

Measuring Water Solubility of Platinum Group Metal Containing Substances

Solubility data available in the literature for the first time

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The water solubility of 22 platinum group metal (pgm) containing substances was evaluated to provide useful data for regulatory compliance and to aid assessment of their environmental impact. The flask method from OECD Guideline 105 (1) for the testing of chemicals (water solubility) was used to test each material. For substances that could not be isolated as pure solids, a simplified water solubility test was carried out. The results provide reliable data on solubility previously unavailable in the literature.

Introduction

There is a paucity of robust data on the water solubility of many pgm compounds. Besides being a fundamental property for each substance, this data is essential for a number of purposes: for example to comply with regulatory requirements (see further discussion below) and as a basis for modelling the environmental effects or environmental distribution of these compounds. Water solubility levels can also serve as an indication for bioavailability of a substance and are thus an important consideration when planning and interpreting ecotoxicology or mammalian toxicology studies.

It has become necessary, as part of the European Union regulation Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (2, 3) to determine the water solubility of every substance placed on the market in quantities greater than one tonne. In order

to achieve this, the industry has organised itself into consortia representing sectors of common interest to share costs and minimise testing.

The work presented in this paper covers pgm compounds for which no reliable data on water solubility was available in the existing literature and which are being considered by the Precious Metal Consortium (PMC) under the auspices of The European Precious Metal Federation (EPMF). To our knowledge, this is the first comprehensive publication of water solubility data of pgm compounds.

Water Solubility Testing

The water solubility of a substance is defined as the saturation mass concentration of the substance in pure water at a given temperature. Water solubility is expressed as the mass of solute per volume of water with the SI unit of kg m^{-3} , but g l^{-1} is also commonly used.

OECD Guideline 105 (1) describes two methods for determining water solubility. These are the column elution method and the flask method. The column elution method involves the use of a micro column charged with an inert carrier material and an excess of test substance. The test material is then eluted with water. Water solubility is determined when the mass concentration (the mass of material dissolved in a given volume) is constant as a function of time. The flask method involves dissolving the test material in water at a higher temperature than the test temperature. The saturated mixture is then cooled and allowed to equilibrate at the test temperature. The mass concentration of the test substance is then determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). According to the Guideline,

solubility below 10^{-2} g l⁻¹ should be evaluated by the column elution method, whereas the flask method is preferred for substances with water solubility above 10^{-2} g l⁻¹.

In this investigation only the flask method was used. The column elution method was not considered to be appropriate for tests on inorganic compounds due to the difficulty of coating the support material with the test substance. A preliminary test was carried out on each substance to determine approximate water solubility. As well as determining which method was to be used it also established how much sample was needed to carry out the test.

A difficulty in following this test method is that several of the substances cannot be isolated as pure solids (some are described as “damp solids”), and whilst a known mass of the material can be tested this does not relate to a known quantity of the pure substance. In such cases a ‘Simplified Water Solubility Test’ was carried out. This test involved preparing a saturated solution, which was then filtered, and the mass concentration of the test substance determined by ICP-OES. In the simplified test the experiment was conducted over 24 hours, which was deemed suitable for fulfilling the water solubility end-point, whereas the flask method is repeated at 48 hours and 72 hours (1).

All of the experimental work for each substance was carried out in duplicate to give extra confidence in the data and allow for calculated errors of the water solubility of each substance.

Some additional water solubility studies were carried out by an external laboratory. This was done for confidentiality reasons, with some companies involved in the study feeling uncomfortable providing their materials to a competitor for analysis. For this reason there is no comparison data between laboratories.

Experimental

Instruments

A Grant OLS200 thermostatically controlled shaking water bath was used to agitate the solutions at a controlled temperature. The Precisa 2625MA-FR analytical balance was used to accurately weigh out the required amount of each substance. A Denley BS400 centrifuge was used to separate the solid and liquid phases of the test material after specific time periods. The concentration of pgm in the resulting solution was determined using a Perkin Elmer Optima 3300

RL ICP-OES. The pH of the test solutions were determined with a Mettler Toledo MP225 pH meter.

Chemicals

De-ionised water with a resistivity of 18.2 MΩ cm, produced by a Milli-Q® Advantage A10 system from Millipore, was used to dissolve the test substances. For ICP-OES measurements, pgm stock standards, prepared in-house and standardised gravimetrically, were used to provide calibration standards. These were used to quantify the pgm content of the saturated solutions obtained from the test method. The pgm materials tested were sourced from EPMF member companies registering these substances under REACH. The tested materials were considered representative samples. For commercial reasons, the producers are not specifically mentioned for each individual material but are listed in the Acknowledgement in this paper.

Preliminary Test

In order to calculate how much sample was required for the analysis, a preliminary test was carried out to determine the approximate solubility. Increasing volumes of water were added to 0.1 g of test material with the mixture being shaken between each addition for 10 minutes. The addition of water was continued until either the substance had completely dissolved or 100 ml of water had been added. In the latter case an approximate solubility of <1 g l⁻¹ was recorded.

OECD 105 Flask Method

From the preliminary test, the quantity of test material necessary to saturate 10 ml of water was calculated. Five times this amount was weighed into a conical flask. This was repeated in five further flasks to allow the study to be carried out in duplicate, for three different analysis times. To each flask, 10 ml of deionised water was added. The flasks were stoppered tightly with rubber bungs and agitated at 200 rpm in a shaking water bath at 30°C. After 24 hours two flasks were removed from the water bath and allowed to equilibrate at room temperature for a further 24 hours. Samples from these flasks were then transferred to centrifuge tubes and centrifuged for 30 minutes to separate the solid from the liquid. The solution was analysed by ICP-OES for the pgm content and the pH was measured. The other four flasks were treated similarly,

and after initial equilibration at 30°C two flasks were removed at 48 hours and the final two after 72 hours.

If the last two vessels varied by less than 15%, the test was deemed satisfactory. If the last two vessels varied by more than 15% then the analysis was repeated with longer equilibration time until the variation was less than 15%, satisfying the criteria specified in the Guideline (1).

Simplified Water Solubility Test

0.2 g of test material was added to 20 ml of deionised water in a conical flask. In cases where the substance was only available as a solution, the equivalent of 0.2 g of the initial solution (for example 2 g of a 10% solution) was used. This was done for rhodium 2-ethylhexanoate solution in 2-ethyl hexanol, dihydrogen tetrachloropalladate, platinum(0) divinyltetramethylsiloxane complex, palladium(II) nitrate and platinum(II) nitrate. The flasks were stoppered tightly with rubber bungs and agitated at 200 rpm in a shaking water bath at 30°C. After 24 hours the solutions were filtered using 0.1 µm cellulose nitrate membrane filters and the pgm content was determined by ICP-OES. The pH of the solution was also measured. The analysis was repeated for each material to provide duplicate data.

Additional Tests

Some additional water solubility studies were carried out by a separate laboratory (AQura GmbH, Marl and Hanau, Germany) on a further five pgm containing substances. The same flask method from OECD Guideline 105 was used for each substance. The following apparatus were used in this additional work: Heidolph Promax 2020 shaking machine; Mettler

Toledo XS205 analytical balance; Lauda Thermostat RMS 6; Heraeus™ Varifuge™ GL centrifuge; Horiba Ultima 2 ICP-OES; Metrohm 736 GP Titrimo burette; Hamilton Mikroelektrode pH electrode. The reagents used in the tests were: purified water produced from a Milli-Q® system; 1.0 g l⁻¹ standards of platinum, palladium, iridium and ruthenium traceable to standard reference materials (SRM) from the National Institute of Standards and Technology (NIST).

Results

The solubility of each of the substances was calculated using the pgm concentrations obtained from the ICP-OES analysis and the pgm assay from the certificate of analysis and conformance provided with each substance. **Table I** shows a summary of the water solubility of each of the test materials analysed by the OECD 105 Flask Method. The results for dicarbonyl(2,4-pentanedionato)rhodium(I) showed a tendency of increasing values at each equilibration time. The experiment was repeated at additional 24 hour intervals until the method criteria were met. In this particular case the samples were repeated with equilibration times up to 192 hours and 216 hours.

Table II shows a summary of the water solubility of each of the test materials analysed by the simplified water solubility test. The amount of test material used was sufficient to produce a saturated solution for substances with water solubility below 10 g l⁻¹. For substances that were soluble at this level, >10 g l⁻¹ was reported as the limit for the water solubility. The pH of each of the test solutions was measured and the results of this can be seen within **Table I** and **Table II**. A summary of the water solubility data obtained from AQura can be seen in **Table III**, along with the pH of each test solution.

Table I Water Solubility of Substances Tested Using OECD 105 Flask Method (1)^a

Substance	CAS number	Water solubility, g l ⁻¹	pH
Potassium hexachloroplatinate(IV)	16921-30-5	11.0 ± 0.08	2.6
Palladium(II) chloride	7647-10-1	4.03 ± 0.014	2.2
Diamminedichloropalladium(II)	14323-43-4	0.63 ± 0.001	5.0
Rhodium(III) iodide	15492-38-3	<0.01	4.3

(Continued)

Table I (Continued)

Substance	CAS number	Water solubility, g l ⁻¹	pH
Rhodium(III) nitrate hydrate	13465-43-5	1170 ± 2.5	-0.9
Ruthenium(III) chloride hydrate	14898-67-0	1140 ± 13.2	0.6
Dicarbonyl(2,4-pentanedionato)rhodium(I)	14874-82-9	0.65 ± 0.044	6.0
Ammonium hexachlororhodate(III)	15336-18-2	99.8 ± 1.80	2.5
Diammonium sodium hexakis(nitrito- <i>N</i>)rhodate	64164-17-6	0.76 ± 0.032	5.6
Tetraammonium decachloro- <i>mu</i> -oxodiruthenate(IV)	85392-65-0	31.1 ± 0.51	1.4
Iridium(IV) oxide	12030-49-8	0.0002 ± 0.00002	6.0
Ammonium hexachlororuthenate(IV)	18746-63-9	26.2 ± 0.06	1.4

^a This method was applied to pure substances

Table II Water Solubility of Substances Tested Using Using the Simplified Test^a

Substance	CAS number	Water solubility, g l ⁻¹	pH
Rhodium trihydroxide	21656-02-0	0.0001 ± 0.00005	7.3
Rhodium 2-ethylhexanoate solution in 2-ethyl hexanol	20845-92-5	0.0098 ± 0.00030	3.5
Ruthenium trihydroxide	12135-42-1	<0.00002	6.0
Dihydrogen tetrachloropalladate	16970-55-1	>10 ^b	1.4
Platinum(0) divinyltetramethylsiloxane complex	68478-92-2	0.0349 ± 0.00052	5.2
Tetrakis(triphenylphosphine) palladium(0)	14221-01-3	<0.00012	6.5
Palladium(II) nitrate	10102-05-3	>10 ^b	1.2
Platinum(II) nitrate	18496-40-7	0.0141 ± 0.00195	1.0
Potassium hexachloropalladate(IV)	16919-73-6	3.41 ± 0.039	1.7
Ammonium hexachloropalladate(IV)	19168-23-1	>10 ^b	1.3

^a See text for description. This method was used for substances in which the quantity of pure material could not be determined, including those supplied as “damp solids”

^b The water solubility of these substances was at or above the level specified in the test

Table III Water Solubility of Substances Investigated by AQura^a

Substance	CAS number	Water solubility, g l ⁻¹	pH
Potassium tetrachloroplatinate(II)	10025-99-7	191 ± 1	2.3
Tetraamminepalladium(II) chloride	13815-17-3	327 ± 2	7.8
Dihydrogen hexachloroiridate(IV) hydrate	16941-92-7	456 ± 5	<0.1
Ruthenium acetate	55466-76-7	660 ± 12	0.8
Palladium(II) 2,4-pentanedionate	14024-61-4	0.0111 ± 0.0005	4.2

^a Tests were carried out using the OECD flask method (1)

Conclusion

A range of pgm containing substances were analysed for water solubility. Each substance was measured in duplicate and an associated error has been quoted in each case. Two methods were used to determine the water solubility. The shake flask method according to OECD 105 guideline was used for pure solids and a simplified water solubility test was used for substances that could not be isolated as pure solids. A column elution method is also described in the guideline for substances with solubility below 10⁻² g l⁻¹ but this was rejected due to difficulties in coating the support material with the test substances. This investigation has provided reliable water solubility data for a range of pgm containing substances which were previously unavailable in the literature.

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