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Solvent extraction of palladium(II) using diamides: A performing molecular system established through a detailed study of extraction kinetics.

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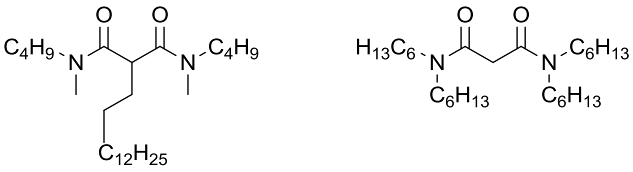
ABSTRACT: Palladium isolation and refining through solvent extraction suffer from limited stability of commercial reagents or limited availability of robust reagents in nitrate media. Several performing extraction solvents based on diamide reagents have been proposed, but their preparation requires synthetic chemistry skills. In the present work, we propose the use of readily accessible *N,N,N',N'*-tetrahexylmalonamide (THMA). This reagent revealed superior distribution ratios and selectivity in comparison with previously used diamides for palladium(II) extraction from nitrate media in the frame of palladium recovery from waste. Furthermore, the benefit of excess dihexylamine (DHA) employed during the preparation of THMA was demonstrated through a gain in kinetics performance. Detailed analysis enabled to determine the best performing formulation of extraction solvent, which can be readily prepared from commercially available chemicals without any complex synthesis procedure nor purification step.

Keywords:

Solvent extraction; Kinetics; Palladium; Diamides; Synergy

1. Introduction

Recycling of platinum Group Metals (PGM) has continuously been the object of extensive R&D efforts due to their elevated cost and importance in many industrial sectors.[1–3] The supply of PGM is limited by their very low natural abundance and the availability of natural ores in only a few countries (South Africa, Russia).[4–6] The recent sanitary crisis has further revealed the weaknesses of the supply chain in most developed countries. Public policies push towards increasing the recovery of PGM from secondary resources to ensure the economy's resilience.[7–10] Various complementary solutions have been proposed, based either on pyrometallurgical or hydrometallurgical processing.[3,11,12] Nevertheless, whatever the technology employed, final isolation and purification of PGM rely generally on a solvent extraction stage.[13,14] The existing industrial extracting molecules, mostly dialkyl sulfides and fatty amines, could not be successfully applied to hydrometallurgical processes dedicated to the recovery of PGM from waste as their selectivity scope or their stability is insufficient.[15] As a consequence, several organic molecules have been developed after molecular design and synthesis route selection.[16] The chemical synthesis of tailor-made molecules is not limited to solvent extraction: They can be employed in solvent impregnated[17,18] or chelating resins,[19] as ion exchange is also a technique of interest for the recovery of PGM in dilute solutions. Amide compounds play a central role, as the amide moiety is very stable in the highly acidic and oxidizing media employed.[20] Monoamides are not efficient enough for PGM extraction. Thus, sulfide containing monoamides and various diamides,[21,22] including aza- or thio-bearing diamides[23,24] have been synthesized and successfully used in solvent extraction of PGM from chloride media. Malonamides proved to lead to very stable Pd(II) complexes, and to efficient extraction from nitrate media.[15,25] Based on these results, we recently proposed a simple process to recover palladium from electronic waste using diamides previously developed in the frame of nuclear fuel reprocessing.[20,26,27] The approach relies on the reformulation of the extraction solvent using existing available molecules. Although the approach seems promising, it relies on a molecule that has to be specifically prepared and which is only available in large quantities through custom synthesis companies, and not through the regular chemical suppliers. To the best of our knowledge, none of the above-presented new molecules has passed the proof of concept stage at the laboratory level due to the complexity of obtaining them on a large scale for further process development. Finally, it is essential to mention that in Europe, the marketing of a new molecule is hampered by REACH regulation, so that efficient solutions based on existing registered molecules are still needed. During our previous work, the fundamental studies performed along with the process development studies revealed that the initial design of the chosen diamide, *N*,*N'*-dimethyl-*N*,*N'*-dibutylteradecylmalonamide (DBMA, Figure 1), was not optimized for selective Pd(II) extraction.[26,28–30] DBMA was selected as this molecule is the former lanthanide/actinide separation molecule, so that it was readily available from French CEA. However, its molecular design has been performed targeting high distribution ratios for lanthanides(III) cations,[31–33] and its ability to also extract palladium(II) was instead a side-effect.[34,35] Thus, the possibility to envision a more simple diamide based solvent dedicated to selective palladium(II) extraction rapidly appeared, using *N*,*N*,*N'*,*N'*-tetrahexylmalonamide (THMA, Figure 1), previously described for uranium(VI) extraction.[36,37] Although the newly proposed diamide is not commercially available, it can be prepared in situ and employed without any purification in the extraction process. Thus, as starting reagents are available and easy to handle, it is possible to prepare the extraction solvent without specific operation in chemical synthesis. Furthermore, the study of the influence of the stoichiometry of reagents employed revealed that a slight excess of amine is beneficial to the performance of the extraction process. A detailed study of the thermodynamic and kinetic features enabled to evidence a synergy phenomenon between amine and diamide for Pd(II) extraction. Finally, the performance of the THMA could be extended to the extraction of Pt(IV) from chloride media.



DBMA **THMA**

Figure 1: Chemical structures of diamides employed in the study

2. Experimental

2.1. Chemical reagents

N,*N'*-dimethyl-*N*,*N'*-dibutylteradecylmalonamide (98% purity, DBMA, Figure 1) was kindly provided by the CEA, France. Production was performed by Pharmasynthèse (former Panchim), France, and the product was used without further purification. Palladium(II) nitrate hydrate ($Pd(NO_3)_2.xH_2O$, ca. 40% Pd, 99.9% purity), palladium(II) chloride (99.9% purity) and platinum(IV) chloride (99.9% purity) were purchased from Strem Chemicals. Iron(III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, ≥98% Fe), neodymium(III) nitrate hexahydrate

($Nd(NO_3)_3.6H_2O$, 99.9% purity), diethyl malonate (99% purity) and dihexylamine (97% purity) were purchased from Sigma-Aldrich and used without further purification. Toluene, Solvesso^{TM} 150, diethyl ether, concentrated nitric acid 69.5% (w/w), concentrated hydrochloric acid 37% (w/w) and anhydrous magnesium sulfate were purchased from Carlo Erba reagents.

2.2. Synthesis and characterization of *N*,*N*,*N*’,*N*’-tetrahexylmalonamide (THMA)

A mixture of diethylmalonate (8.09 g, 0.05 mol) and dihexylamine (20.1 g, 0.105 mol, 2.1 equiv.) was heated under reflux (ca. 180°C) for 7 h. Every 30 min, an argon flow was injected during 1 min to evacuate the produced ethanol through a distillation apparatus (see SI, Figure S1). The reaction mixture was then cooled to room temperature. The resulting product could be used directly in solvent extraction experiments. For characterization and detailed study, purification was performed as follows: The resulting mixture was dissolved in 100 mL diethyl ether and then washed with an aqueous 1M HCl solution to remove unreacted dihexylamine (4 x 30 mL), with an aqueous saturated solution of $NaHCO_3$ (1 x 30 mL) and finally with brine (1 x 30 mL). The recovered organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. *N,N,N’,N’*-tetrahexylmalonamide (THMA, Figure 1) was obtained as a viscous pale yellow liquid (21.5 g, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ *(ppm)*: *3.45 (s, 2H, $COCH_2CO$) 3.34 (dd, J = 15.4, 7.8 Hz, 4H, $N\text{-}CH_2$), 3.32 (dd, J = 15.4, 7.7 Hz, 4H, $N\text{-}CH_2$), 1.57-1.55 (m, 8H, $N\text{-}CH_2\text{-}C\underline{H}_2$), 1.32-1.29 (m, 24H, CH_2,) 0.92 (t, J = 6.7 Hz, 6H, CH_3), 0.88 (t, J = 6.6 Hz, 6H, CH,);* ^{13}C NMR (100.6 MHz, $CDCl_3$) δ *(ppm): 166.6, 48.4, 46.0, 40.8, 31.5, 31.5, 28.9, 27.5, 26.6, 26.5, 22.5, 13.9, 13.9*, IR (neat) ν *(cm^{-1}): 2927, 2903, 2850, 1634 (C=O), 1456, 1420, 1376.*

2.3. Solvent extraction

Aqueous phases containing the desired metallic cations were prepared from the corresponding metallic salts ($Pd(NO_3)_2.xH_2O$, $PdCl_2.2H_2O$, $Fe(NO_3)_3.9H_2O$, $Nd(NO_3)_3.6H_2O$, $PtCl_4$) dissolved in an aqueous HNO_3 or HCl solution of desired concentration as described in the text. Organic phases were prepared by diluting THMA, DMBA and/or DHA in the appropriate diluent (toluene, Solvesso^{TM} 150) to reach the concentrations given in the text.

The organic phases were pre-equilibrated by bringing them into contact for 30 min with a five-fold volume of an aqueous solution of HNO_3 or HCl of molarity identical to that of the aqueous metal solution employed for the extraction step.

Extraction experiments were carried out in 2 mL Eppendorf tubes with equal volumes of the aqueous and organic phases (A/O =1). The two phases were shaken with a thermostated orbital mixer (Eppendorf Thermomixer® C) for 1 h to 24 h at 20°C ± 2°C. Unless otherwise stated in the text, the stirring speed was set at 2000 rpm. Tubes were then centrifuged to ensure good phase separation.

For each extraction performed, aliquots of the aqueous phases (100 µL), before and after extraction, were directly diluted with a 2% HNO_3/HCl aqueous solution (90/10). After extraction, aliquots of the loaded organic phases (500µL) were back-extracted during 1 h with 1 mL of a 0.1M aqueous thiourea solution. Resulting phases were separated and 250 µL of the final aqueous phase were taken and diluted with a 2% HNO_3/HCl aqueous solution (90/10). Evidence from preliminary investigations showed that all extracted metals were totally stripped from loaded organic phases during the process, and that no metal precipitation occurred prior to analysis. Dilution factors have been chosen so that a minimum 10-fold dilution is operated to avoid matrix effects during analysis.

2.4. Analytical determination of metal content

Metals concentration in each solution was determined using inductively coupled plasma atomic emission spectroscopy (ICP/AES, SPECTRO ARCOS ICP Spectrometer, AMETEK Materials Analysis). The selected spectral lines to assay metals were free from interference. The given concentrations were calculated as the average of three replicates at different wavelengths for each metal. Relative standard deviations have been determined and lie between 1 and 3%. Quantification limits (LoQ) in each analyzed phase were determined for each metal from the dilution factor applied and the background equivalent concentration calculated by the spectrometer for each optical line. Confidence intervals were selected taking into account the error of the spectrometer and the precision of the equipment used for dilution. Altogether, the relative errors were found to be between 5% and 10%. All results showed a total mass balance in each metal in the range of ±5% of the initial load in the aqueous phase.

2.5. Expression of results

Assuming that the volume change of both phases is neglected during extraction, the metal distribution ratio (D) and the metal extraction percentage ($\%E$) were determined using equations (1) and (2) below:

$$D = \frac{[M]_{org}}{[M]_{aq}} \tag{1}$$

$$\%E = \left(\frac{V_{org}\,[M]_{org}}{V_{aq}\,[M]_{aq,i}}\right) x\ 100 \tag{2}$$

Where $[M]_{aq,i}$, $[M]_{aq}$ and $[M]_{org}$ denote, respectively, the metal concentration in the initial aqueous phase, the metal concentration in the aqueous phase and the organic phase after extraction, and V_{aq} and V_{org} denote, respectively, the volumes of aqueous and organic phases.

The separation factors were calculated using the following equation (3):

$$S_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}} \tag{3}$$

Where D_{M_1} and D_{M_2} denote the distribution ratios of the metal M_1 and the metal M_2 respectively.

2.6. Interfacial tension measurements

All interfacial tension measurements were carried out using a Krüss spinning drop tensiometer (SDT) equipped with a high resolution USB3 camera. The tensiometer is combined with the ADVANCE software. This software performs image analysis applying either the approximation functions of Vonnegut, or making use of an evaluation algorithm based on a Young-Laplace fit. For the current measurements, Young-Laplace-fit equation was used for interfacial tension determination. The densities of all samples were determined using DSA 5000 densimeter at 23°C. All the organic phases were pre-equilibrated by contacting them for 30 min with a five-fold volume of 3M aqueous nitric acid concentration. The capillary was filled with the heavy phase (3M HNO_3). A drop of the sample (organic phase) was injected with a syringe against the inner wall of the horizontally held capillary, so that the drop remained stuck approximately in the center of the capillary. The capillary was then placed on the filled closure cap so that it was sealed. Calibration of the tensiometer were performed before each measurement to obtain the image scale. Interfacial tension measurements were performed at a controlled temperature of 23°C at a high rotation rate (>5000 rpm). The reported values were recorded after the drops reached equilibrium, and no further decrease in interfacial tension values was observed.

3. Results and discussion

3.1. Extraction of Pd with THMA and DBMA

In addition to their capacity to remove minor actinides, diamides have shown an affinity to extract Pd(II) from nitric acid media. Accordingly, the selective extraction of Pd(II) from nitrate media was reported with DBMA. DBMA remains complicated to prepare (three synthesis steps, and purification on silica gel column), making a competitive process dependent on excellent recycling of extraction solvent. Furthermore, for efficient extraction of Pd(II), it was necessary to increase the concentration of the extractant to 0.6 mol/L, i.e. about 300 g/L, which makes the initial investment in extraction solvent substantial. On the contrary, THMA is a *N,N,N',N'*-tetrasubstituted malonamide that is much simpler to prepare. Furthermore, it revealed to be an excellent candidate for the selective extraction of Pd(II): The Pd(II) extraction performances of THMA have been assessed in comparison with DBMA, in conditions where DBMA presents good Pd(II) distribution ratios and good selectivity regarding Fe(III) and Nd(III) (Table 1). THMA exhibited overall much better extraction of Pd(II) than DBMA across the whole range of extractant concentrations. Palladium distribution ratios D_{Pd} with THMA were between 10 and 100 times higher than that with DBMA, and still using only 0.3M THMA, the concentration of residual Pd(II) in the final aqueous layer was below the detection limit of the ICP-OES analysis ($D_{Pd} > 70$). The quantitative extraction of Pd(II) with THMA can induce a significant reduction in extractant charge in the organic phase since both diamides are structural isomers, having the same number of carbon atoms (27), and thus the same molecular weight (438.7 g.mol^{-1}).

It was previously reported that the selective extraction of Pd(II) over Nd(III) and Fe(III) with DBMA was strongly dependent on two key parameters: The concentration of DBMA for Nd(III) and the aqueous nitric acid concentration for Fe(III).[26] Therefore, the optimized conditions to reach selective Pd(II) extraction with DBMA have been established at 0,5-0,6M DBMA in toluene with a 3M aqueous HNO_3 solution. THMA showed an impressively high selective extraction of palladium in the presence of Fe(III) and Nd(III) compared to DBMA. For instance, at 0.3M THMA, $S_{Pd/Fe}$ and $S_{Pd/Nd}$ were above 11600 and 35000 respectively, and Pd(II) extraction was quantitative. Experimentally, after extraction Pd(II) could not be detected in the aqueous layer ($D_{Pd} > 70$), and Nd(III) could not be detected in the organic layer ($D_{Nd} < 0.002$). Fe(III) was barely quantified in the organic layer ($D_{Fe} = 0.006$). In comparison, for the same concentration for DBMA, $S_{Pd/Fe}$ and $S_{Pd/Nd}$ were 180 and 50, respectively, with Pd(II) distribution ratio of 4 only. The increase in extractant concentrations leads to a decrease in the selectivity regarding Fe(III) or Nd(III) with DBMA as previously reported. When using THMA, the distribution ratios of both Fe(III) and Nd(III) also increased with concentration, but remained very low (below 0.1) so that $S_{Pd/Fe}$ and $S_{Pd/Nd}$ were still much higher than those obtained using the same DBMA concentration (Table 1).

Table 1. Distribution ratios of Pd(II), Fe(III) and Nd(III) and Pd/Fe, Pd/Nd selectivity $S_{Pd/Fe}$, $S_{Pd/Nd}$ after extraction using THMA and DBMA in toluene, from an aqueous 3M HNO_3 phase. Initial $[Pd]_{aq}$ 500 mg/L, 1 h extraction, stirring speed 2000 rpm.

	THMA 0.3M	DBMA 0.3M	THMA 0.5M	DBMA 0.5M	THMA 0.6M	DBMA 0.6M
D_{Pd}	>70*	4.0	>70*	10	>70*	15
D_{Fe}	0.006	0.02	0.05	0.2	0.09	0.31
D_{Nd}	<0.002*	0.08	0.038	0.37	0.069	0.83
$S_{Pd/Fe}$	>11600	200	>1400	50	>778	48
$S_{Pd/Nd}$	>35000	50	>1840	27	>1014	18

Note: * When concentration in the final aqueous phase is below the detection limit, only a lower *D* value can be determined. Similarly, when concentration in the final organic phase is below the detection limit, only a higher *D* value can be determined.

Altogether, this analysis rapidly emphasized the very interesting features of THMA over DBMA in the selective extraction of Pd(II). Regarding the Pd(II) selective isolation process we recently proposed, using THMA instead of DBMA should lead to a more efficient process, based on lower stage numbers in extraction and scrubbing sequences, and using a lower amount of extracting molecule. However, we were surprised to notice a sudden drop in performance when lowering the THMA concentration to 0.2M or below. Particularly low Pd(II) distribution ratios were sometimes obtained, depending on the batches of THMA used. Careful examination of the NMR spectra of the corresponding batches was conducted and revealed residual traces of dihexylamine (DHA) in the solvent. Also, equilibrium was not reached after 1 h extraction: The extraction with THMA is incomplete after 1 h shaking (see SI, Figure S2), whereas with DBMA we found during our previous studies that extraction equilibrium was reached after 10 min only, working in toluene and using the same aqueous layer ([HNO_3] = 3M). This drawback led us to investigate in detail the impact of THMA purity on extraction performances, and especially on the kinetics of Pd(II) extraction.

3.2. Impact of added DHA on Pd(II) extraction with THMA

Synthesis of THMA involves DHA as a starting material. High molecular weight amines and quaternary ammonium salts have been used among nitrogen-containing extractants for the extraction of PGM from chloride media.[38–46] In addition to their extraction properties, their role as a catalyst in the extraction of Pd(II) from aqueous hydrochloric acid solutions has been documented in previous studies.[47–50] Incorporation of an amine moiety into an amide based extractant proved superior performances for Pd(II) from nitrate media. However, Pd(II) extraction with amine-based functions from nitrate media has been rarely reported in the literature.[51–53] Thus, the impact of controlled addition of DHA to pure THMA on the extraction of Pd(II) from nitric acid media was investigated. Firstly, a well-purified batch of THMA was prepared and fully characterized (see SI, Figures S3 and S4, and Table S1). Working with this batch confirmed i) the excellent performance regarding Pd(II) extraction, and ii) the slower kinetics of Pd(II) extraction at low THMA concentrations, compared to previous results with DBMA. Then, the concentration of THMA was set at 0.2M, and DHA was added in quantity varying from 0 to 100 mol% respective to THMA. For a contact period of 24 h, excellent Pd(II) distribution ratios could be obtained even at this relatively low THMA concentration (D_{Pd} = 28 with 0.2M THMA in toluene after 24 h). DHA addition only had marginal effect, since the D could reach only 32-35 (see Figure 3). Finally, using only DHA 0.2M in toluene, very low palladium distribution ratio was found (D_{Pd} = 0.1 at equilibrium, after 24 h) which confirms that secondary amines are not good Pd(II) extracting molecules from nitrate media.

In order to investigate in detail the kinetics effects, extraction conditions were modified in order to disfavor mass transfer through lowering of the interfacial area between aqueous and organic phases. Although it is difficult to determine with precision the interfacial area, it is clear that it depends on the shearing rate, thus on stirring rate. A visual study of the impact of the stirring rate on the mixing of both phases revealed that dispersion of organic phase into aqueous phase occurs at stirring rate between 800 and 1000 rpm (see SI, Figure S5). At higher speed, emulsification of the biphasic system is well visible, and it can be assumed that the concentration in metal is homogeneous in each phase. Mass transfer is, nevertheless, probably still limited by the reduced interfacial area, and thermodynamic equilibrium is reached after longer shaking time. This was well evidenced through the study of Pd(II) extraction yield after 1 min (see SI, Figure S5). Therefore, the stirring speed was set at 1200 rpm.

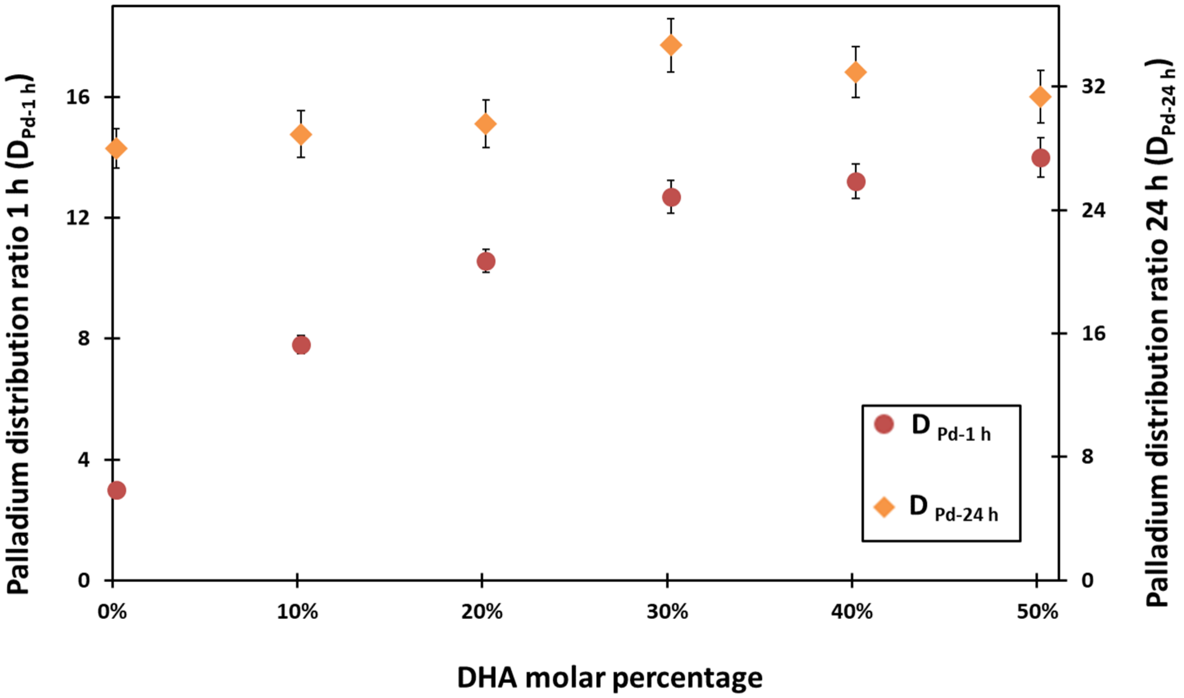


Figure 3. Pd(II) distribution ratio with mixed THMA/DHA systems in toluene. THMA concentration 0.2M, DHA molar percentage 0 mol% to 50 mol%, initial $[Pd]_{aq}$ 500mg/L, $[HNO_3]_{aq}$ 3M, 1 h extraction, stirring speed 1200 rpm.

In these conditions, the palladium distribution ratio (D_{Pd}) drops to 3 (75% extraction percentage) using pure THMA 0.2M in toluene after 1 h. When DHA was added to 0.2M THMA in toluene, the Pd(II) distribution ratio determined after 1 h extraction increased significantly (Figure 3). It reached a maximum at 14 (93% extraction yield) when 50 mol% DHA were added to THMA (thus, the extraction solvent is a 0.2M THMA / 0.1M DHA solution). The increase in the palladium distribution ratio was somehow still limited, and remained below the distribution ratio obtained in the same conditions after 24 h (Figure 3). Then, above 50 mol% of added DHA, there is no more benefit of DHA addition. Moreover, a further increase in the molar percentage of added DHA led to a decrease in the extraction efficiency of Pd(II) (see SI, Figure S6). For instance, when using THMA with 90 mol% added DHA, D_{Pd} dropped to 2 (69% extraction yield).

The marked increase of Pd(II) extraction at short durations could not be related to a change in interfacial surface, as no effect of DHA on interfacial tension was observed (see SI,

Figure S7). Neither did viscosity change significantly up to 50 mol% added DHA. We therefore assume that the addition of DHA does not induce any extra interfacial activity, and that the observed results may instead be linked to chemical limits of the extraction kinetics. An increase in viscosity of the extraction solvent was noticed when the added DHA quantity exceeded 80 mol%. This increase in viscosity can be invoked here to explain the lower extraction yield at short durations as the increase in viscosity leads to reduced diffusion of molecules and ions. High molecular weight amines have been reported to extract nitric acid,[54] and the increase in viscosity probably originates in the aggregation of DHA-nitrate species formed upon extraction of nitric acid by DHA.[55,56] Visually, mixing of both phases was still efficient. A dedicated experimental set-up with a controlled interfacial area would be required to investigate in detail the effect of added DHA on the Pd(II) transfer kinetics. However, the experimental approach we propose is simple for preliminary investigations and we limited the following studies to 50 mol% added DHA.

3.3. Pd extraction kinetics with mixed THMA/DHA systems

In order to precise the effect of DHA on the extraction kinetics, experiments were performed at short extraction durations (1 to 6 min). The concentration of THMA in toluene was still set at 0.2M, and controlled amount of DHA was added (10 mol% to 50 mol%). For each point in each series, a separate experiment was carried out, and the reported extraction time corresponds to the shaking time. The average absolute error in extraction time for each point was determined as the delay between the agitation turnoff and the time required to reach the maximum centrifugation speed. Assuming that afterwards during centrifugation mass transport is negligible, the time absolute errors are estimated at 6 seconds for each point, and are positive. A first-order model was used to interpret the experimental data. The rate of palladium extraction can be expressed as follows:

$$-\frac{d[Pd]_{aq}}{dt} = k([Pd]_{aq,t} - [Pd]_{aq,eq}) \qquad (4)$$

The integration of equation (4) gives equation (5):

$$\ln\left([Pd]_{aq,t} - [Pd]_{aq,eq}\right) = -kt + \ln\left([Pd]_{aq,0} - [Pd]_{aq,eq}\right) \qquad (5)$$

Where k is the rate constant, t is the time, $[Pd]_{aq,t}$ is the concentration of Pd in the aqueous phase at time t, $[Pd]_{aq,eq}$ is the concentration of Pd in the aqueous phase at equilibrium (see SI, Table S2) and $[Pd]_{aq,0}$ is the initial concentration of Pd in the aqueous phase. In Figure 4, the plots of $\ln\left([Pd]_{aq,t} - [Pd]_{aq,eq}\right) = f(t)$ are represented for four chosen samples: (a) Pure THMA, (b) THMA + 10 mol% DHA, (c) THMA + 20 mol% DHA and (d) THMA + 50 mol% DHA. The data of each sample is in agreement with the first order model as they can be modelled by a straight line.

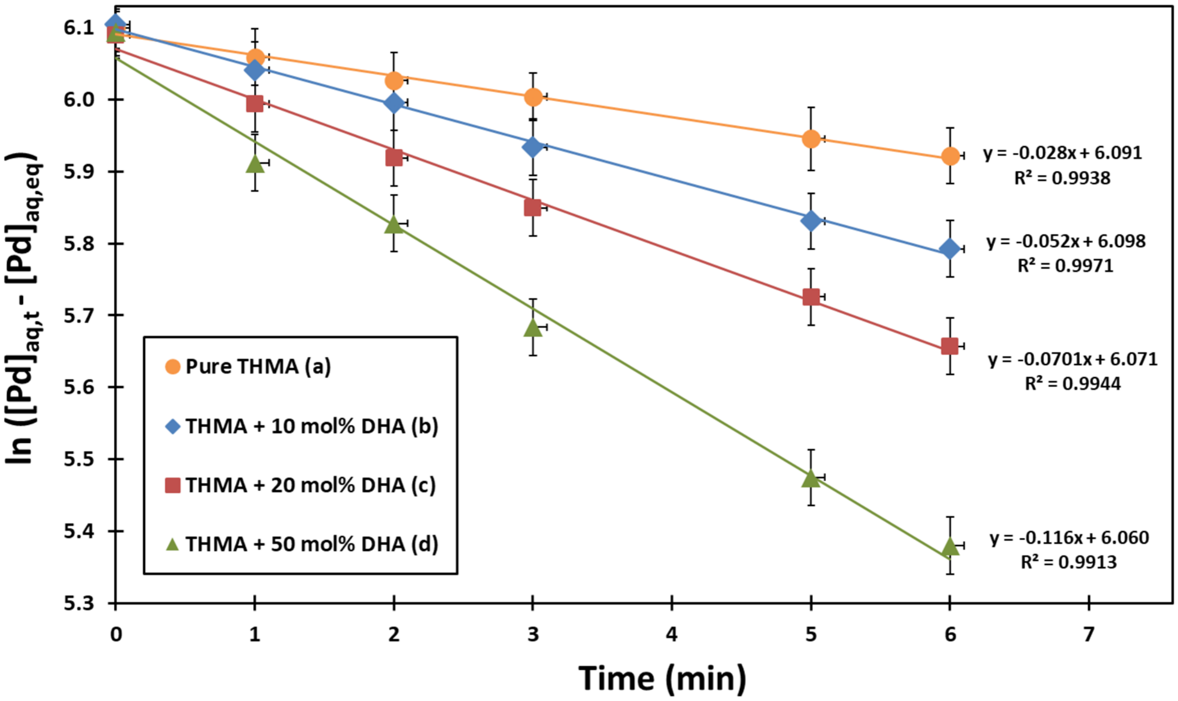


Figure 4. First order model for the extraction of Pd(II) with pure THMA and mixed THMA/DHA systems in toluene. THMA concentration 0.2M, and 10 mol% DHA, 20 mol% DHA and 50 mol% DHA, initial $[Pd]_{aq}$ 500 mg/L, $[HNO_3]_{aq}$ 3M, stirring speed 1200 rpm.

The extraction kinetics of Pd(II) is enhanced in the presence of DHA, with a regular increase in the observed rate constants (Figure 4). The rate constant increased from 0.028 min^{-1} for the extraction with pure THMA to 0.116 min^{-1} with 50 mol% added DHA, corresponding to an extraction half-time of 25 min and 6 min respectively. Thus, without DHA, Pd(II) extraction is slow, but occurs. The addition of 10 mol% DHA leads to doubling of the rate constant (half-time divided by almost 2). The increase is then proportional to the quantity of added DHA (see SI, Figure S8). Interestingly, the observed rate constant (k_{obs}) can be decomposed into two contributions, k_{THMA} (obtained when no DHA is added, k_{THMA} = 0.028 min^{-1}) and k_{DHA} (equation (6)).

$$k_{obs} = k_{THMA} + k_{DHA} \tag{6}$$

The contribution k_{DHA} is then proportional to the DHA quantity (see SI, Figure S8), as given by equation (7), where [DHA] is the concentration in DHA in mol.L^{-1}:

$$k_{DHA} = 0.87\ [DHA] \tag{7}$$

As thermodynamic outcome of the Pd(II) extraction is almost the same in each case (Figure 3), this result demonstrates that DHA has principally a kinetic effect. Analysis of the observed rate constant suggests that two mechanisms occur simultaneously, i) a direct extraction with THMA, and ii) an indirect one mediated by DHA, and of first order respective to DHA. As stated above, a more detailed study employing adequate experimental tools would be necessary to reach a complete mechanistic understanding. These results are, nevertheless, sufficient to justify i) that slow kinetics are only observed at low THMA concentration, and ii) that DHA is involved in the formation of intermediate molecular species responsible for Pd(II) extraction.

The effect of the aqueous nitric acid concentration was studied, and results showed that the kinetics enhancement is strongly dependent on the aqueous nitric acid concentration: When using a 5M aqueous HNO_3 solution, no more effect of added DHA was observed (Figure 5). Palladium distribution ratio obtained after 1 h extraction remained constant (~2) for the entire range of added DHA. After 24 h of extraction, palladium distribution were found to lie around 10 (see SI, Figures S9 and S10). The lack of kinetic effect when using a higher concentration of aqueous HNO_3 is possibly due to the fact that under these conditions, in the organic phase, DHA (pK_a = 11.0 in ethanol-water mixture) is fully protonated by HNO_3. Thus, using a 5M aqueous HNO_3 solution, only the extraction promoted by THMA may be observed.

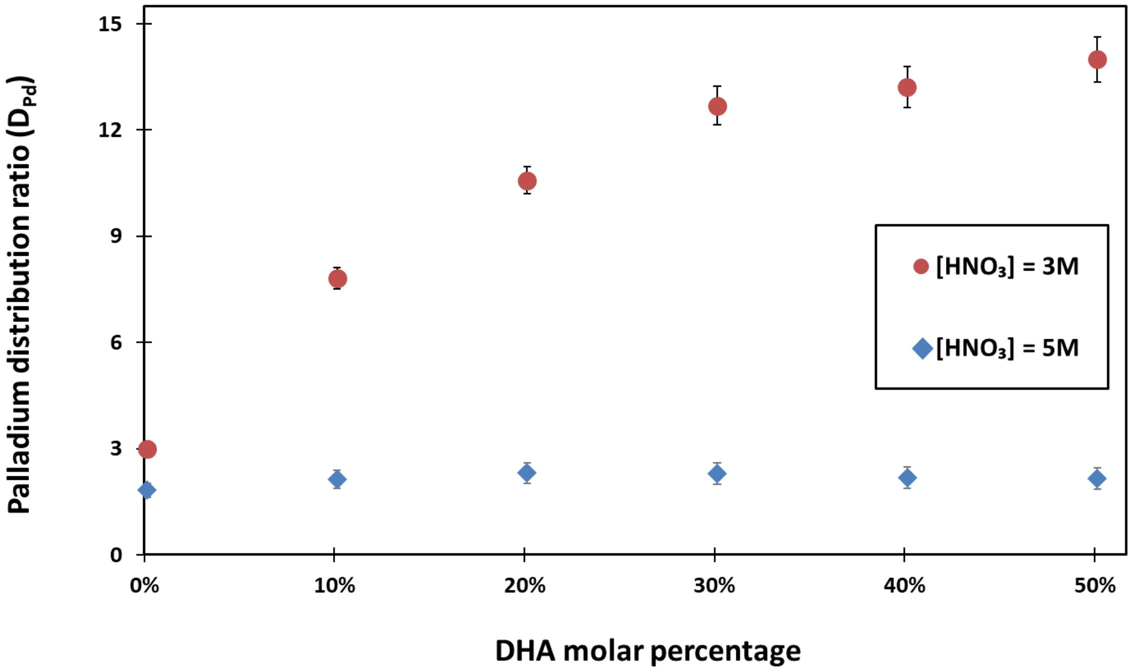


Figure 5. Variation of the Pd(II) distribution ratio with the aqueous nitric acid concentration with mixed THMA/DHA systems in toluene, 0.2M THMA concentration, DHA molar percentage 0% to 50%, initial $[Pd]_{aq}$ 500mg/L, 1 h extraction, stirring speed 1200 rpm.

3.4. Extraction solvent formulation: optimization of added DHA quantity

These results suggest that addition of 50 mol% DHA is the optimum for improvement of extraction kinetics. However, when the THMA quantity is fixed, the addition of extra DHA leads to a higher total amount of extractant employed. Thus, it could be argued that better performance results also from the use of a higher amount of extractant. We therefore examined the impact of controlled DHA addition to THMA when total concentration in extracting molecules is fixed, ie. when [THMA] + [DHA] = 0.2M. Thus, the addition of DHA is here accompanied by a lowering of the THMA concentration. The total mass of used extractant also decreases, as the DHA is lighter than the THMA. As it is preferable to present results using molar quantities than weight, we did not perform the study using a constant weight in extractant. The Pd(II) distribution ratios obtained were plotted against the molar ratio of DHA (x_{DHA}) in the extraction solvent (Figure 6):

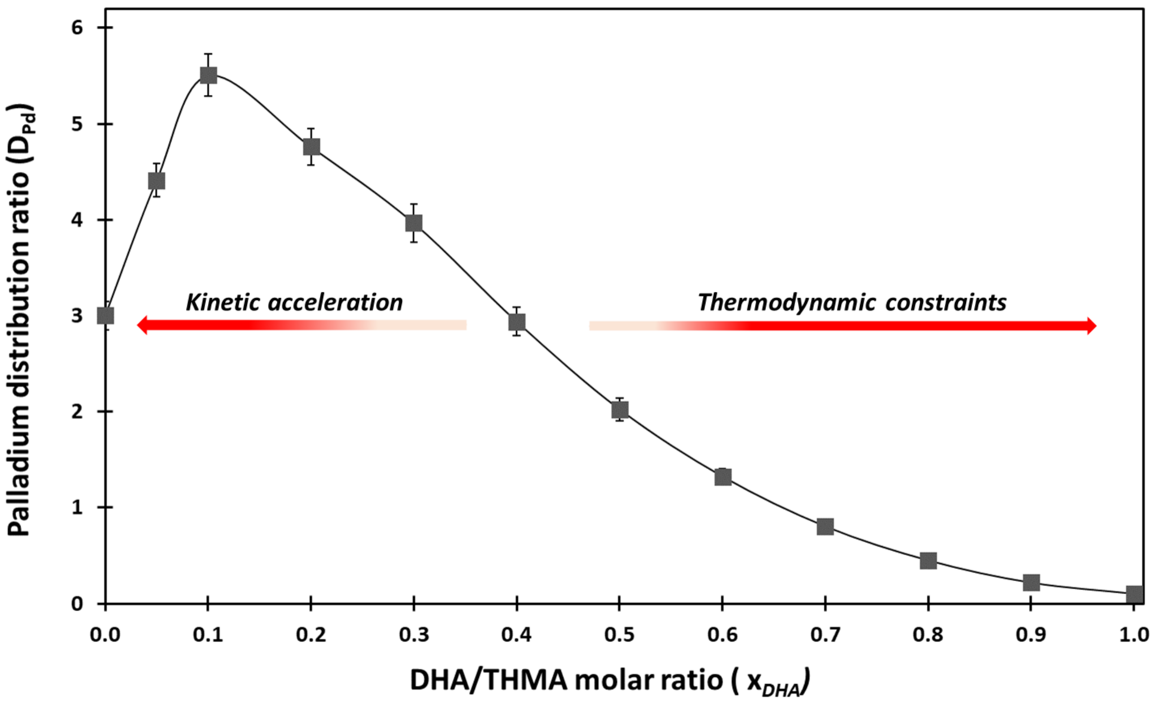


Figure 6. Pd(II) distribution ratio after extraction with THMA/DHA mixtures. [THMA]+[DHA] = 0.2M in toluene, initial $[Pd]_{aq}$ 500 mg/L, $[HNO_3]_{aq}$ 3M, 1 h extraction, stirring speed 1200 rpm.

Palladium distribution ratios rapidly rose as the molar ratio of DHA in the organic phase increased, and maximum of D_{Pd} = 5.5 was reached for x_{DHA} = 0.1. Conversely, by exceeding this limit, palladium distribution ratios decreased continuously, and reached D_{Pd} = 0.14 for pure DHA. As expected, the Pd(II) extraction strongly relies on sufficient THMA concentration in the organic phase. As long as the THMA content in the solvent is sufficient to enable the extraction of Pd(II), the contributory effect of DHA is visible. At the maximum point (x_{DHA} = 0.1), the THMA concentration is still close to 0.2M (0.18M precisely), and the DHA concentration is 0.02M, very close to 10 mol% respective to THMA. Afterwards, Pd(II) extraction efficiency decreases, as the THMA content in the organic phase decreases. Thus, it can be concluded that the benefit of DHA addition is optimum at 10 mol%. Further addition of DHA does increase the kinetics, but the increase is insufficient to counterbalance loss of efficiency due to lower amount of THMA. Extraction half-time is lowered from 13 min to 10 min upon doubling of the DHA quantity from 10 mol% to 20 mol%. Thus, unless kinetics are the most important parameter, we think that it is not worth adding more than 10 mol% DHA. It is worth mentioning here again that these results have been gathered in conditions voluntarily chosen in order to reduce mass transfer during the liquid-liquid extraction process.

The simple set-up we used, and the low quantities of reagents employed enabled a rapid screening of several different conditions. Once optimum conditions are chosen, i) they can be employed for further development in regular conditions, ie. with adequate phase mixing, and ii) the potential kinetics limits have been identified, as well as key parameters to study. The way experimental results are presented is similar to classical studies which evidence synergistic phenomena. In our case, it is clear that mass transfer is limiting, at least on the left side of Figure 6, and that thermodynamic equilibrium is not reached. The results should not be taken as evidence of a synergy. The non-linear behaviour of the extraction results obtained with THMA/DHA mixtures results from an enhancement of the extraction kinetics, counterbalanced by thermodynamic constraints due to poor Pd(II) extraction with pure DHA. The rise in extraction yield when $x_{DHA} \leq 0.1$ ($x_{THMA} \geq 0.9$), where D_{Pd} with THMA/DHA mixtures are higher than D_{Pd} with THMA, have been proven to result from enhancement of kinetics by DHA. Then, for the range of $0.1 \leq x_{DHA} \leq 0.4\text{-}0.6$, a decrease in D_{Pd} was observed, yet they were still higher than D_{Pd} with THMA at a 0.2M concentration, thus probably higher than D_{Pd} at corresponding THMA concentration. The thermodynamical constraints are still partially overcome by the kinetic acceleration. Finally, when $x_{DHA} > 0.6$, the system is entirely governed by thermodynamic limitations. This approach demonstrates that studies of synergism under thermodynamic conditions require proof that there is no kinetic limitation. Kinetics studies are often overlooked, although our results demonstrate that they could be at the origin of an apparent synergy.

3.5. Extraction of Pd with crude THMA

As DHA proved to have a beneficial effect on the extraction of Pd(II) with THMA from nitric acid media, we investigated the possibility to employ unpurified THMA to prepare the extraction solvent. When DHA is employed in excess (more than 2.0 equiv.) respective to diethyl malonate in the synthesis of THMA, the crude reaction mixture only contains residual DHA in addition to THMA. Thus, a batch of crude (unpurified) THMA was evaluated for Pd(II) extraction. This THMA batch was prepared using excess DHA (10 mol%), with the same synthetic procedure, except that all purification stages (dilution in diethyl ether, HCl washing, drying over magnesium sulfate and distillation of diethyl ether) were not performed: The synthesis was run solvent free by heating at 180°C, and the crude mixture was employed directly, after cooling, through dilution of the viscous yellow liquid obtained in toluene. Determination of the molar ratio of residual DHA was performed through integration of corresponding signal areas in ^{1}H NMR spectrum (see SI, Figure S11). Other diluents can be employed, such as aromatic cuts, *eg.* Solvesso^{TM} 150 (*vide infra*). Comparison of the results obtained during Pd(II) extraction between purified THMA and crude THMA in toluene are presented in Table 2:

Table 2. Extraction of Pd(II) with purified THMA and crude THMA synthesized with an excess of DHA (10 mol%). THMA concentration 0.2M in toluene, initial $[Pd]_{aq}$ 500mg/L, $[HNO_3]_{aq}$ 3M, stirring speed 2000 rpm, A/O = 1.

	Purified THMA *C = 0.2 mol/L*	Crude THMA *C = 0.2 mol/L*
Experiment duration	24 h	1 h
D_{Pd}	28	34

These experiments have been carried out with standard shaking (2000 rpm), and proper emulsification of aqueous and organic phases. No issue was encountered with crude THMA compared to purified THMA during phase disengagement, as the protonated amine does not significantly modify interfacial tension. The results suggest that equilibrium is reached after 1 h using crude THMA. Thus, the kinetics limitations associated with THMA are successfully overcome by using crude THMA. The extraction performance of the crude THMA was better compared with the purified one (DHA free). Indeed, the palladium distribution ratio increased from 28 when using purified THMA to 34 when using crude THMA.

3.6. Extraction of Pd(II) and Pt(IV) from chloride media

THMA has proven to be a performing extractant for Pd(II) from nitric acid media. The investigation was further extended to assess the efficiency of THMA in the extraction of Pd(II) from chloride media. From an industrial application perspective, toluene was replaced by Solvesso^{TM} 150 as diluent. These experiments were carried out with crude THMA using the batch and the procedure described above. THMA concentration was set at 0.2M. THMA showed an efficient extraction of Pd(II) (Table 3). So far, results obtained on Pd(II) extraction with malonamides were mitigated: The best results were obtained in 1,2-dichloroethane at 8M HCl,[57] with specific malonamides, with distribution ratios close to 4. In our hands, extraction of Pd(II) with DBMA from chloride media was very low, so that we employed a sodium chloride solution as stripping reagent in the Pd purification process we developed. The possibility to extract Pd(II) with excellent efficiency from chloride media (D_{Pd} = 35.4 at [HCl] = 1M) is particularly striking, as only the hydrophobic part of the molecule was modified, the coordinating head is still the same diamide moiety. Using same conditions, Pd(II) extraction yield with DBMA (0.6M in toluene) was only 2%. Also, extraction of Pt(IV) was evaluated and gave successful results (Table 3). Distribution ratios of both metals strongly depend on the aqueous hydrochloric acid concentration. The distribution ratio of Pd(II) decreased from 35.4 to 1 with HCl concentration increasing from 1M to 6M, whereas that of Pt(IV) increased from 10.3 to 27.4. The separation of Pt(IV) from Pd(II) is efficient at 6M aqueous hydrochloric acid concentration, where the separation factor $S_{Pt/Pd}$ was 27.4.

Table 3. Pd(II) and Pt(IV) distribution ratios (D_{Pd} and D_{Pt}) and Pt/Pd selectivity ($S_{Pt/Pd}$) with crude THMA in Solvesso*TM* 150 from hydrochloric acid media. THMA concentration 0.2M, initial $[Pd]_{aq}$ 500mg/L, initial $[Pt]_{aq}$ 500mg/L, 1 h extraction, A/O = 1, stirring speed 2000 rpm.

	[HCl] = 1M	[HCl] = 6M
D_{Pd}	35.4	1
D_{Pt}	10.3	27.4
$S_{Pt/Pd}$	0.29	27.4

Altogether, these preliminary results on platinum group metals (PGM) extraction from chloride media demonstrate the potential interest of THMA for the extraction and purification of these metals. Significant distribution ratios could be obtained in classical conditions, ie. after 1 h, with crude THMA. As a comparison, the extraction of PGM with alkyl sulfides from chloride media require the addition of a fatty amine to obtain acceptable kinetics. It could be worth envisioning the study of the optimum DHA quantity before adapting the technology to PGM separation from chloride media.[58]

It is finally interesting to take into consideration the cost of reagents: DHA is the expensive reagent employed for THMA synthesis (Table 4):

Table 4. Preliminary cost analysis of THMA synthesis. Costs based on Sigma-Aldrich (France) prices available in May 2021, for synthesis grade reagents, in 2.5 L packaging (DEM = diethyl malonate).

	Price (2.5 L)	M_w (g.mol^{-1})	Density	Cost (€.mol^{-1})	Equiv.	Cost for synthesis of 1 mole THMA
DEM	117 €	160.17	1.15	6.5	1	6.5 €

DHA	280 €	185.35	0.795	26.1	2	52.2 €
THMA	n.a.	438.73				58.7 €

Thus, each 10 mol% added DHA will increase the cost of prepared THMA by 4.5 % (2.6 €). This cost analysis is preliminary, only based on reagents costs. The results are indicative, they should only be considered in comparison with other reagents available from the same supplier in same packaging. For instance, tributyl phosphate (TBP) can be purchased in 2.5 L packaging for 137 € from Sigma-Aldrich (France), thus at a 56 €/kg price, to be compared with the 134 €/kg price for THMA based on reagents employed. In other words, the cost for THMA is expected to be in the same order of magnitude as that of TBP. From same supplier, and based on same packaging, dioctyl sulfide (DOS) is 10-20 times as expensive as TBP. Thus, THMA is one order of magnitude cheaper than DOS, an extracting molecule than can be employed at industrial scale for PGM refining. Altogether, this analysis and the obtained results suggest that THMA should be investigated with careful attention for PGM refining.

4. Conclusion

Tetrahexylmalonamide (THMA) is a performing extracting molecule for Pd(II) extraction from nitrate and from chloride media. Although the pure molecule displays slow kinetics, the possibility to accelerate extraction through the use of excess dihexylamine (DHA) enabled to propose a formulation of extracting molecules in order to prepare a performing extraction solvent. Furthermore, this formulation can be directly obtained after reaction between the two reagents needed to prepare THMA, diethyl malonate (DEM) and DHA. We demonstrated that the crude reaction product can be employed directly for solvent extraction, without work-up nor purification, after sole dilution in the required diluent (eg. Solvesso^{TM} 150), as there is no organic solvent employed for the synthesis. This approach is particularly interesting as both reagents, DEM and THA, are registered chemicals, easy to handle, and not flammable. Consequently, there is no regulation issue with the use of THMA as long as it is prepared *in situ*. Extraction performances were extended to Pd(II) and Pt(IV) extraction from chloride media. Potential applications of the proposed extraction solvent in platinum group metals (PGM) refining is underway. Also, deep understanding of the impact of the molecular topology on extraction outcome will be continued.

The kinetics study was performed *via* simple experimental models. By deliberately lowering the stirring speed, we demonstrated that relevant data can be acquired. A deeper understanding of the kinetics phenomena involved, and the determination of precise absolute mass transfer rate constants require more complex devices (single drop technique, rotating membrane, cell with controlled interface) that cannot be employed for intensive screening. Our approach enabled to precise the importance of different parameters (DHA concentration, THMA concentration, aqueous HNO_3 and Pd(II) concentrations…) so that dimensioning of adapted kinetics studies will be straightforward. More generally, the proposed method is worth considering when kinetics limitations are suspected. Finally, we would like to point attention to possible artefacts and pitfalls related to misinterpretation of solvent extraction results when kinetics are not properly checked: Although the results obtained on THMA/DHA mixtures sound like synergism, they should not be interpreted this way.

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Supporting information

Solvent extraction of Palladium(II) using malonamides: A performing molecular system established through a detailed study of extraction kinetics.

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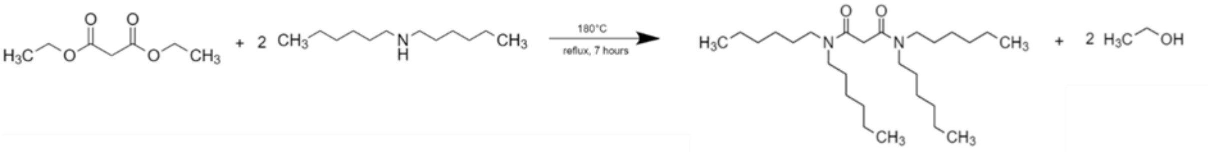
Figure S1: Experimental set-up for the synthesis of *N,N,N',N'*-tetrahexylmalonamide.

Reaction:



Set-up:

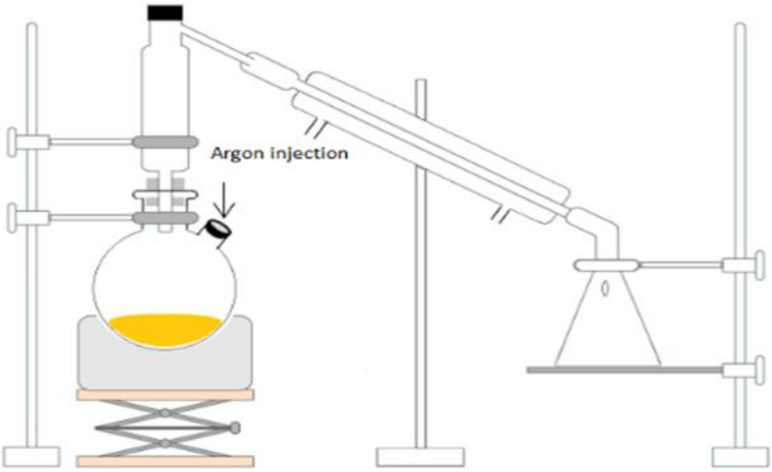


Figure S2: Progress of Pd(II) extraction with 0.2M THMA in toluene as a function of time. $[HNO_3]_{aq}$ 3M, initial $[Pd]_{aq}$ 500mg/L, A/O=1, stirring speed 1200 rpm.

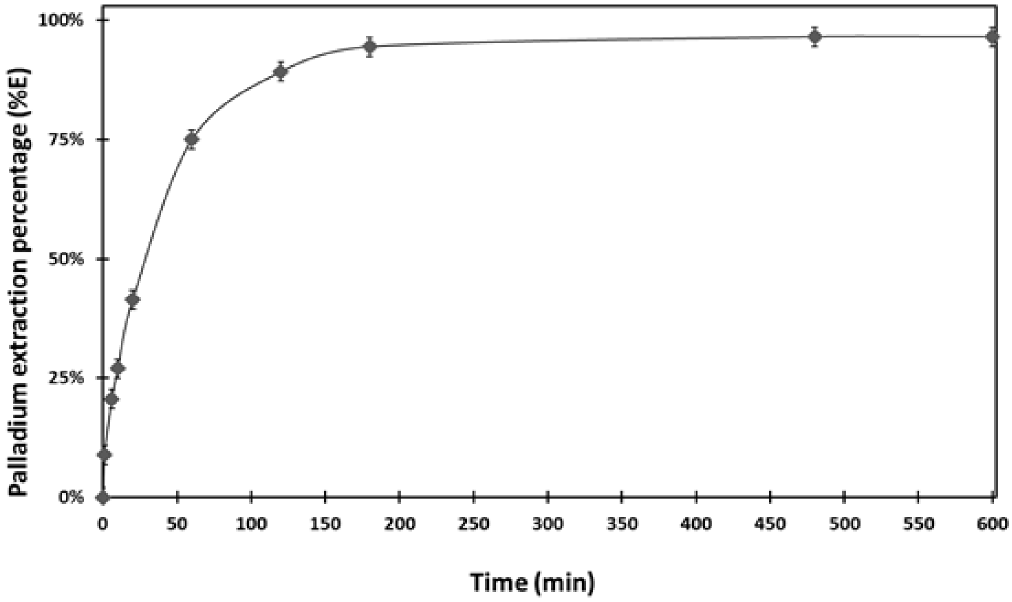


Figure S3: ^{1}H NMR and ^{13}C NMR spectra of THMA (400 MHz, 100 MHz, solvent $CDCl_3$).

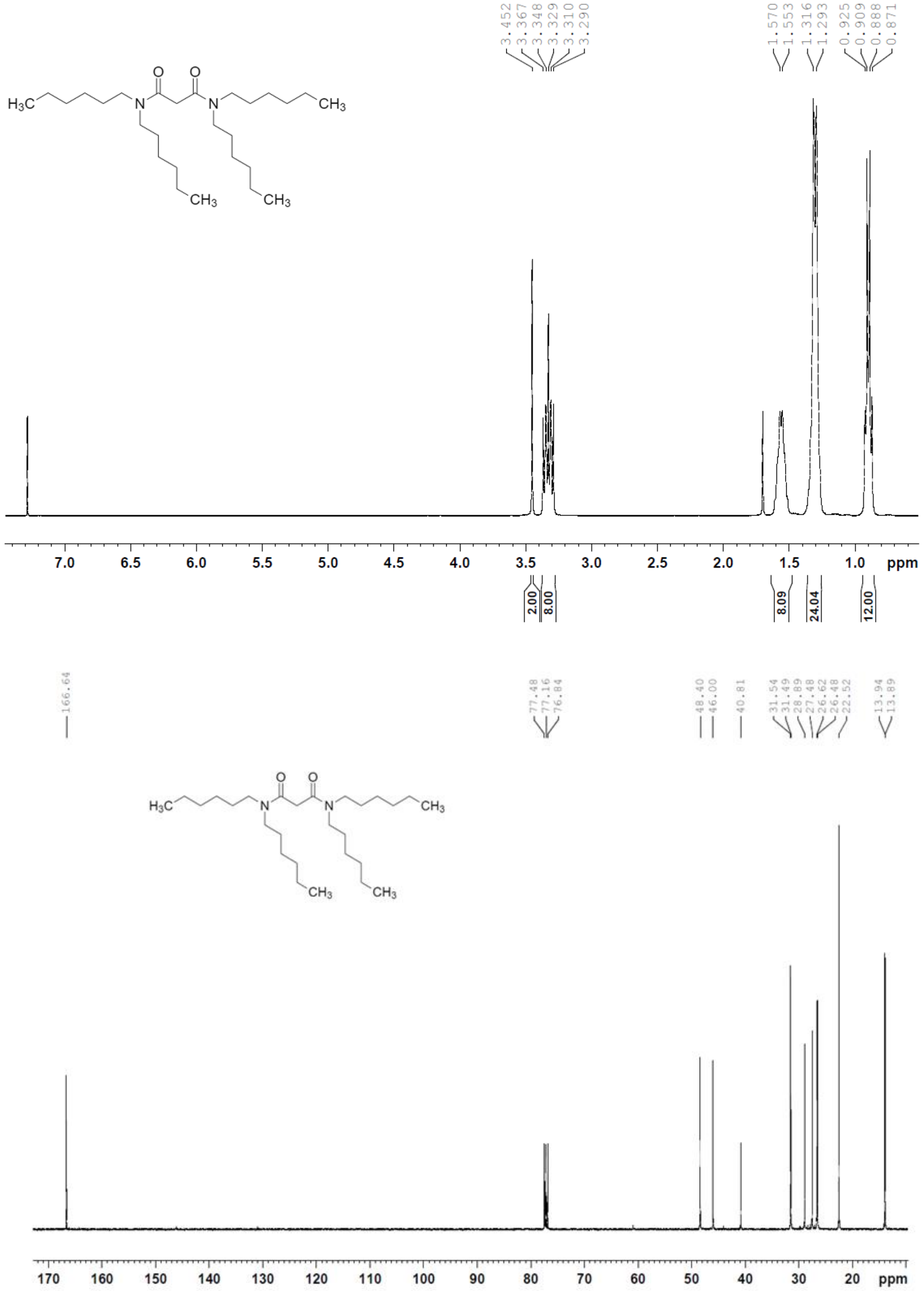


Figure S4: FT-IR spectrum of THMA.

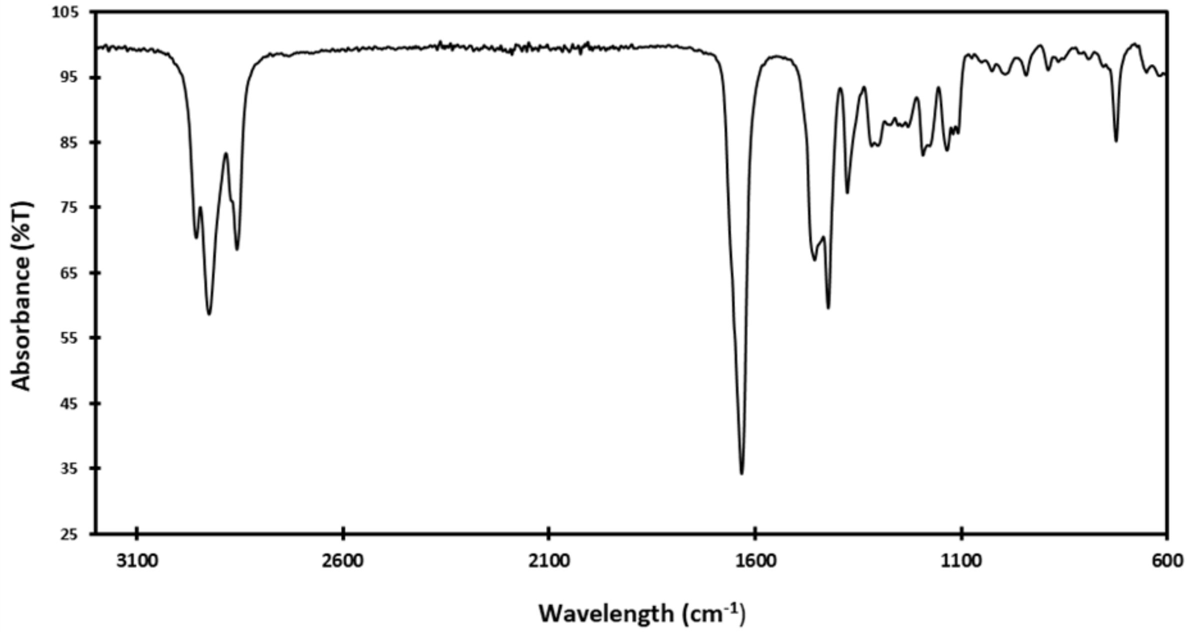


Table S1: FTIR vibrations of THMA.

Wavenumber / cm^{-1}	Assignment
2850 cm^{-1} – 2927 cm^{-1}	ν CH_2 (stretching)
1634 cm^{-1}	ν C=O (stretching)
1456 cm^{-1}	ν CH_2 (bending)
1420 cm^{-1}	ν C-N (stretching)
1376 cm^{-1}	ν C-H (bending)

Figure S5: Effect of stirring speed on the Pd(II) extraction with 0.2M THMA in toluene. $[HNO_3]$ 3M, initial $[Pd]_{aq}$ 500 mg/L, 1 min of extraction.

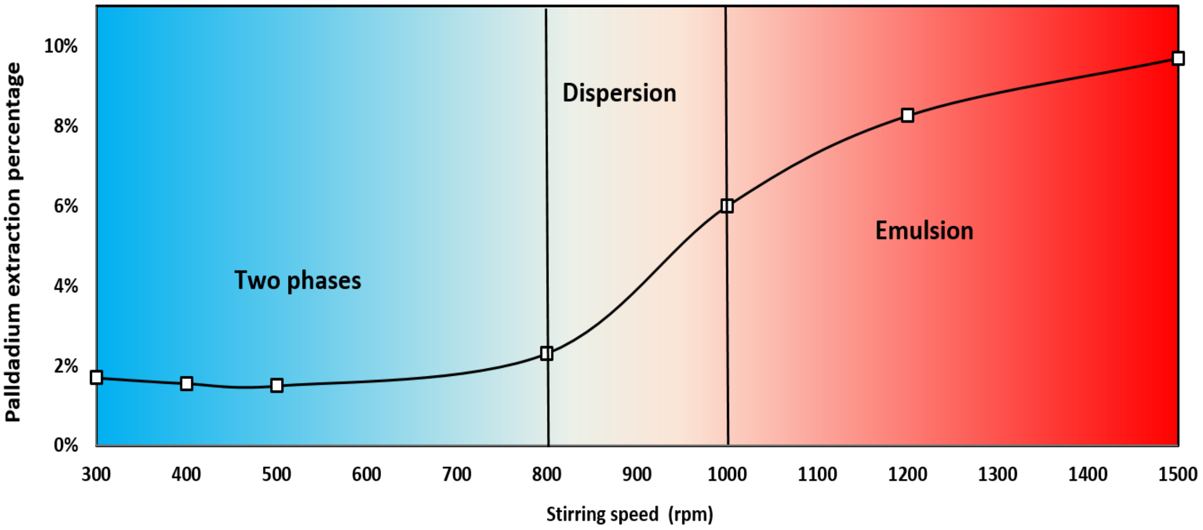


Figure S6: Pd(II) distribution ratio with 0.2M THMA in toluene with added DHA after 1 h of extraction. DHA molar percentage 0 mol% to 100 mol% respective to THMA, initial $[Pd]_{aq}$ 500mg/L, $[HNO_3]_{aq}$ 3M, A/O=1, stirring speed 1200 rpm.

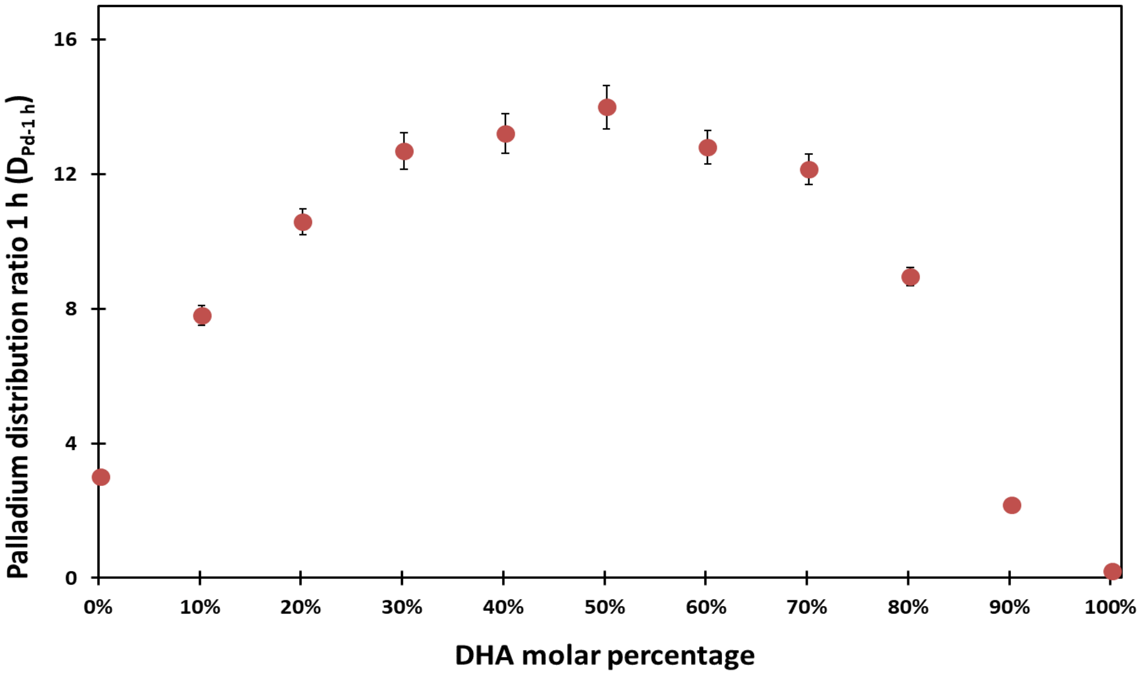


Figure S7: Variation of the interfacial tension upon addition of DHA in the organic phase. 0.2M THMA in toluene, DHA molar percentage 0 mol% to 50 mol% respective to THMA, $[HNO_3]_{aq}$ 3M, T = 23°C.

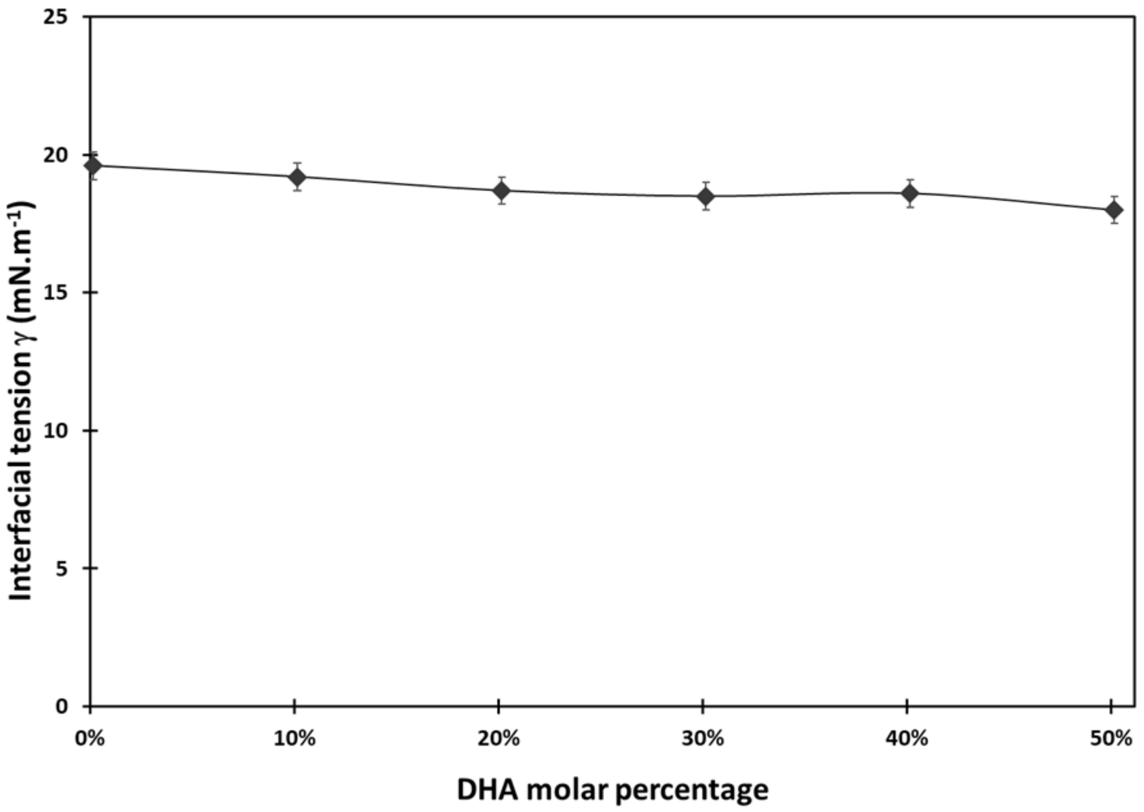


Table S2: Variation of the aqueous concentration of Pd(II) at equilibrium (24 h) after extraction with 0.2M THMA in toluene with added DHA. DHA molar percentage 0 mol% to 50 mol% respective to THMA.

DHA molar percentage	$Pd_{aq,eq}\ (mg.L^{-1})$	k_{obs} **(min^{-1})**	$t_{1/2}$ **(min)**
0 mol%	16.7	0.028	25
10 mol%	15.2	0.052	13
20 mol%	13.2	0.070	10
30 mol%	14.7	0.079	9
40 mol%	13.6	0.104	7
50 mol%	15.4	0.116	6

Figure S8: Evolution of observed rate constant k_{obs} of Pd(II) extraction with 0.2M THMA in toluene from aqueous 3M HNO_3 solution according to the added DHA quantity. Initial $[Pd]_{aq}$ 500 mg/L, $[HNO_3]_{aq}$ 3M, stirring speed 1200 rpm.

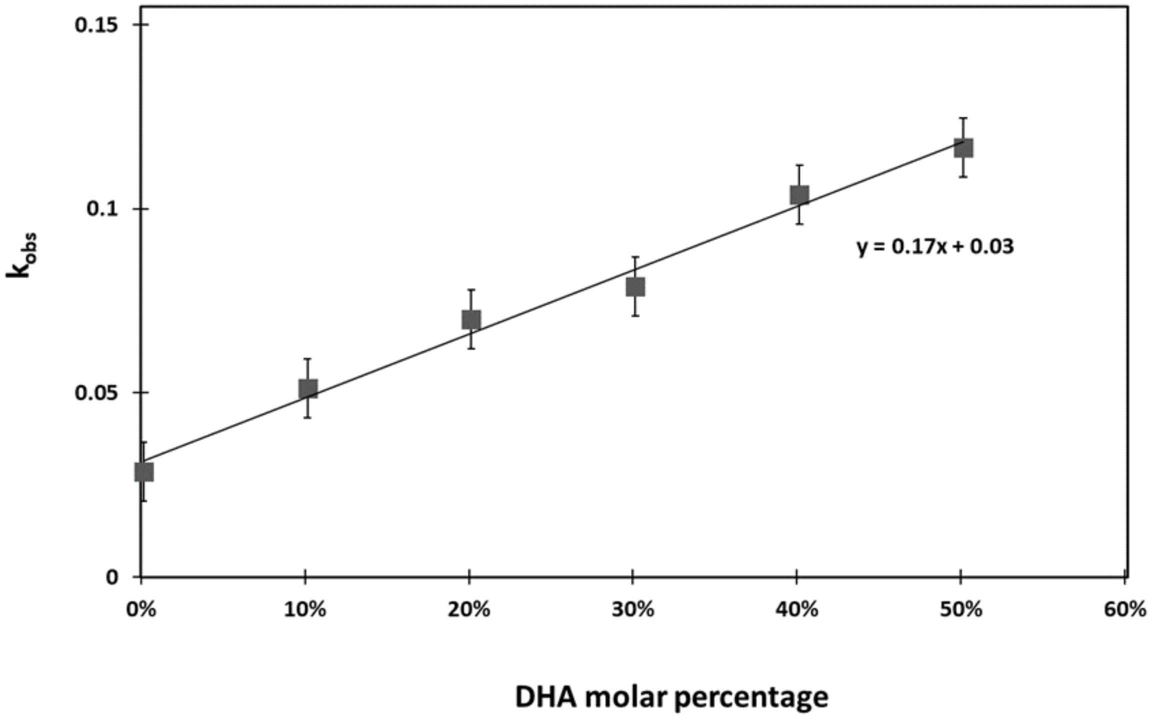


Figure S9: Effect of HNO_3 on Pd(II) extraction with 0.2M THMA in toluene at equilibrium (24 h). Initial $[Pd]_{aq}$ 500 mg/L, A/O=1.

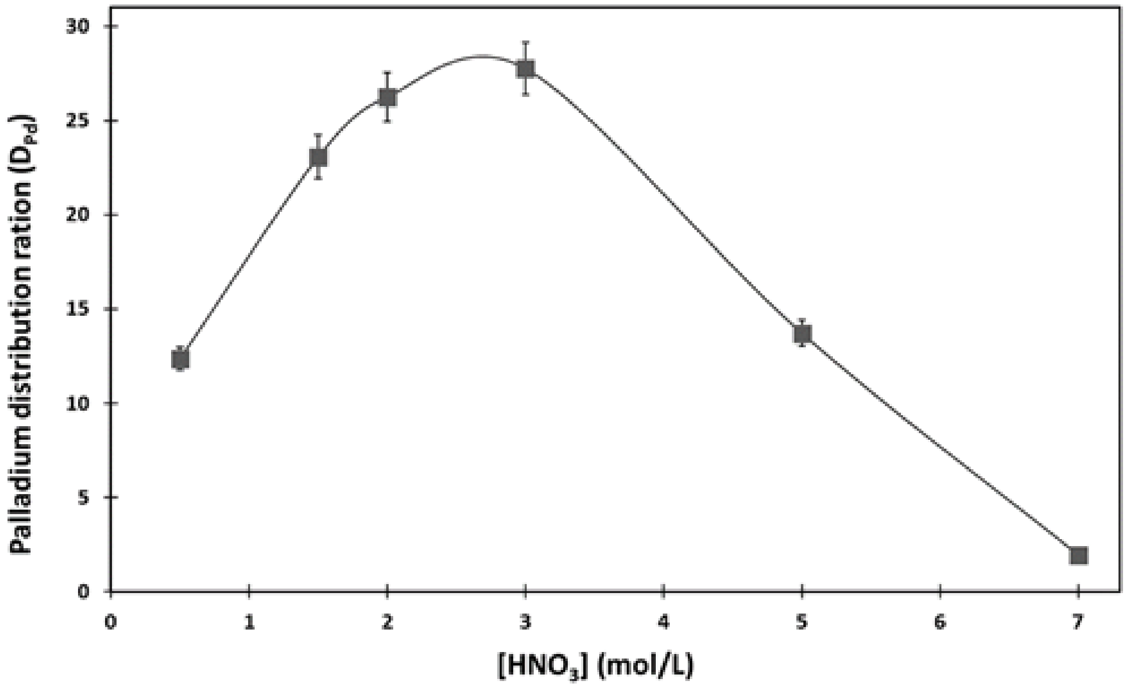


Figure S10: Pd(II) distribution ratio with 0.2M THMA in toluene with added DHA at equilibrium (24 h extraction duration). DHA molar percentage 0 mol% to 50 mol% respective to THMA, initial $[Pd]_{aq}$ 500mg/L, $[HNO_3]_{aq}$ 5M, A/O=1.

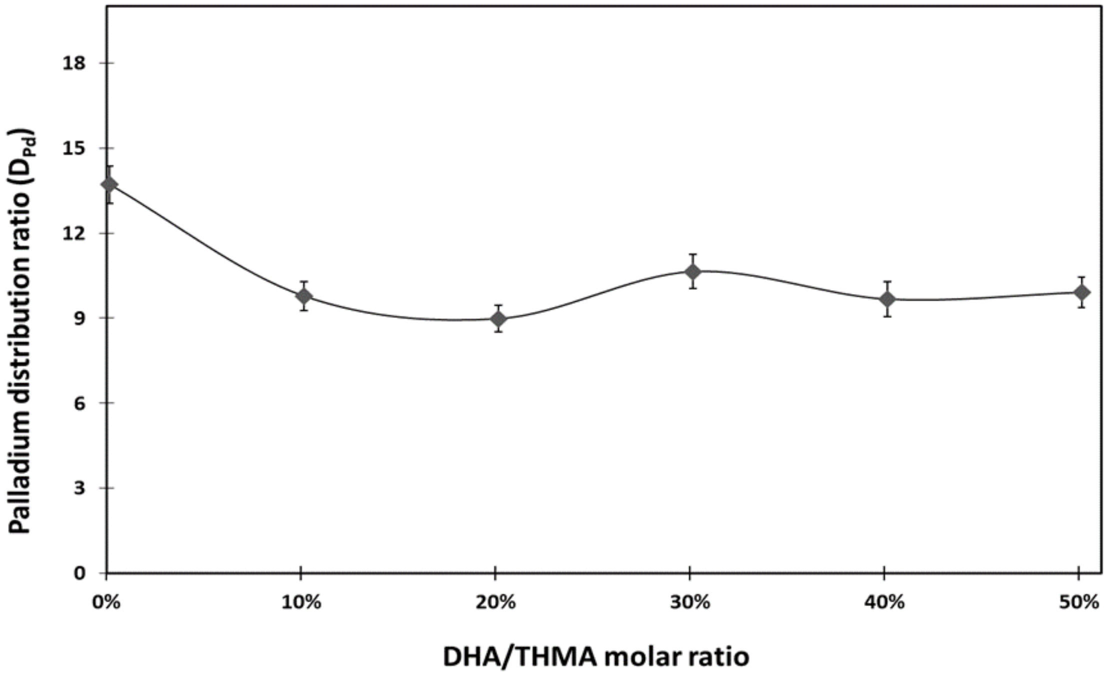
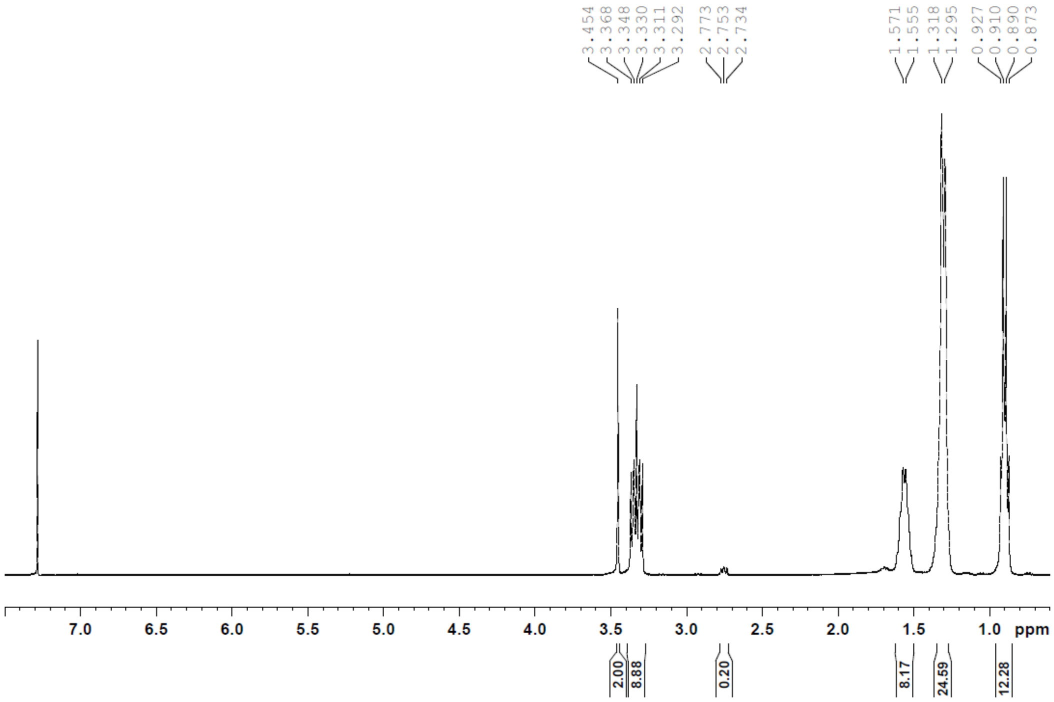
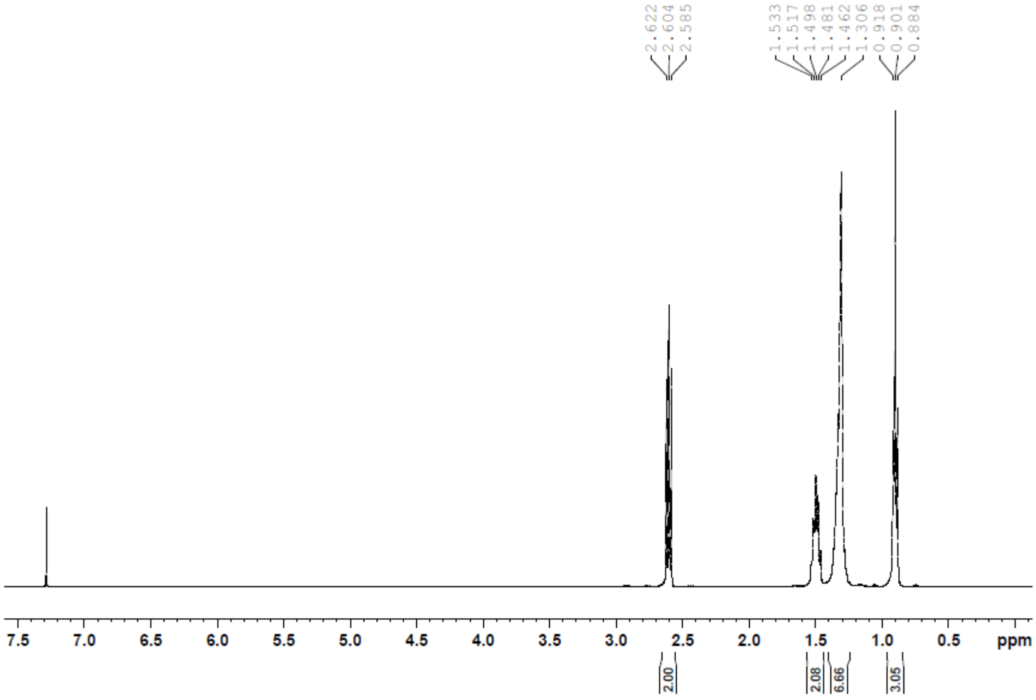


Figure S11: ^{1}H NMR spectra (400 MHz, 100 MHz, solvent $CDCl_3$) of (a) crude THMA and (b) Dihexylamine (DHA).



(a)

(b)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0.918
0.901
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.08
6.66
3.05