The Role of the Thiol Functional Group in the Solubility of Palladium in Oil Analogues

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1. Introduction

In natural systems, a variety of metals are commonly associated spatially with hydrocarbons, e.g., pyrobitumen. These include, gold (Au), palladium (Pd), platinum (Pt), zinc (Zn), copper (Cu), molybdenum (Mo), mercury (Hg), lead (Pb), vanadium (V), and nickel (Ni). Moreover, these metals commonly occur in elevated concentrations in crude oil. Textural evidence of metal-oil interactions is also commonly observed in some sedimentary rocks with high metal concentrations. High concentrations of Au are present in so-called carbon seams (pyrobitumen) in the Witwatersrand goldfield, South Africa (Kucha and Przybylowicz, 1999; Williams-Jones et al., 2009). Sphalerite in many Mississippi valley-type deposits (MVT) commonly contains liquid hydrocarbon fluid inclusions and oil seeps have been reported from some MVT deposits (Kesler et al., 1994). Nickel and V are present in high concentrations in many crude oils (> 1000 ppm in the case of V and > 100 ppm in the case of Ni). Indeed, the Ni/V ratio is widely utilized by oil companies to distinguish marine from continental sources of hydrocarbons (Barwise, 1990). Platinum group elements (PGE) are of particular interest because of their high commercial value and have been found in economic concentrations associated in pyrobitumen in the Kupferschiefer, Poland (Kucha and Przybylowicz, 1999). Black shales in South China likewise have been shown to contain economic concentrations of Pd and Pt (0.4 ppm Pd and 0.3 ppm Pt in the Zunyi deposit; Coveney, 1991). These observations and preliminary experiments showing that crude oils can dissolve metals to potentially exploitable concentrations, suggest that liquid hydrocarbons could constitute important ore fluids (Miedaner et al., 2005; Williams-Jones et al., 2009).

![Figure 1](image1.png)
![Figure 2](image2.png)
![Figure 3](image3.png)

![Figure 4](image4.png)
![Figure 5](image5.png)
![Figure 6](image6.png)
The Role of the Thiol Functional Group in the Solubility of Palladium in Oil Analogues

Figures: 1) Cinnabar associated with bitumen in the Culver-Baer Mercury deposit, California, U.S.A. (Peabody and Einaudi, 1992), 2) Gold in bitumen in the Witwatersrand, South Africa (England and Rasmussen, 2001), 3) Palladium and Pt in the bituminous shale of the Kupferschiefer, Poland (Kucha and Przybyłowicz, 1999), 4) Oil inclusion in a quartz grain, 5) Molybdenum in bituminous shale in South China (Coveney, 1991), 6) Oil seep from the Pine Point MVT deposit, Yukon, Canada (Kesler et al., 1994).

2. Objectives

The objective of this thesis is to experimentally determine the solubility of Pd in selected organic compounds known to be important constituents of natural liquid hydrocarbons, and thereby contribute to the body of knowledge on ore forming processes involving hydrocarbons. Approximately 40 to 50% of crude oil is composed of paraffins, including straight chain alkanes. Sulphur is an important component of marine-derived crude oil (Barwise, 1990). In view of this and the fact that Pd is known to have a strong affinity for sulphur, the objective of this study is to investigate the solubility of Pd in dodecane (figure 7) and dodecanethiol (figure 8).

3. Reasons for the Experimental Parameters

3.1. Why Palladium (Pd)?
Palladium is one of the PGE group of elements (Pd, Pt, Rh, Ru, Ir, and Os) and is most commonly mined from magmatic immiscible sulfide deposits. These deposits are located in South Africa (42%), Russia (40%), and North America (9%). The two main reasons for investigating the solubility of Pd in liquid hydrocarbons are: 1) presence of economic Pd deposits in organic-rich black shales in the Kupferschiefer, Poland and South China; and 2) the observation that Pd is, a soft acid, and therefore should theoretically have high affinity for sulphur, a soft base.

3.1.1. Pearson’s rule
Pearson’s rule (guideline) is based on two properties of ions: 1) radius, and 2) charge. Those two properties determine the affinity of a metal for a ligand. Pearson’s rule predicts metal-ligand interactions, applying the ideas of stereochemistry and valence properties.
The thiol group (HS-) is a soft ligand, which is theoretically reactive with soft metals. Palladium (Pd$^{2+}$) is a soft acid due to its relatively large ionic radius to charge ratio. Due to its d-orbital configuration, Pd can provide empty coordination sites for bonding (Pd(2+)) and non-bonding sites (Pd(0)). Thus, the empty valence orbital (lowest unoccupied molecular orbital (LUMO)) will serve as a Lewis acid (electrophilic sites), whereas non-bonding orbitals (Pd(0)) (the highest occupied molecular orbitals (HOMO)) will serve as Lewis bases (nucleophilic sites) (Negishi, 2002). Not only is Pd a soft acid, it is also a versatile element, which can react with wide range of chemical compounds and still maintain its stereoselectivity and chemoselectivity (Negishi, 2002). Soft acids and bases dominantly form covalent bonds, which are generally stronger than the ionic bonds formed between hard acid and bases. Thus, I chose Pd for its stereoselective and chemoselective nature based on Pearson's rules and its known affinity for hydrocarbons. Dodecane and dodecanethiol were chosen as the solvents, to distinguish the solubilizing effect of an alkane from that of an alkane with a thiol group.

3.2. Why Dodecane?
One of the reasons for choosing dodecane as the solvent in the experiments was that dodecane is liquid over the temperature range of the oil window (50 °C - 150 °C). A second reason for choosing dodecane is that data are available on the time required for steady state dissolution in dodecane (Miedaner et al., 2005). Although these data are for Hg, they do provide a rough guide that can be used for Pd; the kinetics of Hg and Pd in dodecane may be different. The final reason for choosing dodecane as a solvent is that crude oil is composed dominantly of alkanes.

3.3. Why Dodecanethiol?
Having selected dodecane as a solvent, it made most sense to use dodecanethiol to investigate the effect of thiol groups on the solubility of Pd in natural oil systems (this permits the role of the corresponding alkane in dissolution to be eliminated). Thiolate (RS-) is a “soft” base, because of its large molecular radius to small charge ratio (Pearson’s rule). This promotes covalent bonding to the thiol group. Palladium is a soft acid and is therefore predicted to form strong covalent bonds.
The Role of the Thiol Functional Group in the Solubility of Palladium in Oil Analogues

4. Methodology

4.1. Cleaning procedures
Concentrated nitric acid is used to clean the titanium autoclaves (figure 9.1); they are soaked in this acid for a day between experiments. Once they have been cleaned in this manner, the autoclaves further cleaned for 2 hours with distilled water; the main purpose of this is to neutralize any remaining acid. The autoclaves are then dried in an oven.

![Cleaning procedures diagram](image)

Figure 9. The methods used to clean the autoclaves to prepare for the new experimental runs.

4.2. Experimental set-up
Palladium is introduced in two ways, either as palladium wire or as palladium hydroxide. The palladium is placed in an open quartz holder to isolate it from the solvent at the beginning and end of an experiment. In order to prevent dispersion of the palladium hydroxide powder in the solvent, the corresponding quartz holder is capped by a semipermeable stopper. Solvent and holder are then placed in a Ti autoclave. Because of concern over potential reaction with the Ti autoclave, a set of control experiments will be run in which the solute-solvent system is encased in a quartz tube closed by welding after introduction of the reagents and placed in a Ti autoclave containing excess solvent to balance the pressure in the system and prevent the quartz tube from shattering. If the results of the control experiments are the same as those obtained when the solute-solvent system is exposed to the Ti autoclave, further experiments will be run using the latter set-up.

![Experimental set-up diagrams](image)

Figure 10. Different methods used to introduce palladium to the hydrocarbon systems.
4.3. Experimental procedure

4.3.1. Experimental runs
Experiments are performed in light-weight titanium autoclaves treated with nitric acid to produce an inert internal surface coated with TiO$_2$, and involve measuring the solubility of palladium metal or hydroxide in dodecane and dodecanethiol at temperatures up to 300 °C using a thermally regulated oven. The durations of the experiments ranged from 15 to 60 days. After completion of an experiment, the autoclave was quenched, and samples of the quenched solutions, and solutions used to wash the autoclaves (Pd commonly precipitated on the surface of the autoclave), are analyzed using inductively coupled plasma mass spectrometry (ICP-MS).

4.3.2. Ashing
In order to be able to analyse the Pd using ICP-MS, it is necessary to ash the sample. This is done by placing 5 ml of reacted solution in a Ti autoclave and heating the autoclave to 450 °C, to convert the hydrocarbon solvent to dry ash. Next, 10 ml of concentrated HCl is used to leach the Pd from the ash and autoclave walls. This HCl solution and the solutions used to wash the autoclave employed in the experiments is analysed using ICP-MS.
5. Preliminary experimental results

The data presented in Figure 12 show that Pd is very soluble in these simple analogues of natural liquid hydrocarbons at temperatures commonly encountered in oil reservoirs, and that its solubility may be increased by complexation with thiol groups.

![Graph showing Pd concentration in Dodecane and Dodecanethiol](image)

One of the preliminary conclusions of the study is that liquid hydrocarbons could be very effective agents of Pd transport in nature. This and the observed close spatial association of Pd with hydrocarbons in some PGE deposits suggest that liquid hydrocarbons could be important ore fluids for these deposits.

6. Scientific contributions and significance of the Proposed Research

One of the main problems in understanding inorganic-organic interactions in crude oil is the chemical complexity of the latter which will likely preclude developing a thermodynamic model for metal solubility in this medium. One of the main scientific contributions of this study will be to understand the speciation of Pd in simple alkanes and the role of sulfur functional groups in promoting the solubility of this metal.
The Role of the Thiol Functional Group in the Solubility of Palladium in Oil Analogues

7. Future work and schedule

A timeline for the proposed study:

<table>
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<tr>
<th>Dates</th>
<th>Research Plans</th>
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<tr>
<td>1\textsuperscript{st} semester 2012</td>
<td>• Resolve some analytical problems for analyzing Pd in hydrocarbons</td>
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<tr>
<td>2\textsuperscript{nd} semester 2012</td>
<td>• Perform experiments on Pd with crude oil provided by Stat Oil</td>
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<td>• Perform experiments on Pd concentrations in dodecane and dodecanethiol at various temperatures</td>
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<tr>
<td></td>
<td>• Perform experiments of Pd concentrations in benzenedithiol and toluene at various temperatures</td>
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<tr>
<td>Summer 2013</td>
<td>• Perform experiments on partitioning of Pd in water and hydrocarbons</td>
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<tr>
<td>3\textsuperscript{rd} semester 2013</td>
<td>• Start thesis preparation</td>
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<td></td>
<td>• Finish the experimental runs</td>
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<tr>
<td>4\textsuperscript{th} semester 2014</td>
<td>• Thesis preparation</td>
</tr>
<tr>
<td>Summer 2014</td>
<td>• Finish thesis preparation</td>
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<td>Conferences</td>
<td>• Summer 2013: Goldschmidt conference</td>
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The Role of the Thiol Functional Group in the Solubility of Palladium in Oil Analogues

8. References


