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Solubility of platinum in aqueous solutions at 25°C and pHs 4 to 10 under oxidizing conditions

Mohamed Azaroual¹, Bruno Romand^{1, 2}, Philippe Freyssinet¹ and Jean-Robert Disnar²

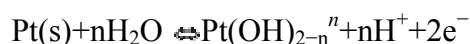
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Abstract

Platinum has been found to be mobile under supergene conditions, including placers and weathering profiles. To elucidate the nature of Pt mobility in supergene environments, the dissolution of platinum metal was investigated under physicochemical conditions similar to those found in such environments. The solubility of platinum metal was measured at 25°C in several systems: Pt-K-HC₈H₄O₄-H₂O (pH 4.02), Pt-Na-HCO₃-Cl-H₂O (pH 6.40), Pt-Na-K-H₂PO₄-HPO₄-H₂O (pH 6.90), Pt-Na-HCO₃-H₂O (pH 8.30), Pt-Na-OH-H₂O (pH 8.54), and Pt-Na-HCO₃-H₂O (pH 9.91). The redox conditions of these experiments were relatively oxidizing, with measured Eh values ranging from +280 to +590 mV. The ionic strength of the aqueous solutions did not exceed 0.30 (molal scale).

The interpretation of the solubility results, in terms of the following reaction and its equilibrium constant,



served to identify the importance of the hydroxylated complex PtOH⁺ in the pH range (4 to 10) and to determine its stability constant at 25°C. Linear regression of the solubility data using the function

$$\log [\text{Pt}] - 2pe = n \text{ pH} + \log K_n$$

yielded a value of 1.01 ± 0.07 for n , the average ligand number, and -31.76 ± 0.55 for the thermodynamic equilibrium constant of reaction. The resulting stability constant (β_1) of PtOH⁺ ($\text{Pt}^{2+} + \text{OH}^- \rightleftharpoons \text{PtOH}^+$) is 24.91 ± 0.50 , assuming the same value of the free energy of formation of Pt²⁺, $\Delta G_f^\circ(\text{Pt}^{2+})$ as that given by Glushko et al. (*Thermodynamic Constants of Matter*, Academy of Science, USSR, 1972). The range of values of $\Delta G_f^\circ(\text{Pt}^{2+})$ proposed to date is +185.63 to +258.74 kJ/mol. The value of Glushko et al. (1972) (+244.11 kJ/mol) appears to fit better with our measurements at pH 4 to 10 and with those of Wood (Wood S. A., "Experimental determination of the hydrolysis constants of Pt²⁺ and Pd²⁺ at 25°C from the solubility of Pt and Pd in aqueous hydroxide solutions," *Geochim. Cosmochim. Acta* **55**, 1759–1767, 1991) at pH 9 to 15.5. Finally, according to these new measurements of the solubility of platinum, the recommended values for Gibbs free energy (ΔG_f° , in kJoule per mole) of the different aqueous species of Pt are +244.11 (Pt²⁺), -55.96 (PtOH⁺), and -234.48 (Pt(OH)₂(aq)).

The integration of data from the literature for chloride and sulfate complexes was used to calculate the speciation of platinum in seawater and in solutions with variable chlorinity (0.1, 1, and 3 mol/L NaCl) at 25°C. These calculations showed that in the absence of strong ligands (i.e., $\text{S}_2\text{O}_3^{2-}$, CN^-), the transport of platinum in supergene environments primarily occurs in the form of PtOH^+ (90%) and $\text{Pt}(\text{OH})_2(\text{aq})$ (9.7%). Chloride complexes (PtCl_4^{2-} and PtCl_3^-) account for less than 1% of the dissolved platinum.

This study clearly shows that the hydroxylated complexes (PtOH^+ and $\text{Pt}(\text{OH})_2(\text{aq})$) can play a very important role in controlling platinum transfer mechanisms in surface fluids (soils, placers, weathering profiles, etc.). Because the charged species PtOH^+ is largely predominant, the mobility and transfer of platinum can also be affected by adsorption-desorption mechanisms onto oxides and hydroxides.

1. Introduction

The understanding of the geochemical cycle of platinum group elements (PGEs) is very important scientifically, industrially, and economically. These metals have always been more or less considered as immobile in supergene environments. McKibben et al. (1990) analyzed the concentrations of Pt, Pd, Au, and Rh in natural hydrothermal solutions at 300°C with pH \sim 5.4 under relatively oxidizing conditions and obtained concentrations in the range of 1 ppb. The authors show that these contents are four to six orders of magnitude higher than those predicted by the thermodynamic data available at the time. Recently, field, laboratory, and theoretical work have investigated the dissolution, transport, and precipitation of PGEs in metallic form or as other minerals.

In supergene environments, and particularly under lateritic conditions, PGEs can be remobilized to form significant supergene enrichments and dispersion haloes in weathering profiles Travis et al., 1976 1993; Augé and Maurizot, 1995). Salpeteur et al. (1995) show that Pd is preferentially leached in comparison to Pt in laterites. Supergene platinum group minerals (PGMs), such as platinum nuggets (Ottemann; Bowles and Bowles), as well as complex minerals such as oxides associated with transition metals (Ti, Cr, Fe, Mn, Co, Ni), can form in various oxidizing supergene environments (Aug; Jedwab and Salpeteur). Bowles et al. (1995) showed by experimentation that organic matter in tropical soils can complex PGEs. Wood (1990) demonstrated the important role of natural dissolved organic acids in maintaining platinum in transportable form in aqueous solutions. Wood et al. (1994) and Wood and Wood showed that oxalate and acetate form aqueous complexes with Pd(II). All this work on natural and experimental systems has shown that PGEs are more mobile than predicted by existing thermodynamic data.

The mechanisms of PGEs transport can only be understood and quantified with the help of thermodynamic and kinetic models that accurately describe the water-rock interaction mechanisms. The application of thermodynamic models to mass transport processes between phases (water-gas-rock) has demonstrated the performance of these models in many contexts, including the construction of genetic models of certain types of metalliferous deposits (Reed; Plumee; Heinrich and Azaroual; and references therein). However, the use of these models to investigate PGEs transport is still premature because of the lack of reliable thermodynamic parameters to describe the thermochemical properties of the different aqueous and solid species of these metals.

Several attempts at theoretical estimation (Mountain; Mountain; Ruaya; Wood and Wood) of the thermochemical parameters of the aqueous species of PGEs have led to relatively inconsistent results, and the discrepancy between the data from different sources may amount to several orders of magnitude. Recent measurements of the solubility of platinum and palladium (Gammons; Gammons; Pan; Wood and Gammons) have demonstrated the limit of these theoretical approaches for determining the stability constants of the aqueous complexes of precious metals. The recent attempt (Sassani and Shock, 1998) to compile data and estimate thermodynamic parameters of PGEs revealed shortcoming making it even more difficult to study the thermodynamic behaviour of PGEs in natural and industrial hydrosystems.

The theoretical estimations of Mountain and Wood (1988a) and Wood and Wood suggested the importance of thiosulfates in the supergene transport of PGEs. Recent experimental investigations of Anthony and Williams (1994) showed that the dissolved Pt concentrations rise sharply with the $S_2O_3^{2-}$ concentration; these authors indicate the formation of the complex $Pt(S_2O_3)_4^{6-}$, of which the stability is sufficiently high to guarantee platinum mobility. Unfortunately, the available measurements do not allow the precise determination of stability constants of these complexes ($Pt(II)-S_2O_3^{2-}$). Mountain and Wood (1988a) considered the possibility of aqueous complexation of PGEs by several ligands in natural waters (Cl^- , HS^- , OH^- , NH_3 , $S_2O_3^{2-}$, OAA^- [organic acid anions]).

Wood (1991) experimentally determined the solubility of Pt at 25°C in solutions of sodium hydroxide of variable ionic strength (10^{-4} to 10). These solubility measurements were made in solutions initially supersaturated in platinum metal (Pt(s)) and lasted from 319 to 465 d. Solubilities ranging from 0.014 to 0.362 mg/L for platinum and up to 6 mg/L for palladium were measured. These experiments clearly demonstrate the effect of OH^- ions on the solubility of PGMs with concentrations increasing with pH (i.e., with $[OH^-]$). The data of Wood (1991) are important because it is the first time that PGM solubility studies have been conducted on low-ionic-strength (<0.001) solutions at 25°C. Wood (1991) interpreted the results of Pt(s) solubility measurements solely by use of the $Pt(OH)_2(aq)$ complex throughout the pH range investigated (9 to 15.5) and obtained a log stability constant of 29.9 ± 1.0 for this complex. However, to our knowledge, the solubility of platinum has never been measured under conditions prevailing in natural systems (pH 6 to 9) at 25°C. This study was designed to address this problem and consisted of performing new solubility measurements on platinum metal, Pt(s), in several systems within the range of pH 4 to 10 at 25°C, conditions that were specifically chosen so as to approach the natural physicochemical conditions of surface systems.

2. Systems studied

The solubility of Pt(s) was measured in several systems with controlled chemical compositions and concentrations within the range of pH 4 to 10. Table 1 shows the experimental conditions of each system studied. The pH and Eh values correspond to those initially measured at 25°C. The concentrations of the buffers were sufficiently low to avoid complication in the interpretation of the results due to possible interactions between these ligands (CO_3^{2-} , HCO_3^- , HPO_4^{2-} , $H_2PO_4^-$, and phthalate: $HC_8H_4O_4^-$) and dissolved platinum. Hydrochloric acid ($[Cl] = 0.004$ molal) was added to the buffer solution so as to examine the potential effect of chloride on the solubility of platinum in the pH range (6 to 8), at contents similar to those observed in supergene environments. Solution D was prepared with NaOH

(2.64×10^{-6} molal), yielding an unbuffered initial pH of 8.3. It is highly improbable that the reliable bases introduced as pH buffers interact significantly with the dissolved platinum.

Table 1. Experimental conditions of the systems studied.a

Series	System	Concentration, molal	I	pH (25)	Eh(25) mV	Time (days)
A	Pt-K-C ₈ H ₅ O ₄ -H ₂ O	[K] = 5.0×10^{-2} [C ₈ H ₅ O ₄] = 5.0×10^{-2}	5.35×10^{-2}	4.02	+537	210
B	Pt-Na-HCO ₃ -Cl-H ₂ O	[Na] = 8.0×10^{-3} [Cl] = 4.0×10^{-3} [HCO ₃] = 8.0×10^{-3}	7.96×10^{-3}	6.40	+355	566*
C	Pt-Na-K-H ₂ PO ₄ -HPO ₄ -H ₂ O	[Na] = 5.0×10^{-2} [K] = 2.5×10^{-2} [H ₂ PO ₄] = 2.5×10^{-2} [HPO ₄] = 2.5×10^{-2}	1.0×10^{-1}	6.90	+557	210
D	Pt-Na-OH-H ₂ O	[Na] = 2.64×10^{-6} [OH] = 2.67×10^{-6}	2.65×10^{-6}	8.30	+280	567
E	Pt-Na-HCO ₃ -H ₂ O	[Na] = 1.0×10^{-2} [HCO ₃] = 1.0×10^{-2}	8.11×10^{-2}	8.54	+358	566*
F	Pt-Na-HCO ₃ -CO ₃ -H ₂ O	[Na] = 2.501×10^{-1} [HCO ₃] = 8.329×10^{-2} [CO ₃] = 8.34×10^{-2}	2.95×10^{-1}	9.91	+404	210

^a In all experiments, 0.5 g of platinum was introduced in wire or powder form (see text). Systems indicated within an asterisk (*) are analyzed by undersaturation and supersaturation. Powder was not used for system D.

Milli-Q distilled water was used to prepare the initial aqueous solutions. All the salts and buffers used were >99.9% pure. No precautions were taken to prevent the dissolution of oxygen and carbon dioxide from the air during preparation of the buffered solutions.

3. Experimental method

Platinum wire and powder were used in the solubility measurement experiments; wire was used for all the systems, but powder was not used for system D. The experiments lasted from 210 to 567 d, and the experimental temperature, reflecting laboratory temperature, fluctuated between 20 and 27°C. This fluctuation is not expected to have a significant effect on the results of the thermodynamic calculations, and no visible influence was noted on the variation in Pt concentrations with time for the long-term experiments.

3.1. Apparatus

Two types of solid platinum were used in our experiments: platinum metal wire (50 mg; 0.2 mm in diameter), and approximately the same mass of platinum powder (50 mg), with particles ranging from 0.27 to 0.47 μm. The platinum wire (99.9% Pt) was supplied by Comptoir des Cendres et Métaux Précieux, Paris, and the platinum powder (99.9% Pt) was supplied by Aldrich.

As platinum dissolves, it is liable to adsorb on the walls of the bottles and cause losses that could potentially jeopardize the determination of metal solubility. This problem was minimized by careful consideration of the type of bottle to be used. High-density polyethylene containers appear to minimize the risk of Pt adsorption, and so we adopted them for the experiments performed during this study. Finally, to avoid contamination problems, new bottles were used for each sampling, and the bottles were only used once. Bottles were initially washed with ultrapure water (resistance = 18.2 MΩ cm) obtained with a Milli-Q system.

3.2. Reagents

Six series of experiments varying in length from 210 to 567 d were performed with 50 mg of platinum in wire form. Platinum powder was not used for the unbuffered pH system (with NaOH). The experimental conditions for each series are given in Table 1. All the pH buffers and products used were of high grade. The following systems were prepared. System A was prepared with pH buffered to 4.02 (Table 1) with potassium phthalate, $\text{KHC}_8\text{H}_4\text{O}_4$. The stock solution was in equilibrium with atmospheric oxygen. System B was prepared with an aqueous solution at pH (6.40) in equilibrium with atmospheric oxygen. The pH was buffered by adding $8.0 \cdot 10^{-3}$ mol/L of 99.5% NaHCO_3 (Normapur Prolabo) and $4.0 \cdot 10^{-3}$ mol/L of 32% HCl (Merck, Pro Analyti). This solution (ionic strength $7.96 \cdot 10^{-3}$) was buffered by carbonates. System C was prepared with an aqueous solution with the pH buffered to 6.90 with 99.5% KH_2PO_4 and 99.8% Na_2HPO_4 (Normapur Prolabo). The ionic strength of this solution was ~ 0.1 . System D was prepared with an unbuffered solution and the initial pH (8.30) was controlled by NaOH (Merck, Pro Analyti). The ionic strength was very low ($2.65 \cdot 10^{-6}$). System E was prepared with a relatively basic pH (8.54) and buffered by the addition of 0.01 mol/L NaHCO_3 in solution. The ionic strength was ~ 0.01 . System F with pH (9.91) was buffered with the HCO_3/CO_3 system ($[\text{NaHCO}_3] = 0.08329$ molal and $[\text{Na}_2\text{CO}_3] = 0.083405$ molal). This solution had the highest ionic strength (0.295).

The experiments that used platinum powder concerned with systems A, B, C, E, and F with exactly the same initial pH and Eh as with platinum wire (Table 1). Platinum powder was not used for system D.

3.3. Loading and sampling procedures

At the time of sampling, the metal wire was first recovered, and 10 mL of solution was then sampled with a syringe, then filtered through 0.1- μm cellulose-acetate filters. Each sample bottle was rinsed with the filtered solution before being filled with the solution sample. Then the filtrate is immediately acidified with hydrochloric acid to reach a pH of ~ 1 . This sample is intended for inductively coupled plasma-mass spectrometry (ICP-MS) analysis to determine the platinum concentration in solution. Samplings and measurements (Eh and pH) were performed in a glove box to avoid equilibrating the aqueous solutions with the atmosphere too rapidly. The parameters pH and Eh were measured (Table 2) immediately after recovering the samples.

3.4. Measurement procedures (solubility, pH, Eh)

The determination of platinum concentration by ICP-MS (VG PQ 2+) is highly attractive because no preconcentration is necessary, the detection limit of platinum being only ~ 1 ppt. The analytical error is between 5 and 10%. Two measurements of dissolved platinum concentrations were taken for each sample. To determine the adsorption rate and total quantity of platinum in solution, the bottles used in these experiments were systematically rinsed with 1% hydrochloric acid solution (pH ~ 1). The rinse solution was then analyzed by ICP-MS. The results showed that the adsorbed portion of Pt did not exceed 5%, which confirms the adequacy of the experimental equipment selected to determine platinum solubility.

A Mettler Delta 350 type pH meter standardized with known pH buffers was used for the experiments. pH measurement errors are ± 0.02 pH units. Eh was measured with an INLAB

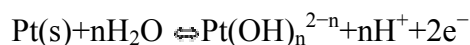
418 platinum electrode. The Eh cell was systematically checked against a reference solution of Pt-Ag/AgCl SCHOTT (+230 mV), and the uncertainty of Eh measurements is estimated at ± 20 mV. Three measurements were taken for pH and Eh. The mean of the measurements is shown in Table 2.

Table 2. Measured dissolved platinum concentrations (in picomolal, pm), pH, and Eh vs. time at 25°C.

A. Pt-K-C ₈ H ₅ O ₄ -H ₂ O					
Time	0 day	158 days	196 days	210 days	210 days
pH (25°)	4.02	4.02	—	4.01	—
Eh (mV)	537	547	—	—	—
[Pt], pm	—	267 \pm 13	318 \pm 16	241 \pm 12	205 \pm 10
	—	318 \pm 16	292 \pm 15	246 \pm 12	210 \pm 11
B. Pt-Na-HCO ₃ -Cl-H ₂ O					
Time	0 day	158 days	315 days	530 days	566 days
pH (25°)	6.40	7.9	8.4	8.5	—
Eh (mV)	355	445	447	404	—
[Pt], pm	—	67 \pm 7	72 \pm 7	231 \pm 12	241 \pm 12
	—	51 \pm 5	87 \pm 9	195 \pm 10	226 \pm 11
C. Pt-Na-K-H ₂ PO ₄ -HPO ₄ -H ₂ O					
Time	0 day	158 days	196 days	210 days	—
pH (25°)	6.90	6.9	—	6.9	—
Eh (mV)	557	438	—	—	—
[Pt], pm	—	51 \pm 3	87 \pm 4	108 \pm 5	—
	—	67 \pm 3	97 \pm 5	92 \pm 5	—
D. Pt-Na-OH-H ₂ O					
Time	0 day	157 days	314 days	529 days	565 days
pH (25°)	8.30	6.5	7.6	6.5	—
Eh (mV)	280	430	392	404	—
[Pt], pm	—	123 \pm 12	97 \pm 10	51 \pm 5	138 \pm 14
	—	97 \pm 10	92 \pm 9	56 \pm 5	143 \pm 14
E. Pt-Na-HCO ₃ -H ₂ O					
Time	0 day	158 days	315 days	530 days	566 days
pH (25°)	8.54	8.96	8.82	8.8	—
Eh (mV)	358	415	443	394	—
[Pt], pm	—	267 \pm 27	318 \pm 32	292 \pm 15	333 \pm 17
	—	277 \pm 28	354 \pm 35	302 \pm 15	308 \pm 15
F. Pt-Na-HCO ₃ -CO ₃ -H ₂ O					
Time	0 day	158 days	196 days	210 days	221 days
pH (25°)	9.91	10.0	—	10.0	—
Eh (mV)	404	362	—	—	—
[Pt], pm	—	615 \pm 31	359 \pm 18	364 \pm 18	282 \pm 14
	—	718 \pm 36	364 \pm 18	354 \pm 18	564 \pm 28

4. Results

The measured Pt concentrations from the wire and powder experiments are shown in Figure 1 plotted vs. time. The measured Pt concentrations from the wire experiments are given in Table 2. For reasons of convenience and presentation (logarithmic scale), the value of [Pt] concentration at zero days (10^{-15} mol/kg H₂O) is assumed arbitrarily. The solubility of platinum (reaction 1) depends on pH and Eh (or pe),



hence, no direct comparison is actually possible. However, pH rises from Figures 1A–F. The measured Eh values fluctuate considerably (Table 2), probably due to the initial oxygenation not being the same for all solutions. Measurements of Pt concentration are reproducible with only one measurement point, except for experiment F, which shows a significant discrepancy. Figure 1 also shows that for systems A, B, C, E, and F, the platinum concentrations obtained with powder are about two orders of magnitude higher than those obtained with wire.

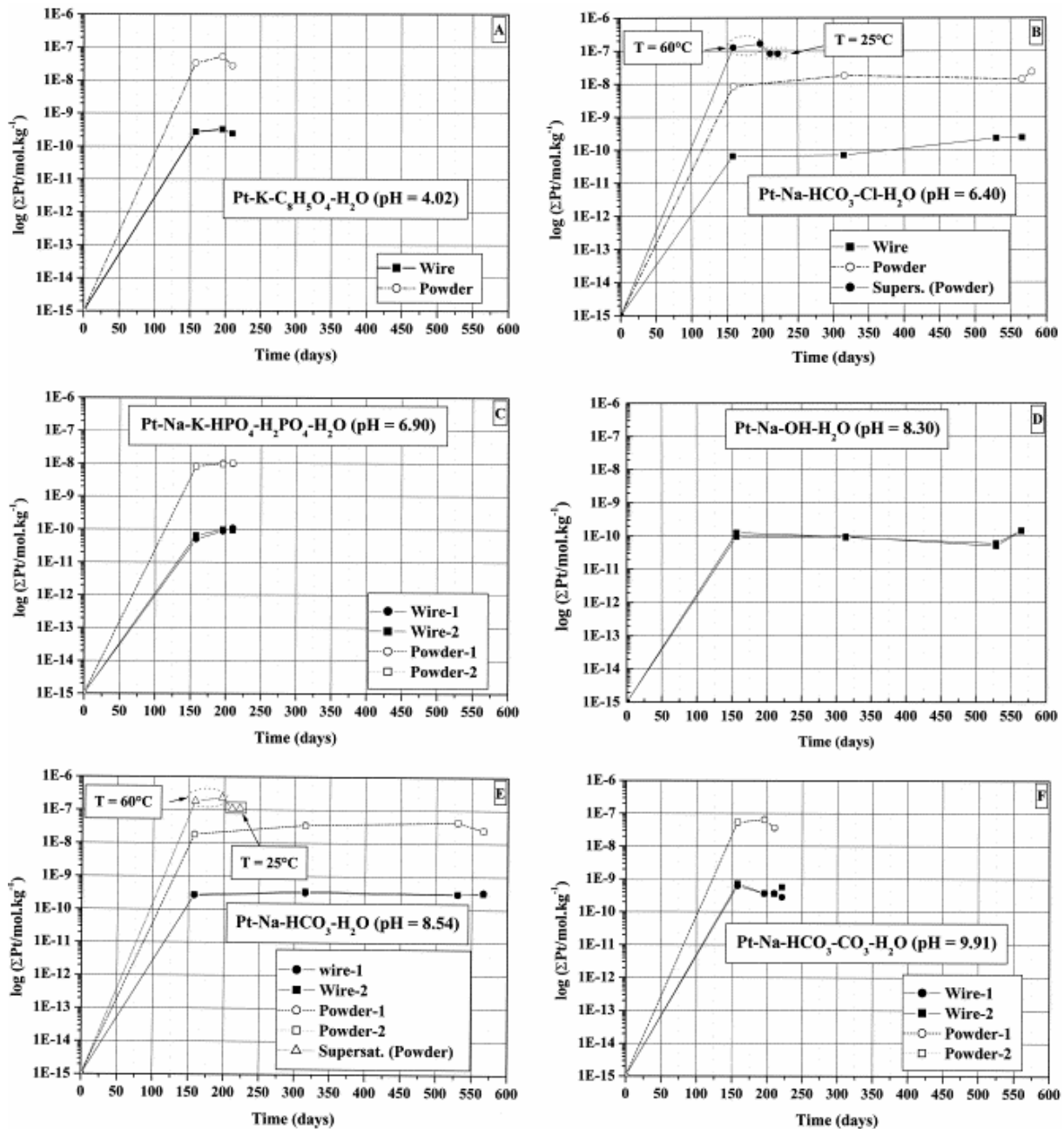


Fig. 1. Plot of total Pt concentrations (log concentration) vs. time (days) for the different solutions of this study in contact with platinum metal at 25 °C. Wire-1, Wire-2 and Powder-1, Powder-2 correspond to the results of the two analyses of each sample.

Even if it cannot be demonstrated that the systems investigated reached equilibrium, the graphs generally show that the dissolved platinum concentrations no longer change after 150 d. For the long-term experiments (>550 d), the Pt concentrations of B, D, and E are practically constant for both powder and wire experiments. This behavior strongly suggests that equilibrium was reached with the respective solids. Figure 1B shows a slight variation in platinum concentrations, particularly for platinum wire, which agrees with the change in pH from 6.4 to 8.5 (Table 2, B) during the experiment. Conversely, Figure 1D shows a slight decrease in Pt concentrations associated with a decrease in pH (Table 2, D) from 8.4 (initial pH) to 6.5 for the point measured at 529 d. The pH was not measured for the last point (at 565 d) where the Pt concentration had increased. When the pH of the aqueous solution is strongly

buffered (Fig. 1E and Table 2, E), the concentrations of dissolved platinum remain unchanged for both the powder and wire experiments.

Figure 1 also shows the results of experiments from supersaturation over a short period performed with platinum powder (Figs. 1B,E). The initial supersaturation was obtained by proceeding in exactly the same way as for undersaturation, but by raising the solution temperature to 60°C for 50 d. The solutions were then cooled rapidly to ambient temperature, and the Pt concentration was monitored. The Pt concentrations are higher than those obtained with powder by undersaturation. After 200 d, the Pt concentrations decreased and became closer to those obtained with powder at 25°C.

5. Data reduction

In aqueous media, platinum can exist in three oxidation states, namely 0, II and IV. Before interpreting the results, it is necessary to know the valence of the platinum in the system so as to correctly formulate the equilibrium reactions. Gammons (1996) shows that under strongly oxidizing conditions, the chloride complexes of Pt(IV) are more stable than their homologues of Pt(II) at 25°C. The author also shows that Pt(II) is more stable in solutions where the Pt concentration is controlled by the solubility of platinum metal. Wood (1991) presents arguments implying that dissolved platinum, under experimental conditions similar to those of the present study, is in the form of Pt(II).

In our experiments, the maximum Cl concentration was 4 mmolal for one case, and the maximum Eh measured was +590 mV for another case without chloride. Examination of the redox potential of the reactions $\text{Pt(s)} \rightleftharpoons \text{Pt}^{2+} + 4\text{e}^-$ ($E^0 = +1.27$ V) and $\text{Pt(s)} \rightleftharpoons \text{Pt}^{4+} + 2\text{e}^-$ ($E^0 = +2.28$ V) shows that it is very unlikely to stabilize Pt(IV) under the conditions adopted for our experiments. The Eh values (+280 to +590 mV) of the solutions used are substantially lower than the value of E^0 for the Pt(0)/Pt(IV) pair (+2.28 V). Finally, the dissolved platinum in the systems investigated is undoubtedly in the form Pt(II). Consequently, in the absence of strong ligands, the dissolution reaction of platinum metal (Pt(s)) can be described by reaction 1, for which the equilibrium constant (K_n) is expressed by

$$K_n = \frac{a_{\text{Pt(OH)}_n^{2-n}} (a_{\text{H}^+})^n (a_{\text{e}^-})^2}{a_{\text{Pt(s)}} (a_{\text{H}_2\text{O}})^n}$$

$$\log K_n = \log a_{\text{Pt(OH)}_n^{2-n}}$$

$$\log K_n = \log a_{\text{Pt(OH)}_n^{2-n}} + \log (a_{\text{H}^+})^n + \log (a_{\text{e}^-})^2 - \log a_{\text{Pt(s)}} - \log (a_{\text{H}_2\text{O}})^n,$$

$$\log a_{\text{Pt(OH)}_n^{2-n}} - 2 \text{pe} = n \text{pH} + \log K_n,$$

where a_i is the activity of the aqueous species i and pe is the negative of base 10 logarithm of the activity of the electron. The parameters of the left-hand side of Eqn. 3 and pH are known, and thus the ligation number n and K_n can be determined graphically (Fig. 2). Only the Pt concentrations of the systems that used platinum wire are plotted. If a parameter was not measured, we assumed that the parameter was constant and adopted its value measured at the previous point.

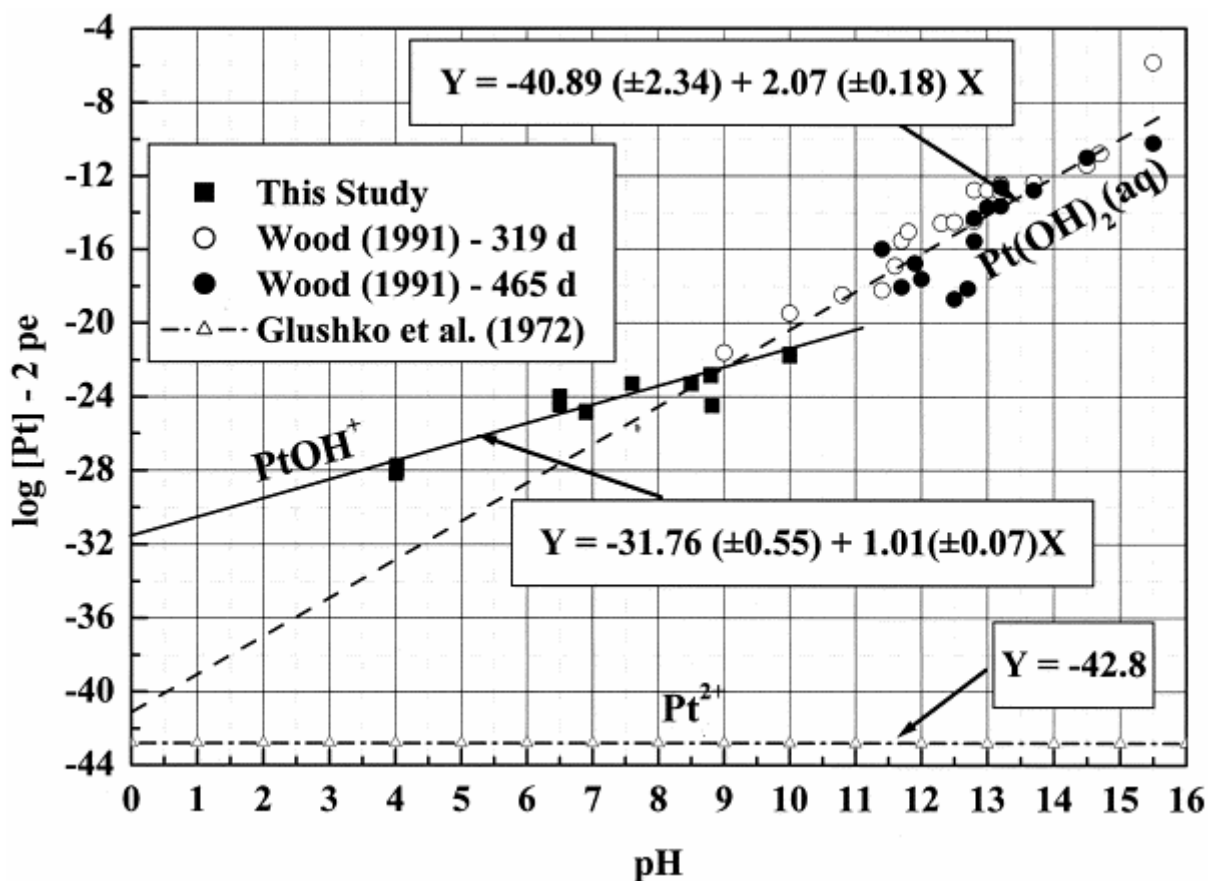


Fig. 2. Aqueous speciation of platinum in the Pt(II)-O-H system in equilibrium with platinum metal at 25 °C. Literature data (Wood, 1991 and Glushko et al., 1972) are included in order to examine the relative importance of platinum hydroxide complexes.

It should nevertheless be noted that the interpretation of the results of our measurements according to reaction 1 is based on various assumptions. The dissolved Pt concentrations are assumed to represent equilibrium concentrations with platinum metal (Pt(s)). First, the measurement points with the greatest weight in Figure 1 correspond to experiments that lasted 567 d. A total of 17 data points was used to determine the equilibrium constant of reaction 1. Second, we assume the absence of metastable precipitates of the (Pt(OH)₂(s)) hydroxide type, of which the solubility is certainly higher than that of platinum metal. The formation of this type of metastable compound is possible in such an experiment, particularly during equilibration by supersaturation. Our method, which consisted in tracking over time (kinetics) the variation in the dissolution of Pt metal, helps identify any formation of metastable compounds. In the case of Pt hydroxide formation, the Pt dissolution curves (Fig. 1) would have shown concentration peaks before reaching equilibrium. Despite the relatively short duration of the experiments by supersaturation performed during this study (Figs. 1B,E), the variation in the Pt concentrations suggests the approach of equilibrium with an amorphous phase.

Only the solubility results obtained with wire are used in further speciation calculations because those obtained with powder do not appear to have approached equilibrium with platinum metal. In fact, the results obtained with powder give Pt concentrations that are two orders of magnitude higher than those obtained with wire. Moreover, platinum concentration is fairly uniform over time and shows no tendency to reach concentration values comparable to those of the wire experiments.

Difficulties encountered with experiments that used precious metal powders (Pt, Au, etc.) are reported in the literature (Vlassopoulos; Wood and Wood), as are descriptions of particle losses in filtration or colloidal forms that complicate the analysis of dissolved platinum.

5.1. Powder experiment results

Because the rates of dissolution reactions are proportional to the reactive surface area, researchers prefer to use ground material to increase this surface area, thus enabling accelerated reaction rates. In the case of platinum powder, we observed a systematic difference of two orders of magnitude between the solubilities obtained with platinum wire and those obtained with platinum powder (Fig. 1). This raises the question of the crystallinity of the solid phase controlling the measured Pt concentrations.

It is also known that above some finite surface area, the solubility of solids is dependent on grain size (Stumm and Gislason). This can be expressed by the Freundlich-Ostwald equation (Enüstüm and Turkevitch, 1960), which was applied with success by Azaroual et al. (1997) to explain the commonly observed excess of dissolved silica in basinal sedimentary aquifers. In the present work, however, it was not possible to apply this approach to estimate the grain size controlling the measured platinum concentrations because of a lack of surface area data, particularly the energy at the platinum-water interface.

Another mechanism can be singled out to explain the platinum concentrations measured in powder systems, namely the precipitation of a platinum hydroxide ($\text{Pt}(\text{OH})_2(\text{s})$) on the surface of the particles of platinum metal powder. The hydroxide, which is more soluble than platinum metal, imposes higher dissolved platinum concentrations. One could very easily fall into this case because of the nonuniformity of the particle size of the powder used; the supplier only provides a very approximate indication of size from 0.2 to 0.4 μm . Ultrafine particles (hence very reactive), which dissolve very rapidly to exceed the solubility of platinum metal by several orders of magnitude, always exist after grinding the solids. The return of the system to equilibrium, with the initial solid, is prevented by the formation of unstable hydroxides. This second hypothesis does not appear to be more realistic because the behavior of platinum in the powder experiments by supersaturation (Figs. 1B,E) closely imitates the behavior observed in the powder experiments by undersaturation. Platinum powder may also generate Pt colloids in solution that may be analyzed despite the filtration at 0.1 μm before analysis. This point is discussed below in comparison with the wire experiment results. For the time being, it is difficult to advance the interpretation of the powder results in terms of thermodynamic constants of the hydroxide ($\text{Pt}(\text{OH})_2(\text{s})$) or energy of the platinum powder-water interface.

5.2. Wire experiment results

The plot of $\log [\text{Pt}]_{\text{T}} - 2\text{pe}$ as a function of pH (Fig. 2) shows that the measurement points lie along a line with slope 1.01 ± 0.07 . This indicates that dissolved Pt concentrations occur as the hydroxylated species PtOH^+ ($n = 1$ in Eqn. 1). Except for a_{H^+} and a_{e^-} , the activities are assumed to be equal to the concentrations. Although neglecting ionic strength effects may introduce some error into the results, it is likely that the error from this source is less than the overall uncertainty in the experimental measurements. The dispersion of the measurement points in Figure 2 suggests no possible improvement of the quality of the adjusted parameters (K_n and n) when activity coefficients are incorporated. Moreover, the effect of the propagation

of measurement errors in the Pt concentration, pH and Eh would be more significant than the errors induced by ignoring the activity coefficients (Wood, 1991).

Fig. 3 and Fig. 4. show the distribution of Pt(II) species in pure water at 25°C. The experimental data of Wood (1991) are combined with those obtained during the present study so as to calculate the distribution of the hydroxy species (PtOH^+ and $\text{Pt(OH)}_2(\text{aq})$) of Pt(II) in a space $\log [\text{Pt}] - 2 \text{ PE} = \text{pH}$ (Fig. 3). The Gibbs free energy of the aqueous species Pt^{2+} used (see Discussion) in Figure 3 is that of Glushko et al. (1972). According to Fig. 3 and Fig. 4., the concentration of Pt^{2+} species is insignificant and the hydroxy species predominate. The Eh-pH diagram (Fig. 4) presents a superimposition of the results obtained with Pt wire and powder. The hypothesis that Pt solubility is controlled by a solid hydroxide ($\text{Pt(OH)}_2(\text{s})$), in the basis of thermodynamic data given by Brookins (1987), is not justified because this would significantly modify the redox equilibrium. Instead, the high Pt concentrations measured in the powder experiments must be related to the very fine particles analyzed in the 0.1- μm -filtered solutions.

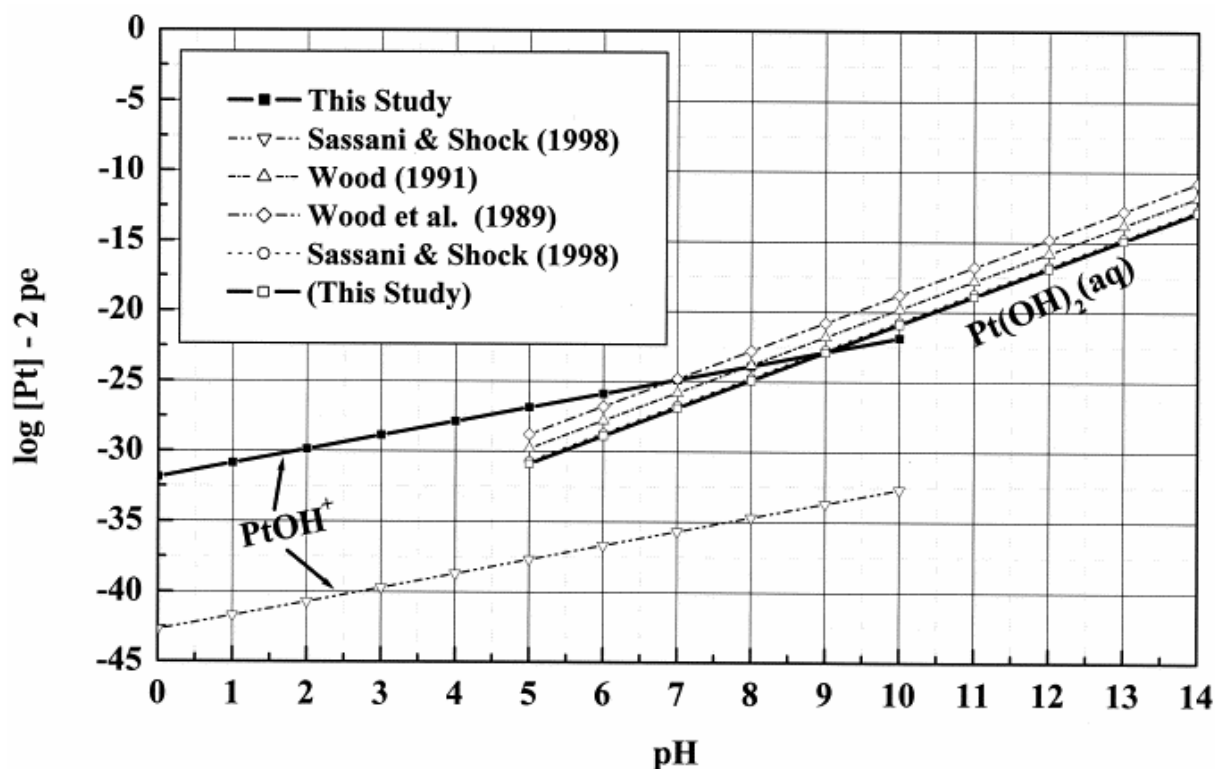


Fig. 3. Solubilities of platinum in the Pt(II)-O-H system in equilibrium with platinum metal at 25 °C. This Study: corresponds to data obtained and/or recommended (Wood, 1991) during this study. Other bibliographic data are plotted for comparison: Sassani and Wood.

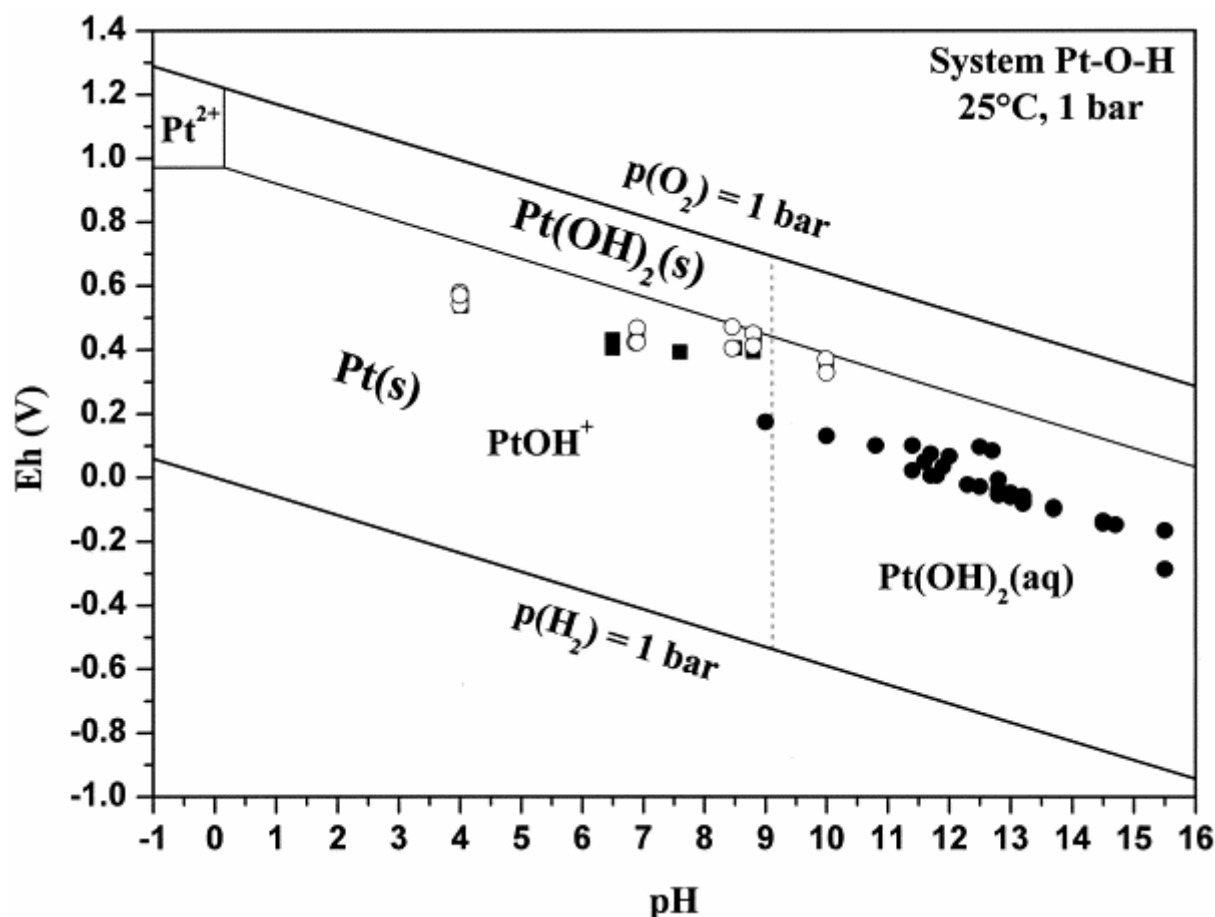


fig. 4.. Eh-pH diagram for the system Pt(II)-O-H. The activity of dissolved platinum $a_{\text{Pt}} = 10^{-10}$. Symbols: \square , wire experiment (this study); \circ , powder experiment (this study); \bullet , data of Wood (1991). The thermodynamic data used are those obtained and/or recommended during this study (see text). The value of Gibbs free energy (+285.08 kJ/mol) given in Brookins (1987) for $\text{Pt}(\text{OH})_2(\text{s})$ is also included.

The boundary between the zones of predominance of $\text{Pt}(\text{OH})_2(\text{aq})$ and PtOH^+ lies at about pH 9 (Fig. 3 and Fig. 4.). Because of the degree of uncertainty (± 2.34) on the equilibrium constant of reaction 1 obtained from the measurements of Wood (1991), this limit lies between pH 7 and 11. Wood (1991) used a finer regression method and gave the value of the stability constant of $\text{Pt}(\text{OH})_2(\text{aq})$ with an uncertainty of ± 1.0 . According to this value, the $\text{PtOH}^+/\text{Pt}(\text{OH})_2(\text{aq})$ equal activity boundary lies between pH 8 and 10.

The results obtained during this study agree with those of Wood (1991). It should be noted that the thermodynamic data obtained during the present study and that of Wood (1991), particularly the values of the stability constants of $\text{Pt}(\text{OH})_2(\text{aq})$ and PtOH^+ , do not depend directly on the Gibbs free energy of Pt^{2+} (reaction 1). The new solubility measurements of platinum metal at 25°C (this study) enable us to address this discrepancy by calculating the total speciation of platinum in the aqueous solutions of our experiments.

The equilibrium constant of reaction 5, written with $N = 0$,



may vary by several orders of magnitude according to the value of $\Delta G_f^\circ(\text{Pt}^{2+})$ used. The calculation of the solubility of Pt(s) and of the aqueous speciation of platinum from the concentrations measured in the different systems investigated (Table 1) enable us to select the value that best takes account of our measurements. The value (+244.11 kJ/mol) proposed by Glushko et al. (1972) helps to account for the complete speciation of platinum and is in good agreement with the measured solubilities (Fig. 2). Consequently, we recommend the values of the Gibbs free energy (ΔG_f° , in kiloJoule per mole) of the different aqueous species of Pt(II), +244.11 (Pt^{2+}), -55.96 (PtOH^+), and -234.48 ($\text{Pt}(\text{OH})_2(\text{aq})$) used to plot Fig. 3 and Fig. 4.. The equilibrium constants for complexation and solubility reactions used in these figures are indicated in Table 3.

Table 3. Thermodynamic constants of platinum hydroxide complexes and platinum solubility

$\text{Pt}^{2+} + \text{OH}^- \rightleftharpoons \text{Pt}(\text{OH})^+$	16.45	a
	<i>24.91 ± 0.50</i>	b
	23.89	e
$\text{Pt}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Pt}(\text{OH})_2(\text{aq})$	32.42	a
	28.81	c
	29.97	e
	<i>29.91 ± 1.0</i>	d
	28.3	b
$\text{Pt}(\text{s}) \rightleftharpoons \text{Pt}^{2+} + 2\text{e}^-$	-45.15	a
	-42.80	f
	-41.71	d
	-33.86	g
$\text{Pt}(\text{s}) + \text{H}_2\text{O} \rightleftharpoons \text{PtOH}^+ + \text{H}^+ + 2\text{e}^-$	-42.69	a
	<i>-31.76 ± 0.55</i>	b
$\text{Pt}(\text{s}) + 2\text{H}_2\text{O} \rightleftharpoons \text{Pt}(\text{OH})_2(\text{aq}) + 2\text{H}^+ + 2\text{e}^-$	<i>-40.89 ± 2.34</i>	c
	-40.72	a
	-39.8	d

^a Sassani and Shock (1998).

^b This study.

^c Computed from data of Wood (1991) for $\text{Pt}(\text{OH})_2(\text{aq})$ and that of Glushko et al. (1972) for Pt^{2+} .

^d Wood (1991).

^e Goldberg and Hepler (1968).

^f Glushko et al. (1972).

^g Wilde et al. (1989).

^h Wood et al. (1989). Italic values are those recommended on the basis of this study.

6. Discussion

In the present study, low concentrations of potential complexing ligands (e.g., Cl^-) preclude the existence of significant concentrations of complexes other than those containing hydroxides. The greatest uncertainties are associated with the measurement of Eh. The Eh measurement error estimated for our experiments is ± 20 mV. An error of this order implies an uncertainty of 0.4 log units on the thermodynamic constant ($\log K_1$) of reaction 1. Wood (1991) suggests evidence implying that Pt electrodes are reliable for characterizing the

Pt(0)/Pt(II) pair. However, van Middlesworth and Wood (1999) do not discard the possibility of Eh measurement errors in Wood's (1991) experiments.

The results obtained during this study offer a new set of stability constants of the PtOH⁺ complex. The overlap of the conditions of certain of our measurements with those of Wood (1991) allows us to reconsider these data and to propose consistent thermodynamic constants for PtOH⁺ and Pt(OH)₂⁰ as well as the Gibbs free energy of the aqueous species Pt²⁺ (Table 4). A bibliographic review by Sassani and Shock (1998) of the available data reveals wide disagreement between the different sources. By using their semiempirical algorithms, these authors recalculated a value of ΔG_r^o(Pt²⁺) of about +258.74 kJ/mol, which is higher than all the previous values determined from experiments (see appendix of Sassani and Shock, 1998).

Table 4. Cumulative stability constants (log β) of platinum hydroxide complexes from 25 to 300°C.

T (°C)	log β ₁			log β ₂			
	a	b	c	a	b	c	c
25	<i>24.91</i>	14.2	16.45	<i>28.81</i>	28.3		32.42
50	—		15.54	—			30.52
100	—	14	14.24	—	24		27.72
150	—		13.41	—			25.88
200	—	14	12.91	—	22		24.72
250	—		12.71	—			24.15
300	—	14	12.82	—	21		24.21

^a Log β₁ and log β₂ obtained in this study.

^b Data from Wood et al. (1989).

^c Data from Sassani and Shock (1998). Italic values are those recommended on the basis of this study.

In this recent compilation of thermodynamic data on PGEs, Sassani and Shock (1998) propose new thermodynamic data based on algorithms of Shock et al. (1992). In these same species, they established the parameters of the revised Helgeson-Kirkham-Flowers (HKF) equations (Helgeson; Tanger and Johnson).

Sassani and Shock (1998) used the revised HKF equations (Tanger and Helgeson, 1988) and semiempirical algorithms to calculate the thermodynamic properties of platinum in the standard state. The HKF approach allows extrapolation of these data to high temperatures and high pressures. However, the data of Sassani and Shock (1998) do not agree with the results of platinum solubility measurements (Fig. 3) at pH 4 to 15.5 (present study and that of Wood, 1991). Sassani and Shock (1998) show that the data available at 25°C are not sufficiently accurate to enable their extrapolations. In fact, the results of the calculations of the thermodynamic constants that used revised HKF equations is closely dependent on the set of values of these constants at 25°C and 1 bar (standard conditions).

To determine the speciation of platinum in certain fluids typical of supergene conditions and seawater, we examined the literature for data on the chloride and sulfate complexes of platinum. The stability constants of chloride and sulfate complexes of Pt(II) (Gammons; Wood and Sassani) are taken into account. The data of these authors are combined to the recommended Gibbs free energy of Pt²⁺ (Glushko et al., 1972) to reevaluate the stability constants of platinum chloride (PtCl⁺, PtCl₂(aq), PtCl₃⁻, and PtCl₄²⁻) and sulfate (PtSO₄(aq), Pt(SO₄)₂²⁻, Pt(SO₄)₃⁴⁻) aqueous complexes (Table 5).

Table 5. Stability constants (log β) of Pt(II) complexes from 25 to 300°C of chloride and sulfate ligands.

Reaction	25	50	100	150	200	250	300	Source
Pt ²⁺ + Cl ⁻ ⇌ PtCl ⁺	<i>6.33</i>	—	—	—	—	—	—	a
	—	5.4	5.0	4.9	5.0	5.3	5.7	b
	8.68	8.19	7.32	6.89	6.74	6.81	7.14	c
Pt ²⁺ + 2Cl ⁻ ⇌ PtCl ₂ (aq)	<i>13.14</i>	—	—	—	—	—	—	a
	—	9.50	8.60	8.10	8.20	8.50	9.30	b
	15.49	13.90	12.67	11.75	11.34	11.38	11.94	c
Pt ²⁺ + 3Cl ⁻ ⇌ PtCl ₃ ⁻	<i>16.14</i>	—	—	—	—	—	—	a
	—	12.3	11.2	10.5	10.4	10.6	11.3	b
	18.49	16.8	14.47	13.08	12.35	12.17	12.57	c
Pt ²⁺ + 4Cl ⁻ ⇌ PtCl ₄ ²⁻	<i>17.66</i>	—	—	—	—	—	—	a
	—	14.0	12.7	12.0	11.9	12.0	12.6	b
	20.01	17.7	14.44	12.39	11.16	10.59	10.67	c
Pt ²⁺ + SO ₄ ²⁻ ⇌ PtSO ₄ (aq)	<i>0.56</i>	—	—	—	—	—	—	a
	2.91	—	—	—	—	—	—	c
Pt ²⁺ + 2SO ₄ ²⁻ ⇌ Pt(SO ₄) ₂ ²⁻	<i>2.38</i>	—	—	—	—	—	—	a
	4.70	—	—	—	—	—	—	c
Pt ²⁺ + 3SO ₄ ²⁻ ⇌ Pt(SO ₄) ₃ ⁴⁻	<i>3.67</i>	—	—	—	—	—	—	a
	6.00	—	—	—	—	—	—	c

^a This study (see text).

^b Wood et al. (1992).

^c Sassani and Shock (1998). Italic values are those recommended on the basis of this study.

7. Geochemical implications

The aqueous speciation of Pt(II) was calculated by EQ3NR software (Wolery, 1992) for seawater (data of Nordstrom et al., 1979) and for solutions of NaCl (0.1, 1.0, and 3.0 mol/L). The platinum concentration was arbitrarily taken as 10⁻¹¹ molal for all the calculations.

The calculation of the speciation of platinum in seawater (Fig. 5), taking account of our data for hydroxyl complexes and those of Sassani and Shock (1998) for chloride complexes, shows the following distribution: PtOH⁺ (90%), Pt(OH)₂⁰(aq) (9.7%), PtCl₄²⁻ (0.2%), and PtCl₃⁻ (0.1%). The data of Sassani and Shock (1998) indicate a speciation represented at 99% by the Pt(OH)₂(aq) species and 1% by PtCl₄²⁻. The data obtained in our study bring the thermodynamic estimates of Sassani and Shock (1998) into question because the stability constants of the chloride complexes calculated from the data of these authors are higher than those of Wood et al. (1992) by two to four orders of magnitude even at 25°C (Table 4 and Table 5). This is due primarily to the fact that Sassani and Shock chose to base their extrapolation on a different set of thermodynamic data at 25°C.

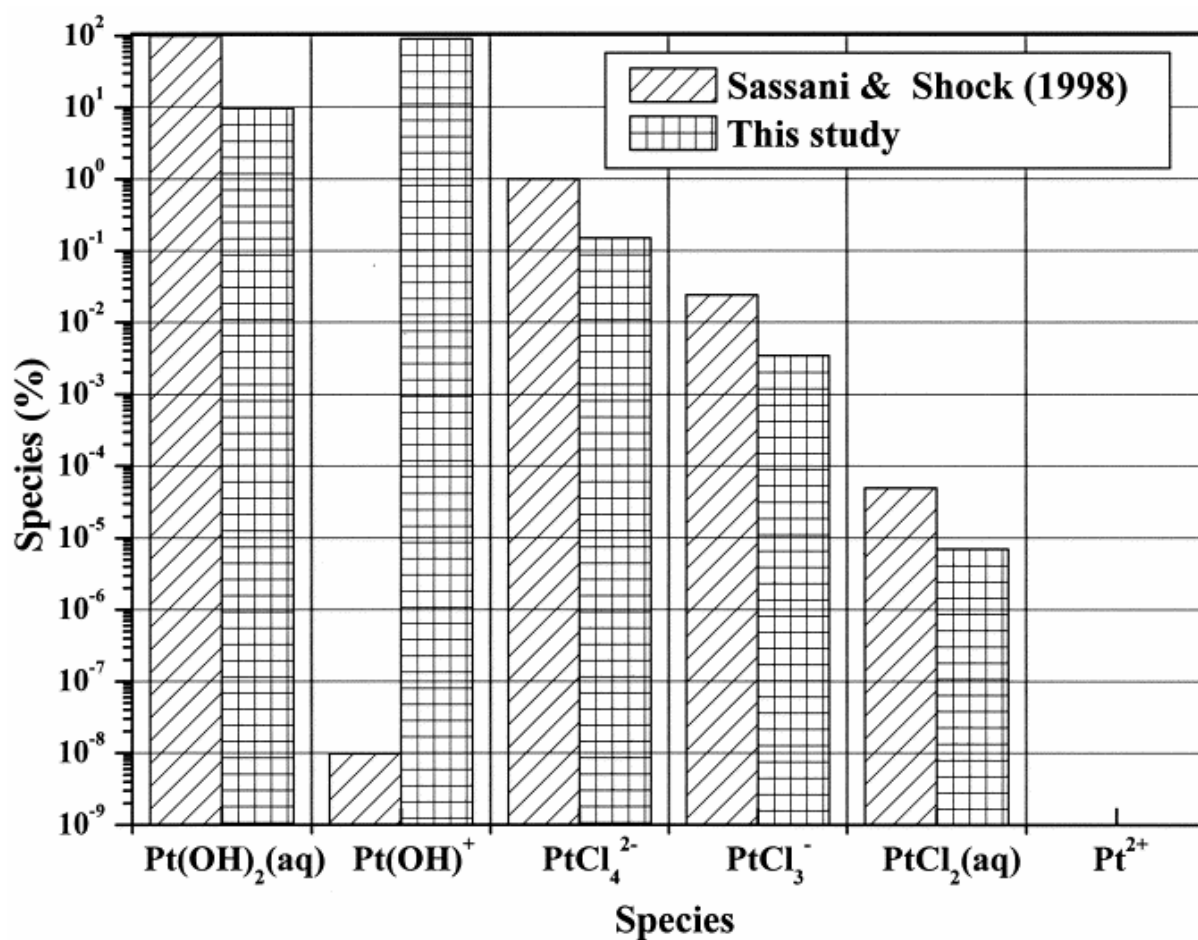


Fig. 5. Platinum speciation in seawater at 25 °C. Seawater composition was taken from Nordstrom et al. (1979). The following values were used in the calculation: pH = 8.22; [Cl⁻] = 0.55 molal and Eh = +500 mV. [Pt²⁺] = 2.71 x 10⁻¹⁷ (This study) and 8.6 x 10⁻¹⁹ (Sassani and Shock, 1998).

Because of the variability of the chemical composition of the fluids in rivers, soils, etc., it is difficult to draw conclusions concerning the relative importance of the hydroxyl and chloride species of Pt in such environments. In fact, organic ligands and thiosulfates may be present in non-negligible contents in these fluids. We have therefore calculated the speciation of Pt in solutions with variable NaCl concentrations as a function of pH (Fig. 6). This figure compares the distribution of the aqueous species of Pt as a function of pH by using our constants and those of Sassani and Shock (1998). For values of pH >10, the neutral species (Pt(OH)₂(aq)) is predominant (Figs. 6A–F), whereas for values of pH <4, the chloride complex PtCl₄²⁻ is predominant. For moderate pH values (4 to 9), a significant difference is observed in the species distribution calculated with our data and those of Sassani and Shock (1998); their data underestimate the importance of the PtOH⁺ species even for solutions with low Cl⁻ contents (Fig. 6B). In contrast, the data recommended in our study indicate a speciation in which the PtOH⁺ species may be important (Fig. 6A), particularly in surface waters ([Cl⁻] <0.1 mol/L). In fact, for pH <9 and in the absence of other strong ligands (i.e., S₂O₃²⁻, CN⁻, etc.), our study shows that the PtOH⁺ species may account for more than 50% of dissolved Pt. Even in the case of relatively saline solutions up to 1 mol/L NaCl, this species can account for over 80% of dissolved Pt at pH values around 7 (Fig. 6E).

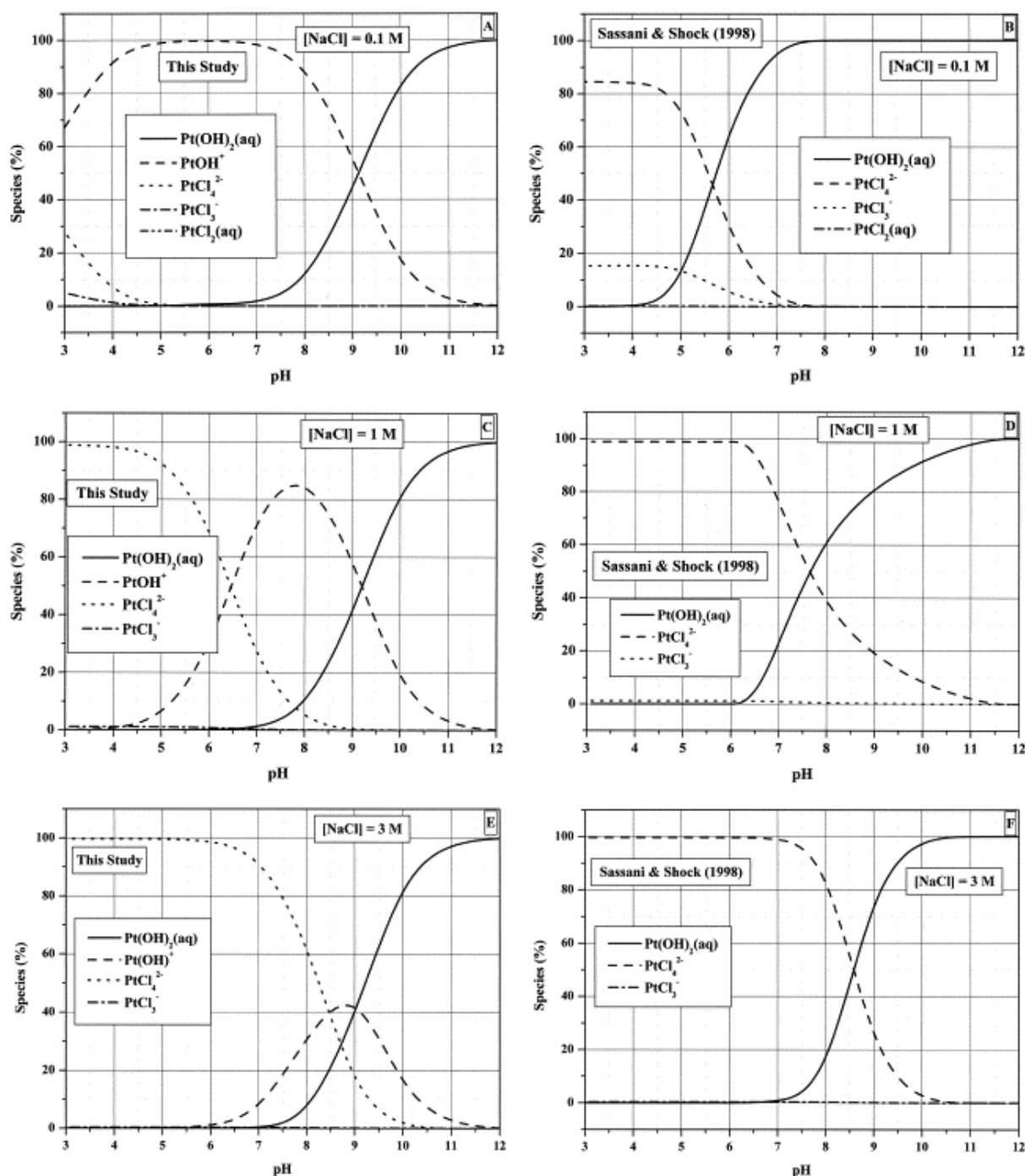


Fig. 6. Calculated platinum speciation in NaCl solutions (0.1, 1.0 and 3.0 M) vs. pH according to the data acquired and/or recommended during this study compared to that based on data from Sassani and Shock (1998).

8. Conclusions

The thermodynamic properties of the aqueous species of platinum are not well known, and serious disagreements exist among data derived during different studies at temperatures varying between 25 (Table 3 and Table 4) and 300°C (Table 5). The present work acquired new solubility measurements of platinum metal at pH 4 to 10 and at 25°C. A comparison of

the experimental results using Pt wire and powder shows significant differences in the Pt concentrations measured in solutions. Consequently, the use of the Pt powder results can lead to an overestimation of Pt concentrations in solutions, which does not allow the evaluation of thermodynamic parameters of Pt(s) solubility in the range of pH 4 to 10. Only the Pt wire results were used to determine the stability constant of the PtOH^+ species.

The results demonstrate the importance of the hydroxylated species of platinum (PtOH^+) in the transport of Pt in surface fluids and have yielded a set of consistent thermodynamic data for the species Pt^{2+} , PtOH^+ , and $\text{Pt}(\text{OH})_2(\text{aq})$. The recommended values of the free energies of formation (in kJ/mol) are +244.11 (Pt^{2+}), -55.96 (PtOH^+), and -234.48 ($\text{Pt}(\text{OH})_2(\text{aq})$).

The speciation of platinum in seawater comprises PtOH^+ (90%), $\text{Pt}(\text{OH})_2(\text{aq})$ (9.7%), PtCl_4^{2-} (0.2%), and PtCl_3^- (0.1%). This confirms the predictions of Wood et al. (1992) concerning the importance of the hydroxylated complexes in the transport of platinum in subsurface aqueous systems. The proportion of platinum transported by chlorides in surface hydrogeochemical environments is expected to be insignificant.

Despite the preconception that platinum is considered inert the results of our experiments show that surface fluids display a strong potential for Pt, causing the deposition of platinum metal, its incorporation into other minerals, or both. Other experiments on the thermodynamic stability of platinum complexes with the thiosulfate, organics, etc., will help to advance our knowledge on the transport of precious metals, such as Pt, and construct better models of the speciation of platinum. Blair 1993

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