)$$

where $\lambda \epsilon_{20}$ is the molar absorptivity of MCl_2^0 , $\lambda \epsilon_{30}$ is the molar absorptivity of MCl_3^- , $\lambda \epsilon_{40}$ is the molar absorptivity of MCl_4^{2-} , and the equilibrium constants $c_1 K_{30}$ and $c_1 K_{40}$ are defined as:

$$c_1 K_{n0} = \frac{[MCl_n^{2-n}]}{[MCl_{n-1}^-][Cl^-]} \quad (19)$$

Whereas molar absorptivities are insensitive to medium composition at constant temperature, our determinations of $c_1 K_{40}$ variation with ionic strength using Eqn. 18, adopted the $PdCl_4^{2-}$, $PdCl_3^-$, and $PdCl_2^0$ molar absorptivities ($\lambda = 279$ nm) determined by Elding (1972) at 25°C in 1.00 mol/L NaCl: $\lambda \epsilon_{40} = 10500 \text{ cm}^{-1} \text{ M}^{-1}$, $\lambda \epsilon_{30} = 1500 \text{ cm}^{-1} \text{ M}^{-1}$, $\lambda \epsilon_{20} = 465 \text{ cm}^{-1} \text{ M}^{-1}$. In addition, since the equilibrium constant $c_1 K_{30}$ describes an isocoulombic reaction ($MCl_2^0 + Cl^- \rightleftharpoons MCl_3^-$), $c_1 K_{30}$ is expected to be only weakly dependent on ionic strength. Since $PdCl_2^0$ is a minor species under the conditions of our experiments, the $c_1 K_{30}$ value of Elding (1972) was assumed constant ($c_1 K_{30} = 260 \text{ M}^{-1}$) in this work for ionic strengths between 0.10 mol/L and 1.0 mol/L. $c_1 K_{40}$ was then determined using Eqn. 18 rearranged as follows:

$$c_1 K_{40} = \frac{\epsilon_{20}(c_1 K_{30}[Cl^-])^{-1} + \lambda \epsilon_{30} - \lambda a(c_1 K_{30}[Cl^-])^{-1} - \lambda a}{(\lambda a - \lambda \epsilon_{40})[Cl^-]} \quad (20)$$

3. MATERIAL AND METHODS

Ultraviolet absorbance spectra of Pd^{II} and Pt^{II} were obtained using a HP 8453 diode array spectrometer (Hewlett Packard, Palo Alto, CA). A 10 cm open-top quartz cell and a closed 1-cm quartz cell were used to obtain absorbance spectra between 200 and 400 nm. Solutions were kept at constant temperature ($25 \pm 0.1^\circ\text{C}$) using a thermocooler (Neslab, Portsmouth, NH) and a water-jacketed spectrophotometric cell holder. Solution pH was measured with an Orion glass-body, standard bulb combination pH electrode (model 81–02) connected to an Orion model 720A pH meter in the absolute mV mode. Total carbon in sample solutions was measured with a CM 5130 coulometer (UIC Inc., Binghamton, NY).

Sodium chloride, sodium perchlorate and sodium borate decahydrate were obtained from Sigma (St. Louis, MO). Pd^{II} and Pt^{II} were obtained as $PdCl_2^0$ (99.999%) and K_2PtCl_4 (99.99%) from Aldrich (Milwaukee, WI). Sodium bicarbonate, hydrochloric acid and sodium hydroxide were obtained from J.T. Baker (Phillipsburg, NJ), and boric acid was from Fisher Scientific (Pittsburgh, PA).

Palladium and platinum experiments were performed over a range of chloride concentrations between 0.1 mol/L and 1.0 mol/L, and over a range of pH between 3.0 and 8.5. Solution pH was measured on the free

hydrogen ion concentration scale. The pH electrode was calibrated via titrations of unbuffered NaCl solutions with standardized HCl. Nernstian electrode behavior was observed for each background electrolyte solution used in this work.

Palladium experiments were conducted in an open-top 10 cm quartz cell. NaCl solutions containing Pd^{II} were titrated with HCl and a mixed titrant consisting of sodium bicarbonate and sodium hydroxide. The absorbance and pH of solutions containing $1 \times 10^{-5} \text{ M Pd}^{II}$ were measured concurrently. Background electrolytes were 1.0 mol/L NaCl, 0.7 mol/L NaCl, 0.5 mol/L NaCl, 0.3 mol/L NaCl, and 0.1 mol/L NaCl. Solutions used for measurement of absorbance baselines were identical to experimental solutions but contained no Pd or Pt. Two types of experiments were performed using Pd. In the first, HCO_3^- concentrations were equal to or less than $3 \times 10^{-4} \text{ M}$. In the second, HCO_3^- concentrations were equal to approximately 0.03 mol/L.

Platinum experiments were conducted in a closed, 1 cm quartz cell. Pt^{II} hydrolysis constants were obtained using solutions composed of $1 \times 10^{-4} \text{ M Pt}^{II}$, 0.001 M $Na_2B_4O_7 \cdot 10H_2O$, and $B(OH)_3$ at concentrations between 0.0026 mol/L and 0.024 mol/L. UV spectra were obtained as a function of pH after equilibration periods of 24, 48 and 96 h. Background NaCl concentrations in this investigation were 1.0 mol/L NaCl, 0.5 mol/L NaCl and 0.1 mol/L NaCl. These experiments were very similar to those conducted for Pd^{II}, except that equilibration periods were on the order of 48 to 96 h. Platinum carbonate complexation experiments were conducted in 0.5 mol/L NaCl plus 0.03 mol/L $NaHCO_3$ with Pt^{II} concentrations equal to $1 \times 10^{-4} \text{ M}$. Observations of Pt absorbances at 260nm, where $PtCl_6^{2-}$ absorbs strongly (Gammons, 1996) indicated that conversion of Pt^{II} to Pt^{IV} was insignificant under our experimental conditions.

Pd experiments used to examine $PdCl_4^{2-}/PdCl_3^-$ partitioning (i.e., determination of $c_1 K_{40}$ in Eqn. 20) were performed in a closed 1-cm quartz cell at low pH. In these experiments two solutions, 0.04 mol/L HCl and 0.04 mol/L HCl plus 0.96 mol/L $NaClO_4$, each containing $1 \times 10^{-4} \text{ M Pd}^{II}$, were combined and absorbance spectra were observed at constant Cl^- concentrations as a function of ionic strength ($0.11 \leq I \leq 1.0 \text{ mol/L}$).

Data analyses were performed using SAS/STAT version 8.02 (1999–2000). Non-linear least squares analyses for determination of B_1^* and B_1 were obtained using Equation 10 at constant chloride concentration. Absorbance ratios ($\lambda A^\circ/\lambda A$) were used as the dependent variable, while $[H^+]^{-1}$ and $[HCO_3^-]$ were used as independent variables. Subsequently, the formation constants defined in Equations 4 and 5, (β_1^* and β_1) were calculated using Equations 13 and 14 and MCl_2^0 stability constants ($c_1 K_{40}$) appropriate to each ionic strength. Pd analyses were conducted using absorbance data at $\lambda = 279$ and Pt analyses utilized absorbance data at $\lambda = 230$ nm.

4. RESULTS AND DISCUSSION

Figure 1 shows palladium spectra obtained in 0.5 mol/L NaCl between pH 4.0 and 8.2. The absorbance peak at $\lambda = 279$ nm is dominantly due to the absorbance contributions of $PdCl_4^{2-}$. The observed decrease in absorbance at 279 nm with increasing pH indicates that $PdCl_3OH^{2-}$ does not absorb strongly at this wavelength. The observed (Fig. 2) linearity of $\lambda A^\circ/\lambda A$ vs. $[H^+]^{-1}$ at low HCO_3^- concentrations ($[HCO_3^-] \leq 3 \times 10^{-4} \text{ M}$) indicates that Equation 10 can be simplified by setting λC_1^* and $\lambda C_1[HCO_3^-]$ equal to zero.

$$\frac{\lambda A^\circ}{\lambda A} = 1 + B_1^*[Cl^-]^{-1}[H^+]^{-1} \quad (21)$$

In contrast to the linear plots of $\lambda A^\circ/\lambda A$ vs. $[H^+]^{-1}$ data obtained at low HCO_3^- concentrations (Fig. 2), $\lambda A^\circ/\lambda A$ vs. $[H^+]^{-1}$ data obtained at high HCO_3^- concentrations (0.03 M) were clearly non-linear. The observed non-linearity at high HCO_3^- concentrations indicates that $\lambda C_1[HCO_3^-]$ is non-zero, whereupon terms containing λC_1 can not be neglected unless

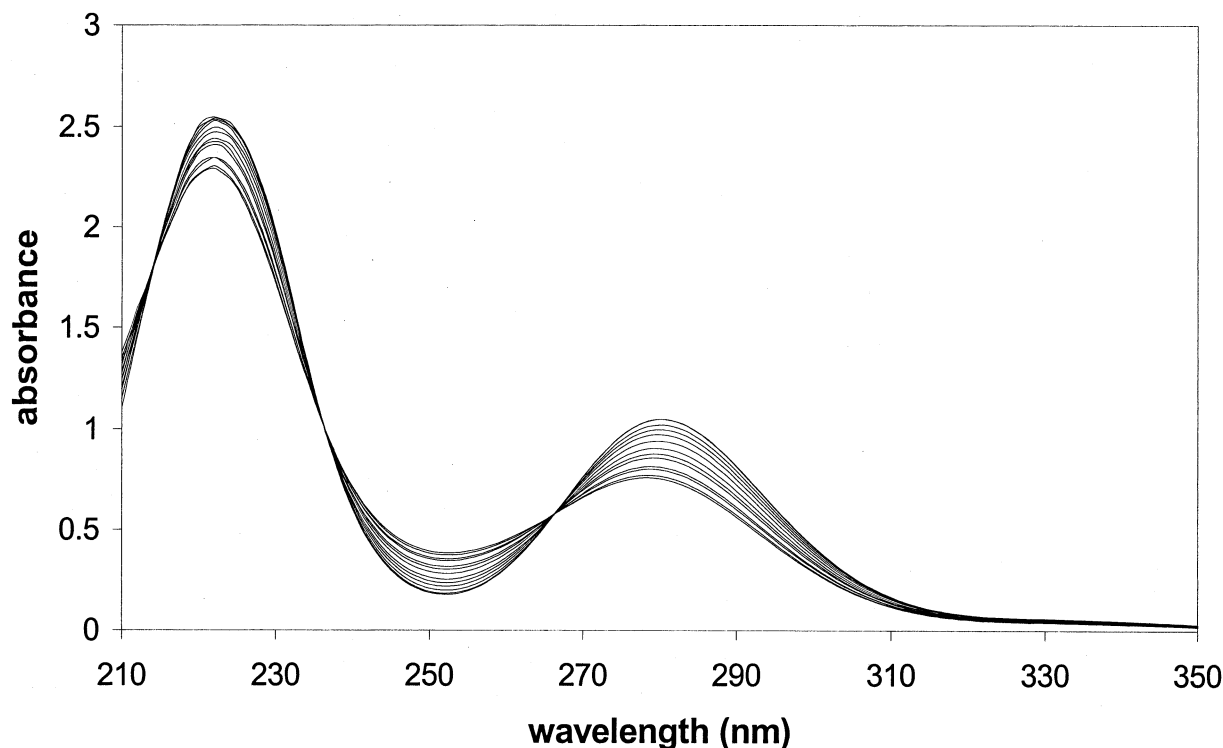


Fig. 1. Palladium absorbance spectra in 0.5 mol/L NaCl (25°C) for pH between 3.0 and 8.2.

$[\text{HCO}_3^-]$ is very small. With λC_1^* set equal to zero, the simplified form of Equation 10 used in our data analysis is given as:

$$\frac{\lambda A^\circ}{\lambda A} = \frac{1 + B_1^*[\text{Cl}^-]^{-1}[\text{H}^+]^{-1} + B_1[\text{Cl}^-]^{-1}[\text{H}^+]^{-1}[\text{HCO}_3^-]}{1 + \lambda C_1[\text{Cl}^-]^{-1}[\text{H}^+]^{-1}[\text{HCO}_3^-]} \quad (22)$$

$\lambda A^\circ/\lambda A$ vs. $[\text{H}^+]^{-1}$ data at low HCO_3^- concentrations were analyzed by using Eqn. 21 to obtain an initial estimate for B_1^* .

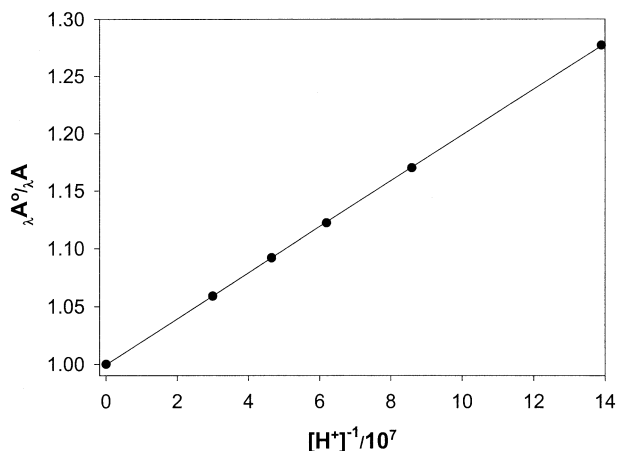


Fig. 2. Pd absorbance behavior ($\lambda = 279$ nm) at low bicarbonate ion concentrations in 0.5 mol/L NaCl at 25°C. The linearity in plots of $\lambda A^\circ/\lambda A$ vs. $[\text{H}^+]^{-1}$ shows that species such as $\text{Pd}(\text{OH})_2^0$ and $\text{PdCl}_2(\text{OH})_2^{2-}$, whose concentrations would be proportional to $[\text{H}^+]^{-2}$, are not significant under the experimental conditions used in our work.

Subsequently, in non-linear least squares analyses, Equation 22 was used iteratively on high HCO_3^- data sets to obtain B_1 and on low HCO_3^- data sets to determine B_1^* . In fits of data at high HCO_3^- concentrations the parameter B_1^* was held constant (i.e., the average of four B_1^* results obtained using low HCO_3^- data). During each fit of data at low HCO_3^- concentrations, estimates of B_1 and λC_1 obtained in the previous iteration were held constant (i.e., the average two B_1 and λC_1 results obtained using high HCO_3^- data). The self-consistent $B_1^*(\text{Pd})$ and $B_1(\text{Pd})$ data obtained in these analyses are given in Table 1. λC_1 is not of thermodynamic interest and consequently is not shown here. This information, however, is provided in Cosden (2002) along with compilations of all primary data.

In contrast to Pd, the complexation kinetics of Pt are quite slow. Our observations indicated that somewhat more than 24 h were required for equilibration of PtCl_4^{2-} and $\text{PtCl}_3\text{OH}^{2-}$. Figure 3 shows $\lambda A^\circ/\lambda A$ vs. $[\text{H}^+]^{-1}$ data obtained for Pt^{II} after 48 and 96 h of equilibration. Based on our observations of λA vs. time, four days were allowed for equilibration in Pt hydrolysis experiments. At equilibrium, our $\lambda A^\circ/\lambda A$ vs. $[\text{H}^+]^{-1}$ data for Pt at $\lambda = 230$ nm were linear at high NaCl concentrations and slightly non-linear at lower NaCl concentrations. As such, the following equation was used for determination of $B_1^*(\text{Pt})$.

$$\frac{\lambda A^\circ}{\lambda A} = \frac{1 + B_1^*[\text{Cl}^-]^{-1}[\text{H}^+]^{-1}}{1 + \lambda C_1^*[\text{Cl}^-]^{-1}[\text{H}^+]^{-1}} \quad (23)$$

No terms for carbonate complexation are included in Equation 23 because $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$ was used as a buffer in all Pt^{II} hydrolysis experiments. Ancillary experiments at high $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$ concentrations indicated that, due to kinetic and/or

Table 1. $B_1^*(\text{Pd})$ and $B_1(\text{Pd})$ determinations in NaCl at 25°C. The uncertainties listed for average $B_1^*(\text{Pd})$ results at each ionic strength indicate the standard deviation of the mean. The uncertainties listed for average $B_1(\text{Pd})$ results depict the range of two measurements at each ionic strength.

| Medium | $B_1^*(\text{Pd})$ | $B_1(\text{Pd})$ |
|--------------|---|--|
| 0.105 M NaCl | $(9.39 \pm 0.27) \times 10^{-10}$ | $(1.02 \pm 0.17) \times 10^{-7}$ |
| | $(1.03 \pm 0.03) \times 10^{-9}$ | $(1.34 \pm 0.18) \times 10^{-7}$ |
| | $(1.15 \pm 0.02) \times 10^{-9}$ | |
| | $(1.20 \pm 0.01) \times 10^{-9}$ | |
| | $(1.08 \pm 0.06) \times 10^{-9}$ average | $(1.18 \pm 0.16) \times 10^{-7}$ average |
| 0.305 M NaCl | $(1.18 \pm 0.02) \times 10^{-9}$ | $(2.66 \pm 0.11) \times 10^{-7}$ |
| | $(9.21 \pm 0.03) \times 10^{-10}$ | $(2.57 \pm 0.09) \times 10^{-7}$ |
| | $(1.02 \pm 0.01) \times 10^{-9}$ | |
| | $(1.08 \pm 0.00) \times 10^{-9}$ | |
| | $(1.05 \pm 0.05) \times 10^{-9}$ average | $(2.62 \pm 0.05) \times 10^{-7}$ average |
| 0.505 M NaCl | $(9.22 \pm 0.25) \times 10^{-10}$ | $(2.11 \pm 0.06) \times 10^{-7}$ |
| | $(9.30 \pm 0.10) \times 10^{-10}$ | $(2.25 \pm 0.06) \times 10^{-7}$ |
| | $(1.07 \pm 0.01) \times 10^{-9}$ | |
| | $(9.74 \pm 0.05) \times 10^{-10}$ | |
| | $(9.74 \pm 0.34) \times 10^{-10}$ average | $(2.18 \pm 0.07) \times 10^{-7}$ average |
| 0.705 M NaCl | $(1.07 \pm 0.01) \times 10^{-9}$ | $(1.25 \pm 0.07) \times 10^{-7}$ |
| | $(9.12 \pm 0.03) \times 10^{-10}$ | $(2.39 \pm 0.30) \times 10^{-7}$ |
| | $(9.55 \pm 0.07) \times 10^{-10}$ | |
| | $(9.46 \pm 0.07) \times 10^{-10}$ | |
| | $(9.71 \pm 0.34) \times 10^{-10}$ average | $(1.82 \pm 0.57) \times 10^{-7}$ average |
| 1.005 M NaCl | $(1.53 \pm 0.02) \times 10^{-9}$ | $(8.46 \pm 1.37) \times 10^{-8}$ |
| | $(8.83 \pm 0.01) \times 10^{-10}$ | $(1.29 \pm 0.22) \times 10^{-7}$ |
| | $(9.29 \pm 0.02) \times 10^{-10}$ | |
| | $(8.70 \pm 0.08) \times 10^{-10}$ | |
| | $(1.05 \pm 0.16) \times 10^{-9}$ average | $(1.07 \pm 0.22) \times 10^{-7}$ average |

thermodynamic factors, formation of Pt borate complexes was not significant under our experimental conditions. The results of $\log B_1^*(\text{Pt})$ determinations are shown in Table 2.

The equilibrium constant results shown in Tables 1 and 2 indicate that $B_1^*(\text{Pd})$ and $B_1^*(\text{Pt})$ are weakly dependent on ionic strength (I) over the range of conditions ($0.105 \leq I \leq 1.00$ M) used in our work. The average of all $B_1^*(\text{Pd})$ values between 0.1 mol/L and 1.0 mol/L is $(1.03 \pm 0.06) \times 10^{-9}$ where the uncertainty indicates the observed range of the average $B_1^*(\text{Pd})$ results ($0.1 \leq I \leq 1.0$ mol/L) shown in Table 1. Consequently,

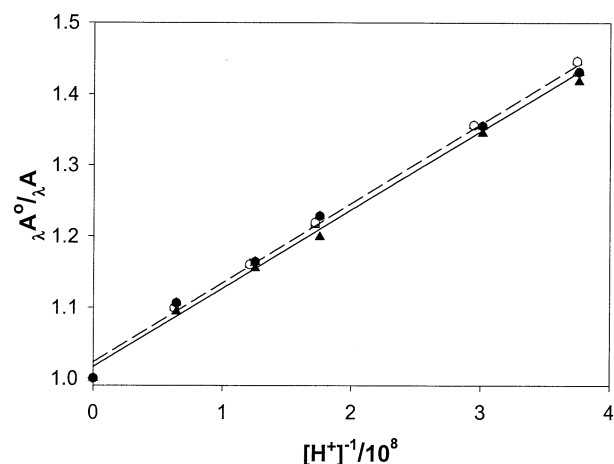


Fig. 3. Pt^{II} absorbance ratios are shown as a function of $[\text{H}^+]^{-1}$ after 48 and 96 h of equilibration. Filled points and solid line represent 96 h. equilibration and open points show data after 48 h. For periods shorter than 24 h large positive and negative deviations from this regression were observed.

over a wide range of salinities, the partition between $\text{PdCl}_3\text{OH}^{2-}$ and palladium that is solely complexed by Cl^- in seawater ($\Sigma[\text{PdCl}_n]$) can be well represented as

$$\log \frac{[\text{PdCl}_3\text{OH}^{2-}]}{\Sigma[\text{PdCl}_n]} = \log B_1^*(\text{Pd}) - \log[\text{Cl}^-] + \text{pH} \quad (24)$$

with $\log B_1^*(\text{Pd}) = -8.98$.

It should be noted that the $B_1^*(\text{Pd})$ results obtained in this work are only weakly influenced by carbonate complexation. The $B_1^*(\text{Pd})$ results obtained using Equation 21 (i.e., assuming insignificant carbonate complexation) at ionic strengths between 0.3 mol/L and 1.0 mol/L are within 2% of the $B_1^*(\text{Pd})$ results (Table 1) obtained using Equation 22. At 0.1 mol/L ionic strength the $B_1^*(\text{Pd})$ result using Equation 21 is 19.8% larger than the result obtained using Equation 22.

The results in Table 1 indicate that the $\text{PdCl}_3\text{OH}^{2-}$ concentration in seawater ($[\text{Cl}^-] \approx 0.56$ mol/L) is approximately

Table 2. $B_1^*(\text{Pt})$ results obtained at 25°C for chloride concentrations between 0.1 molar and 1.0 molar. Average values are shown with uncertainties in the form B_1^* (average) \pm range/2.

| Medium | $B_1^*(\text{Pt})$ |
|--------|---|
| 0.1 M | $(1.08 \pm 0.02) \times 10^{-9}$ |
| | $(1.37 \pm 0.05) \times 10^{-9}$ |
| | $(1.23 \pm 0.15) \times 10^{-9}$ average |
| 0.5 M | $(1.12 \pm 0.15) \times 10^{-9}$ |
| | $(9.49 \pm 0.49) \times 10^{-10}$ |
| | $(1.03 \pm 0.09) \times 10^{-9}$ average |
| 1.0 M | $(7.84 \pm 3.29) \times 10^{-10}$ |
| | $(8.79 \pm 0.05) \times 10^{-10}$ |
| | $(8.32 \pm 0.48) \times 10^{-10}$ average |

equal to the sum concentration of non-hydrolyzed chloride complexes (PdCl_4^{2-} plus PdCl_3^- etc.) at pH = 8.7. The range of results obtained for $B_1^*(\text{Pt})$ between 0.10 mol/L and 1.0 mol/L ionic strength (Table 2) is very similar to the range of $B_1^*(\text{Pd})$. $B_1^*(\text{Pt})$ results between 0.1 mol/L and 1.0 mol/L can be represented as $B_1^*(\text{Pt}) = (1.03 \pm 0.2) \times 10^{-9}$. Consequently, the extent of Pt^{II} hydrolysis in seawater ($[\text{Cl}^-] = 0.555$ mol/L, $S = 34.8$) should be quite similar to that of Pd^{II} .

The B_1 result obtained for formation of $\text{PdCl}_3\text{CO}_3^{3-}$ is sufficiently large that $\text{PdCl}_3\text{CO}_3^{3-}$ is a significant species in seawater. This result is not altogether surprising because previous work on the complexation of Hg^{II} by OH^- and CO_3^{2-} indicated that the complexation of "soft" (class B) metal ions by carbonate can be quite strong. Formation constants for the reactions $\text{Hg}^{2+} + \text{OH}^- \rightleftharpoons \text{HgOH}^+$ and $\text{Hg}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{HgCO}_3^0$ at 25°C and 3 mol/L ionic strength have both been estimated as $10^{10.65}$ (Ahlberg, 1962; Hietanen and Högfeltdt, 1976).

Since $B_1(\text{Pd}) \cong 1.8 \times 10^{-7}$ at 0.7 mol/L ionic strength and the HCO_3^- concentration in seawater is approximately 1.9 mM, the $[\text{PdCl}_3\text{CO}_3^{3-}]/\Sigma[\text{PdCl}_n]$ ratio in seawater is approximately 0.063 at pH 8. Under the same conditions the $[\text{PdCl}_3\text{OH}^{2-}]/\Sigma[\text{PdCl}_n]$ ratio is approximately 0.18. Using the formation constant results in Table 1 at 0.7 mol/L ionic strength, it follows from the formation constants defined in Equations 4, 5, 13 and 14, that

$$\frac{[\text{PdCl}_3\text{CO}_3^{3-}]}{[\text{PdCl}_3\text{OH}^{2-}]} = \frac{B_1}{B_1^*} [\text{HCO}_3^-] = 187[\text{HCO}_3^-]. \quad (25)$$

Since the HCO_3^- concentration throughout the normal pH range of seawater is approximately 1.9×10^{-3} M, the $[\text{PdCl}_3\text{CO}_3^{3-}]/[\text{PdCl}_3\text{OH}^{2-}]$ concentration ratio in seawater is approximately 0.35 and is largely independent of pH. Thus, within the normal pH range of seawater, using Equations 24 and 25, the speciation of Pd^{II} can be expressed as

$$\log\left(\frac{[\text{PdCl}_3\text{OH}^{2-}] + [\text{PdCl}_3\text{CO}_3^{3-}]}{\Sigma[\text{PdCl}_n]}\right) = -8.86 - \log[\text{Cl}^-] + \text{pH}. \quad (26)$$

Given the general similarity of Pd^{II} and Pt^{II} chemical equilibria, it appears reasonable to expect that, under equilibrium conditions, the sum of $\text{MCl}_3\text{OH}^{2-}$ and $\text{MCl}_3\text{CO}_3^{3-}$ concentrations for both metals in seawater amounts to approximately 25% of the Pd^{II} and Pt^{II} that is present in the form of chloride complexes at pH 8.

Equations 13 and 14 can be used to transform the B_1^* and B_1 data in Tables 1 and 2 to β_1^* and β_1 defined in Equations 4 and 5. At chloride concentrations between 0.1 mol/L and 1.0 mol/L the predominant chloride complexes of Pd and Pt are limited to MCl_3^- and MCl_4^{2-} species. Transformation of B_1^* and B_1 data to β_1^* and β_1 via Equations 13 and 14 requires use of the equilibrium constants (c_1K_{40}) relating MCl_4^{2-} and MCl_3^- concentrations. c_1K_{40} (Pd) values determined using (a) Eqn. 20 and (b) absorbance data obtained over a range of ionic strengths between 0.11 mol/L and 1.0 mol/L are shown in Table 3. Least squares analysis of the $\log c_1K_{40}$ data shown in Table 3 indicated that $\log c_1K_{40}$ is well described by the following equation:

Table 3. Average c_1K_{40} (Pd) results at 25°C.

| Ionic strength | Average c_1K_{40} |
|----------------|---------------------|
| 0.11 | 12.07 |
| 0.20 | 13.63 |
| 0.31 | 15.15 |
| 0.52 | 17.31 |
| 0.84 | 20.63 |
| 1.00 | 23.70 |

$$\log c_1K_{40} = c_1K_{40}^0 + \frac{1.022I^{1/2}}{1 + 2.9I^{1/2}} + b \cdot I \quad (27)$$

where $c_1K_{40}^0 = 0.897$ and $b = 0.216$

Eqn. 27 was used to calculate the c_1K_{40} (Pd) values required for calculation of β_1^* and β_1 via Equations 13 and 14. c_1K_{40} (Pt) and c_1K_{40} (Pd) are expected to have very similar dependences on ionic strength. As such, c_1K_{40} (Pt) values at ionic strength 0.1 mol/L, 0.5 mol/L and 1.0 mol/L were obtained using c_1K_{40} (Pd) calculated using Equation 27 plus the c_1K_{40} (Pt)/ c_1K_{40} (Pd) stability constant ratio obtained by Elding (1972, 1978) at 25°C and $I = 1.0$ mol/L:

$$c_1K_{40}(\text{Pt}) = 5.27(c_1K_{40}(\text{Pd})) \quad (28)$$

Calculated $\log\beta_1^*(\text{Pd})$, $\log\beta_1^*(\text{Pt})$ and $\log\beta_1(\text{Pd})$ results are given in Table 4.

Since the stoichiometry of the MCl_4^{2-} hydrolysis reaction is identical for Pd^{II} and Pt^{II} , it is expected that the dependence of $\log\beta_1^*$ on ionic strength should be very similar for the two elements. Furthermore, based on the activity coefficient behavior expected for MCl_4^{2-} hydrolysis (Byrne and Yao, 2000), the influence of ionic strength on $\log\beta_1^*$ should be relatively small. The hydrolysis constant ($\beta_1^*(\text{M})$) appropriate to Equation 4 can be written as the product of an equilibrium constant for an isocoulombic reaction (${}_{\text{OH}}\beta_1(\text{M}) = ([\text{MCl}_3\text{OH}^{2-}][\text{Cl}^-])/([\text{MCl}_4^{2-}][\text{OH}^-])$) and the equilibrium constant for water hydrolysis ($K_w = [\text{H}^+][\text{OH}^-]$). Since the ionic strength dependence for the isocoulombic reaction should be weak, and the ionic strength dependence for K_w is small (Baes and Mesmer, 1976), their product, $\beta_1^*(\text{M})$, should be only weakly dependent on ionic strength. Consistent with these expectations, Table 4 shows that $-8.98 \leq \log\beta_1^*(\text{Pd}) \leq -8.72$ between $I = 0.1$ mol/L and $I = 1.0$ mol/L, while $-9.08 \leq \log\beta_1^*(\text{Pt}) \leq -8.85$. The ionic strength dependence of $\log\beta_1^*(\text{M})$ for each element is similar in that the largest values of $\log\beta_1^*(\text{M})$ for each element are obtained at $I = 0.1$ mol/L.

As an assessment of the quality of our hydrolysis constant determinations, the results in Table 1 can be compared with the $B_1^*(\text{Pd})$ results of Byrne and Yao (2000) obtained in CO_2 -free 0.5 mol/L NaCl (25°C) and the 25°C result of Kump and Byrne

Table 4. Palladium and Platinum $\log\beta_1^*(\text{M})$ results at 25°C, and $\log\beta_1(\text{M})$ results for Palladium (25°C).

| Ionic strength | $\log\beta_1^*(\text{Pd})$ | $\log\beta_1^*(\text{Pt})$ | $\log\beta_1(\text{Pd})$ |
|----------------|----------------------------|----------------------------|--------------------------|
| 0.105 M | -8.72 | -8.85 | -6.68 |
| 0.305 M | -8.89 | | -6.50 |
| 0.505 M | -8.97 | -8.97 | -6.62 |
| 0.705 M | -8.98 | | -6.71 |
| 1.005 M | -8.96 | -9.08 | -6.95 |

Table 5. Comparison of PdCl_4^{2-} , PtCl_4^{2-} and PtCl_6^{2-} hydrolysis constant results. $\log B_1^*(\text{Pd}^{\text{II}})$ and $\log B_1^*(\text{Pt}^{\text{II}})$ results were obtained at 25°C.

| $\text{PdCl}_4^{2-} + \text{H}_2\text{O} = \text{PdCl}_3\text{OH}^{2-} + \text{Cl}^- + \text{H}^+$ | | |
|--|---------------------------|--|
| Ionic strength | $-\log B_1^*$ (this work) | $-\log B_1^*$ (Milic and Burgarcic, 1984) |
| 0.5 M | 9.01 | 9.53 |
| 0.7 M | 9.01 | — |
| 1.0 M | 8.98 | 9.30 |
| 1.5 M | — | 9.17 |
| 2.0 M | — | 9.09 |
| 2.5 M | — | 9.05 |
| 3.0 M | — | 9.13 |
| $\text{PtCl}_4^{2-} + \text{H}_2\text{O} = \text{PtCl}_3\text{OH}^{2-} + \text{Cl}^- + \text{H}^+$ | | |
| Ionic strength | $-\log B_1^*$ (this work) | $-\log B_1^*$ (Peshchevitski et al., 1962) |
| 1.0 M | 9.07 | 8.66 |
| $\text{PtCl}_6^{2-} + \text{H}_2\text{O} = \text{PtCl}_5\text{OH}^{2-} + \text{Cl}^- + \text{H}^+$ | | |
| Ionic strength | temperature | $-\log B_1^*$ (Pt^{IV}) |
| variable | 50°C | 5.3 (Davidson and Jameson, 1965) |
| variable | 25-50°C | 7.25 (Nikolaeva et al., 1965) |

(1989) obtained in CO_2 -free $S = 36$ seawater. The result of Byrne and Yao at 25°C in 0.5 mol/L NaCl is $B_1^*(\text{Pd}) = (9.70 \pm 0.015) \times 10^{-10}$, while the Table 1 result in 0.505 mol/L NaCl at 25°C is $(9.74 \pm 0.34) \times 10^{-10}$. In CO_2 -free seawater ($S = 36$, $I = 0.73$ mol/L) at 25°C, the Kump and Byrne (1989) result is $B_1^*(\text{Pd}) = (1.21 \pm 0.34) \times 10^{-9}$ and the Table 1 result for 0.705 mol/L NaCl is $(9.71 \pm 0.34) \times 10^{-10}$.

Hydrolysis constants obtained in this work by ultraviolet spectroscopy are compared in Table 5 with results obtained in previous work by titrimetry. The Table 5 results of Milic and Bugarcic (1984), obtained using Pd^{II} concentrations more than one hundred times higher than those used in the present study, are in fair agreement with our spectroscopic $\log B_1^*(\text{Pd})$ results. Taken together, the present study and the work of Milic and Bugarcic indicate that $\log B_1^*(\text{Pd}) \leq -9.0$ for ionic strengths between 0.3 and 3.0 mol/L. Based on the results shown in Table 5, PdCl_4^{2-} is a dominant species in seawater relative to hydrolyzed forms of Pd. This conclusion contrasts sharply with the conclusions of van Middlesworth and Wood (1999), wherein $[\text{PdCl}_3\text{OH}^{2-}] \gg [\text{PdCl}_4^{2-}]$ throughout the normal pH range of seawater. Problems in the interpretations of van Middlesworth and Wood (1999) are discussed at length in Byrne and Yao (2000).

The $\log B_1^*(\text{Pt}^{\text{II}})$ result obtained at 25°C and 1.0 mol/L ionic strength in this work is in fair agreement with the Table 5 result of Peshchevitski et al. (1962) obtained at the same conditions. Furthermore, inspection of the Peshchevitski et al. (1962) graphical data suggests that our $B_1^*(\text{Pt}^{\text{II}})$ results agree with the Peshchevitski et al. (1962) results within their analytical precision. Based on the $\log B_1^*(\text{Pt}^{\text{II}})$ results shown in Table 5, PtCl_4^{2-} is a dominant species in seawater relative to hydrolyzed forms of Pt. This conclusion differs sharply with the conclusions of Azaroual et al. (2001), wherein $[\text{PtOH}^+] \gg [\text{PtCl}_4^{2-}]$ throughout the normal pH range of seawater. Problems in the hydrolysis constant interpretations of Azaroual and coauthors are described in Byrne (in press).

Since Pt^{IV} is a potentially important or even dominant form

of Pt in natural aqueous solutions (Gammons, 1996), Table 5 also shows available Pt^{IV} hydrolysis constant results. The results of Nikolaeva et al. (1965) and Davidson and Jameson (1965) show that $B_1^*(\text{Pt}^{\text{IV}})$ is poorly defined relative to $B_1^*(\text{Pt}^{\text{II}})$. While available results appear to establish that PtCl_6^{2-} hydrolysis is substantially stronger than PtCl_4^{2-} hydrolysis, at present no work has produced well-defined $B_1^*(\text{Pt}^{\text{IV}})$ results under well-defined physical-chemical conditions.

The B_1^* data shown in Tables 1 and 2 indicate that the speciation of Pt^{II} and Pd^{II} in estuaries should be strongly dependent on both pH and salinity. As an example, using $\log B_1^* = -9.0$ as a reasonable estimate for both Pt^{II} and Pd^{II} at 25°C and $S = 35$, the $[\text{MCl}_3\text{OH}^{2-}]/\Sigma[\text{MCl}_n]$ ratio at pH = 8.2 is approximately 0.3. At $S = 5$ the $I = 0.1$ mol/L results in Tables 1 and 2 indicate that the $[\text{MCl}_3\text{OH}^{2-}]/\Sigma[\text{MCl}_n]$ ratio at pH = 8.2 is greater than two. Thus, the results obtained in this work indicate that hydrolyzed forms of Pd^{II} and Pt^{II} are important at low salinities.

Palladium complexation observations in the presence of HCO_3^- indicate that complex Pd^{II} species containing carbonate (e.g., $\text{PdCl}_3\text{CO}_3^{3-}$) are important in the environment. As an example, in an estuarine environment at $S \approx 5$ ($I = 0.1$ mol/L), with $[\text{HCO}_3^-] \approx 1.9 \times 10^{-3}$ M and pH = 8.2, the $[\text{PdCl}_3\text{CO}_3^{3-}]/\Sigma[\text{PdCl}_n]$ ratio calculated using our $\log B_1(\text{Pd})$ results (Table 1) is approximately equal to 0.5. At somewhat lower chloride concentrations it would be expected that mixed hydroxy-carbonato species could become important along with many other types of mixed ligand species. At sufficiently low chloride concentrations, species such as MCl_2OH^- and $\text{MCl}_2\text{CO}_3^{2-}$ should also become important. Given the extraordinary affinity of Pd^{II} for a wide variety of ligands, and especially ligands that are strong electron-donors, the speciation of Pd^{II} in the environment is likely to be quite complex.

The equilibrium behaviors of Pd^{II} and Pt^{II} are quite similar. Linear free energy relationships between $\log \beta_4(\text{Pd})$ and $\log \beta_4(\text{Pt})$ for a wide variety of single ligand-type complexes indicate (Hancock et al., 1977) that

$$\log\beta_4(\text{Pt}) \cong 1.2\log\beta_4(\text{Pd}) \quad (29)$$

where $\beta_4 = [\text{MCl}_4^{2-}][\text{M}^{2+}]^{-1}[\text{Cl}^-]^{-4}$.

In spite of this observation, and the general similarity in the $\log \beta_1^*$ results obtained in this work, our results indicate that Pd^{II} and Pt^{II} may be strongly fractionated in the environment. Differences in the environmental behavior of Pt^{II} and Pd^{II} are expected due to dissimilar equilibration kinetics rather than thermodynamics. While the PdCl_4^{2-} to $\text{PdCl}_3\text{OH}^{2-}$ transformation is complete on time scales shorter than one second (Byrne and Yao, 2000), the $\text{PtCl}_4^{2-}/\text{PtCl}_3\text{OH}^{2-}$ equilibration occurs on a time scale of days. Consequently, the speciation of Pt^{II} , unlike Pd^{II} , will reflect both past and present environments. Particularly during riverine to estuarine transitions, the estuarine speciation of Pt^{II} may reflect prior progress toward equilibrium under riverine conditions. The slow ligand exchange kinetics of Pt^{II} is likely to strongly influence the comparative scavenging behavior of Pt^{II} and Pd^{II} . Although Pt^{II} is somewhat more reactive than Pd^{II} in a thermodynamic sense, the kinetic inertness of Pt^{II} should make this element substantially less particle-reactive than Pd^{II} .

The influence of kinetics on $\text{Pt}^{\text{II}}/\text{Pd}^{\text{II}}$ fractionation may be more profound than would be surmised from observed differences in PtCl_4^{2-} and PdCl_4^{2-} hydrolysis kinetics. The equilibration periods required for Pt^{II} carbonate complexation experiments were so long (possibly weeks) that the experiments were discontinued. Relative to the kinetics of $\text{PtCl}_3\text{CO}_3^{3-}$ formation, the $\text{PtCl}_4^{2-}/\text{PtCl}_3\text{OH}^{2-}$ equilibration rate (requiring days) appears unusually fast. Formation of $\text{PtCl}_3\text{OH}^{2-}$ can involve a pathway wherein a coordinated Cl^- is quickly replaced by a ubiquitous ligand (H_2O) followed by a very rapid dissociation step ($\text{PtCl}_3\text{H}_2\text{O}^- \rightarrow \text{PtCl}_3\text{OH}^{2-} + \text{H}^+$). This pathway is, of course, not available for $\text{PtCl}_3\text{CO}_3^{3-}$ formation. The influence of comparative kinetics on $\text{Pt}^{\text{II}}/\text{Pd}^{\text{II}}$ fractionation may provide interesting opportunities for assessing the relationship between solution speciation and trace metal behavior in the environment.

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