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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.

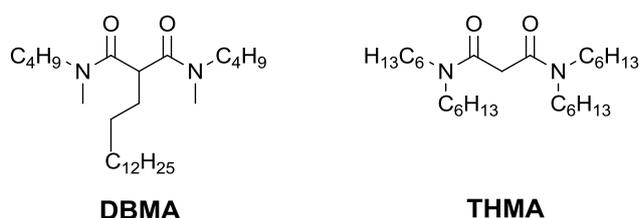
Keywords:

Solvent extraction; Kinetics; Palladium; Diamides; Synergy

1 **1. Introduction**

2 Recycling of platinum Group Metals (PGM) has continuously been the object of
3 extensive R&D efforts due to their elevated cost and importance in many industrial sectors.¹⁻³
4 The supply of PGM is limited by their very low natural abundance and the availability of
5 natural ores in only a few countries (South Africa, Russia).⁴⁻⁶ The recent sanitary crisis has
6 further revealed the weaknesses of the supply chain in most developed countries. Public
7 policies push towards increasing the recovery of PGM from secondary resources to ensure the
8 economy's resilience.⁷⁻¹⁰ Various complementary solutions have been proposed, based either
9 on pyrometallurgical or hydrometallurgical processing.^{3,11,12} Nevertheless, whatever the
10 technology employed, final isolation and purification of PGM rely generally on a solvent
11 extraction stage.^{13,14} The existing industrial extracting molecules, mostly dialkyl sulfides and
12 fatty amines, could not be successfully applied to hydrometallurgical processes dedicated to
13 the recovery of PGM from waste as their selectivity scope or their stability is insufficient.¹⁵
14 As a consequence, several organic molecules have been developed after molecular design and
15 synthesis route selection.¹⁶ The chemical synthesis of tailor-made molecules is not limited to
16 solvent extraction: They can be employed in solvent impregnated^{17,18} or chelating resins,¹⁹ as
17 ion exchange is also a technique of interest for the recovery of PGM in dilute solutions.
18 Amide compounds play a central role, as the amide moiety is very stable in the highly acidic
19 and oxidizing media employed.²⁰ Monoamides are not efficient enough for PGM extraction.
20 Thus, sulfide containing monoamides and various diamides,^{21,22} including aza- or thio-bearing
21 diamides^{23,24} have been synthesized and successfully used in solvent extraction of PGM from
22 chloride media. Malonamides proved to lead to very stable Pd(II) complexes, and to efficient
23 extraction from nitrate media.^{15,25} Based on these results, we recently proposed a simple
24 process to recover palladium from electronic waste using diamides previously developed in
25 the frame of nuclear fuel reprocessing.^{20,26,27} The approach relies on the reformulation of the
26 extraction solvent using existing available molecules. Although the approach seems
27 promising, it relies on a molecule that has to be specifically prepared and which is only
28 available in large quantities through custom synthesis companies, and not through the regular
29 chemical suppliers. To the best of our knowledge, none of the above-presented new molecules
30 has passed the proof of concept stage at the laboratory level due to the complexity of
31 obtaining them on a large scale for further process development. Finally, it is essential to
32 mention that in Europe, the marketing of a new molecule is hampered by REACH regulation,
33 so that efficient solutions based on existing registered molecules are still needed. During our

1 previous work, the fundamental studies performed along with the process development
2 studies revealed that the initial design of the chosen diamide, *N,N'*-dimethyl-*N,N'*-
3 dibutylteradecylmalonamide (DBMA, Figure 1), was not optimized for selective Pd(II)
4 extraction.^{26,28–30} DBMA was selected as this molecule is the former lanthanide/actinide
5 separation molecule, so that it was readily available from French CEA. However, its
6 molecular design has been performed targeting high distribution ratios for lanthanides(III)
7 cations,^{31–33} and its ability to also extract palladium(II) was instead a side-effect.^{34,35} Thus, the
8 possibility to envision a more simple diamide based solvent dedicated to selective
9 palladium(II) extraction rapidly appeared, using *N,N,N',N'*-tetrahexylmalonamide (THMA,
10 Figure 1), previously described for uranium(VI) extraction.^{36,37} Although the newly proposed
11 diamide is not commercially available, it can be prepared in situ and employed without any
12 purification in the extraction process. Thus, as starting reagents are available and easy to
13 handle, it is possible to prepare the extraction solvent without specific operation in chemical
14 synthesis. Furthermore, the study of the influence of the stoichiometry of reagents employed
15 revealed that a slight excess of amine is beneficial to the performance of the extraction
16 process. A detailed study of the thermodynamic and kinetic features enabled to evidence a
17 synergy phenomenon between amine and diamide for Pd(II) extraction. Finally, the
18 performance of the THMA could be extended to the extraction of Pt(IV) from chloride media.



20 **Figure 1:** Chemical structures of diamides employed in the study

21

22 2. Experimental

23 2.1. Chemical reagents

24 *N,N'*-dimethyl-*N,N'*-dibutylteradecylmalonamide (98% purity, DBMA, Figure 1) was
25 kindly provided by the CEA, France. Production was performed by Pharmasynthèse (former
26 Panchim), France, and the product was used without further purification. Palladium(II) nitrate
27 hydrate ($\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, ca. 40% Pd, 99.9% purity), palladium(II) chloride (99.9% purity)
28 and platinum(IV) chloride (99.9% purity) were purchased from Strem Chemicals. Iron(III)
29 nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 98\%$ Fe), neodymium(III) nitrate hexahydrate

(Nd(NO₃)₃·6H₂O, 99.9% purity), diethyl malonate (99% purity) and dihexylamine (97% purity) were purchased from Sigma-Aldrich and used without further purification. Toluene, SolvessoTM 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 NaHCO₃ (1 x 30 mL) and finally with brine (1 x 30 mL). The recovered organic layer was dried over anhydrous MgSO₄ 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).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 3.45 (s, 2H, COCH₂CO) 3.34 (dd, *J* = 15.4, 7.8 Hz, 4H, N-CH₂), 3.32 (dd, *J* = 15.4, 7.7 Hz, 4H, N-CH₂), 1.57-1.55 (m, 8H, N-CH₂-CH₂), 1.32-1.29 (m, 24H, CH₂) 0.92 (t, *J* = 6.7 Hz, 6H, CH₃), 0.88 (t, *J* = 6.6 Hz, 6H, CH); ¹³C NMR (100.6 MHz, CDCl₃) 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(NO₃)₂·xH₂O, PdCl₂·2H₂O, Fe(NO₃)₃·9H₂O, Nd(NO₃)₃·6H₂O, PtCl₄) dissolved in an aqueous HNO₃ 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, SolvessoTM 150) to reach the concentrations given in the text.

1 The organic phases were pre-equilibrated by bringing them into contact for 30 min with a
2 five-fold volume of an aqueous solution of HNO₃ or HCl of molarity identical to that of the
3 aqueous metal solution employed for the extraction step.

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

9 For each extraction performed, aliquots of the aqueous phases (100 µL), before and
10 after extraction, were directly diluted with a 2% HNO₃/HCl aqueous solution (90/10). After
11 extraction, aliquots of the loaded organic phases (500µL) were back-extracted during 1 h with
12 1 mL of a 0.1M aqueous thiourea solution. Resulting phases were separated and 250 µL of the
13 final aqueous phase were taken and diluted with a 2% HNO₃/HCl aqueous solution (90/10).
14 Evidence from preliminary investigations showed that all extracted metals were totally
15 stripped from loaded organic phases during the process, and that no metal precipitation
16 occurred prior to analysis. Dilution factors have been chosen so that a minimum 10-fold
17 dilution is operated to avoid matrix effects during analysis.

18

19 **2.4. Analytical determination of metal content**

20 Metals concentration in each solution was determined using inductively coupled
21 plasma atomic emission spectroscopy (ICP/AES, SPECTRO ARCOS ICP Spectrometer,
22 AMETEK Materials Analysis). The selected spectral lines to assay metals were free from
23 interference. The given concentrations were calculated as the average of three replicates at
24 different wavelengths for each metal. Relative standard deviations have been determined and
25 lie between 1 and 3%. Quantification limits (LoQ) in each analyzed phase were determined
26 for each metal from the dilution factor applied and the background equivalent concentration
27 calculated by the spectrometer for each optical line. Confidence intervals were selected taking
28 into account the error of the spectrometer and the precision of the equipment used for dilution.
29 Altogether, the relative errors were found to be between 5% and 10%. All results showed a
30 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:

$$D = \frac{[M]_{org}}{[M]_{aq}} \quad (1)$$

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

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):

$$S_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}} \quad (3)$$

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 HNO₃). 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

1 performed before each measurement to obtain the image scale. Interfacial tension
2 measurements were performed at a controlled temperature of 23°C at a high rotation rate
3 (>5000 rpm). The reported values were recorded after the drops reached equilibrium, and no
4 further decrease in interfacial tension values was observed.

6 3. Results and discussion

7 3.1. Extraction of Pd with THMA and DBMA

8 In addition to their capacity to remove minor actinides, diamides have shown an
9 affinity to extract Pd(II) from nitric acid media. Accordingly, the selective extraction of Pd(II)
10 from nitrate media was reported with DBMA. DBMA remains complicated to prepare (three
11 synthesis steps, and purification on silica gel column), making a competitive process
12 dependent on excellent recycling of extraction solvent. Furthermore, for efficient extraction of
13 Pd(II), it was necessary to increase the concentration of the extractant to 0.6 mol/L, i.e. about
14 300 g/L, which makes the initial investment in extraction solvent substantial. On the contrary,
15 THMA is a *N,N,N',N'*-tetrasubstituted malonamide that is much simpler to prepare.
16 Furthermore, it revealed to be an excellent candidate for the selective extraction of Pd(II): The
17 Pd(II) extraction performances of THMA have been assessed in comparison with DBMA, in
18 conditions where DBMA presents good Pd(II) distribution ratios and good selectivity
19 regarding Fe(III) and Nd(III) (Table 1). THMA exhibited overall much better extraction of
20 Pd(II) than DBMA across the whole range of extractant concentrations. Palladium distribution
21 ratios D_{Pd} with THMA were between 10 and 100 times higher than that with DBMA, and still
22 using only 0.3M THMA, the concentration of residual Pd(II) in the final aqueous layer was
23 below the detection limit of the ICP-OES analysis ($D_{Pd} > 70$). The quantitative extraction of
24 Pd(II) with THMA can induce a significant reduction in extractant charge in the organic phase
25 since both diamides are structural isomers, having the same number of carbon atoms (27), and
26 thus the same molecular weight (438.7 g.mol⁻¹).

27 It was previously reported that the selective extraction of Pd(II) over Nd(III) and
28 Fe(III) with DBMA was strongly dependent on two key parameters: The concentration of
29 DBMA for Nd(III) and the aqueous nitric acid concentration for Fe(III).²⁶ Therefore, the
30 optimized conditions to reach selective Pd(II) extraction with DBMA have been established at
31 0,5-0,6M DBMA in toluene with a 3M aqueous HNO₃ solution. THMA showed an
32 impressively high selective extraction of palladium in the presence of Fe(III) and Nd(III)

1 compared to DBMA. For instance, at 0.3M THMA, $S_{Pd/Fe}$ and $S_{Pd/Nd}$ were above 11600 and
 2 35000 respectively, and Pd(II) extraction was quantitative. Experimentally, after extraction
 3 Pd(II) could not be detected in the aqueous layer ($D_{Pd} > 70$), and Nd(III) could not be detected
 4 in the organic layer ($D_{Nd} < 0.002$). Fe(III) was barely quantified in the organic layer ($D_{Fe} =$
 5 0.006). In comparison, for the same concentration for DBMA, $S_{Pd/Fe}$ and $S_{Pd/Nd}$ were 180 and
 6 50, respectively, with Pd(II) distribution ratio of 4 only. The increase in extractant
 7 concentrations leads to a decrease in the selectivity regarding Fe(III) or Nd(III) with DBMA
 8 as previously reported. When using THMA, the distribution ratios of both Fe(III) and Nd(III)
 9 also increased with concentration, but remained very low (below 0.1) so that $S_{Pd/Fe}$ and $S_{Pd/Nd}$
 10 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

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

14 Altogether, this analysis rapidly emphasized the very interesting features of THMA
 15 over DBMA in the selective extraction of Pd(II). Regarding the Pd(II) selective isolation
 16 process we recently proposed, using THMA instead of DBMA should lead to a more efficient
 17 process, based on lower stage numbers in extraction and scrubbing sequences, and using a
 18 lower amount of extracting molecule. However, we were surprised to notice a sudden drop in
 19 performance when lowering the THMA concentration to 0.2M or below. **Particularly low**
 20 **Pd(II) distribution** ratios were sometimes obtained, depending on the batches of THMA used.
 21 Careful examination of the NMR spectra of the corresponding batches was conducted and
 22 revealed residual traces of dihexylamine (DHA) in the solvent. Also, equilibrium was not
 23 reached after 1 h extraction: The extraction with THMA is incomplete after 1 h shaking (see
 24 SI, Figure S2), whereas with DBMA we found during our previous studies that extraction
 25 equilibrium was reached after 10 min only, working in toluene and using the same aqueous

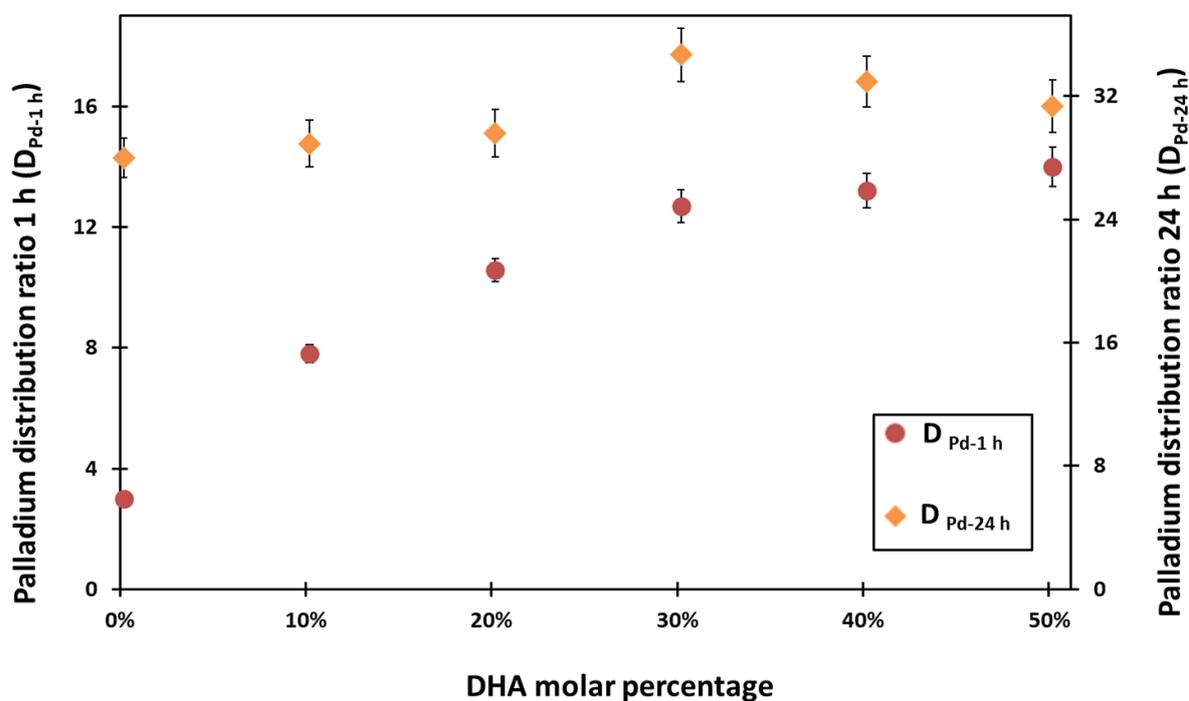
1 layer ($[\text{HNO}_3] = 3\text{M}$). This drawback led us to investigate in detail the impact of THMA
2 purity on extraction performances, and especially on the kinetics of Pd(II) extraction.

3 **3.2. Impact of added DHA on Pd(II) extraction with THMA**

4 Synthesis of THMA involves DHA as a starting material. High molecular weight
5 amines and quaternary ammonium salts have been used among nitrogen-containing
6 extractants for the extraction of PGM from chloride media.³⁸⁻⁴⁶ In addition to their extraction
7 properties, their role as a catalyst in the extraction of Pd(II) from aqueous hydrochloric acid
8 solutions has been documented in previous studies.⁴⁷⁻⁵⁰ Incorporation of an amine moiety into
9 an amide based extractant proved superior performances for Pd(II) from nitrate media.
10 However, Pd(II) extraction with amine-based functions from nitrate media has been rarely
11 reported in the literature.⁵¹⁻⁵³ Thus, the impact of controlled addition of DHA to pure THMA
12 on the extraction of Pd(II) from nitric acid media was investigated. Firstly, a well-purified
13 batch of THMA was prepared and fully characterized (see SI, Figures S3 and S4, and Table
14 S1). Working with this batch confirmed i) the excellent performance regarding Pd(II)
15 extraction, and ii) the slower kinetics of Pd(II) extraction at low THMA concentrations,
16 compared to previous results with DBMA. Then, the concentration of THMA was set at
17 0.2M, and DHA was added in quantity varying from 0 to 100 mol% respective to THMA. For
18 a contact period of 24 h, excellent Pd(II) distribution ratios could be obtained even at this
19 relatively low THMA concentration ($D_{\text{Pd}} = 28$ with 0.2M THMA in toluene after 24 h). DHA
20 addition only had marginal effect, since the D could reach only 32-35 (see Figure 3). Finally,
21 using only DHA 0.2M in toluene, very low palladium distribution ratio was found ($D_{\text{Pd}} = 0.1$
22 at equilibrium, after 24 h) which confirms that secondary amines are not good Pd(II)
23 extracting molecules from nitrate media.

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

1 of Pd(II) extraction yield after 1 min (see SI, Figure S5). Therefore, the stirring speed was set
2 at 1200 rpm.



3
4 **Figure 3.** Pd(II) distribution ratio with mixed THMA/DHA systems in toluene. THMA
5 concentration 0.2M, DHA molar percentage 0 mol% to 50 mol%, initial $[Pd]_{aq}$ 500mg/L,
6 $[HNO_3]_{aq}$ 3M, 1 h extraction, stirring speed 1200 rpm.

7
8 In these conditions, the palladium distribution ratio (D_{Pd}) drops to 3 (75% extraction
9 percentage) using pure THMA 0.2M in toluene after 1 h. When DHA was added to 0.2M
10 THMA in toluene, the Pd(II) distribution ratio determined after 1 h extraction increased
11 significantly (Figure 3). It reached a maximum at 14 (93% extraction yield) when 50 mol%
12 DHA were added to THMA (thus, the extraction solvent is a 0.2M THMA / 0.1M DHA
13 solution). The increase in the palladium distribution ratio was somehow still limited, and
14 remained below the distribution ratio obtained in the same conditions after 24 h (Figure 3).
15 Then, above 50 mol% of added DHA, there is no more benefit of DHA addition. Moreover, a
16 further increase in the molar percentage of added DHA led to a decrease in the extraction
17 efficiency of Pd(II) (see SI, Figure S6). For instance, when using THMA with 90 mol% added
18 DHA, D_{Pd} dropped to 2 (69% extraction yield).

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

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

14

15 **3.3. Pd extraction kinetics with mixed THMA/DHA systems**

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

$$26 \quad -\frac{d[Pd]_{aq}}{dt} = k([Pd]_{aq,t} - [Pd]_{aq,eq}) \quad (4)$$

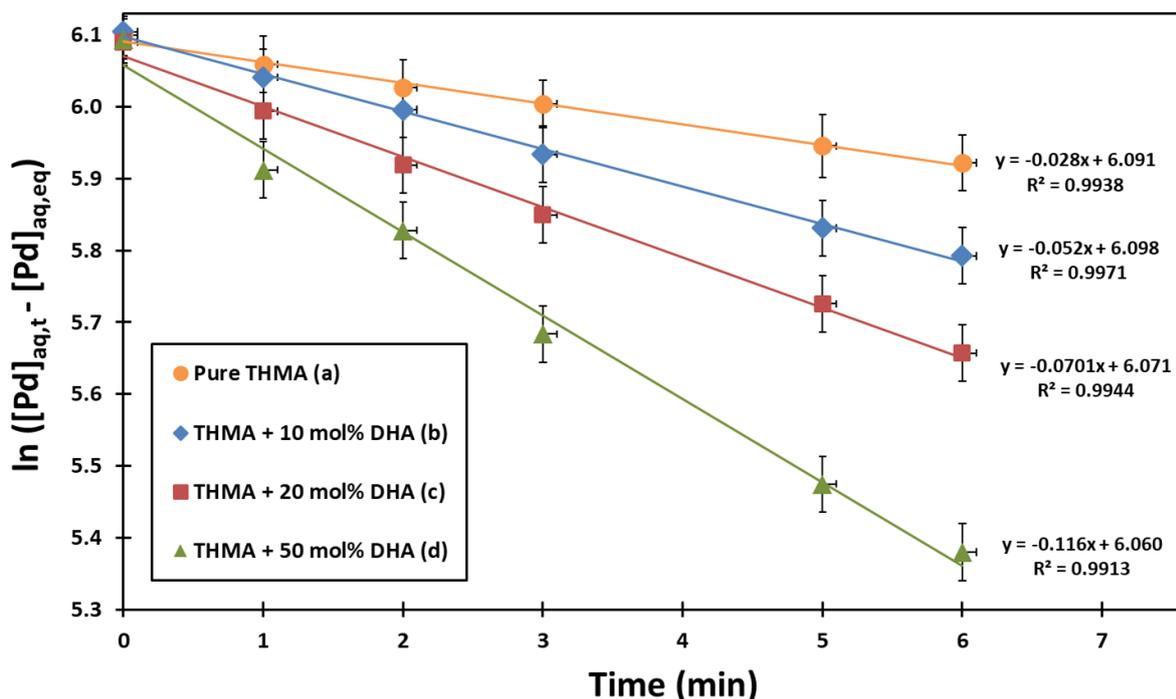
26

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

$$28 \quad \ln([Pd]_{aq,t} - [Pd]_{aq,eq}) = -kt + \ln([Pd]_{aq,0} - [Pd]_{aq,eq}) \quad (5)$$

28

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



8
 9 **Figure 4.** First order model for the extraction of Pd(II) with pure THMA and mixed
 10 THMA/DHA systems in toluene. THMA concentration 0.2M, and 10 mol% DHA, 20 mol%
 11 DHA and 50 mol% DHA, initial $[Pd]_{aq}$ 500 mg/L, $[HNO_3]_{aq}$ 3M, stirring speed 1200 rpm.

12
 13 The extraction kinetics of Pd(II) is enhanced in the presence of DHA, with a regular
 14 increase in the observed rate constants (Figure 4). The rate constant increased from 0.028
 15 min^{-1} for the extraction with pure THMA to 0.116 min^{-1} with 50 mol% added DHA,
 16 corresponding to an extraction half-time of 25 min and 6 min respectively. Thus, without
 17 DHA, Pd(II) extraction is slow, but occurs. The addition of 10 mol% DHA leads to doubling
 18 of the rate constant (half-time divided by almost 2). The increase is then proportional to the
 19 quantity of added DHA (see SI, Figure S8). Interestingly, the observed rate constant (k_{obs}) can

1 be decomposed into two contributions, k_{THMA} (obtained when no DHA is added,
2 $k_{THMA} = 0.028 \text{ min}^{-1}$) and k_{DHA} (equation (6)).

$$k_{obs} = k_{THMA} + k_{DHA} \quad (6)$$

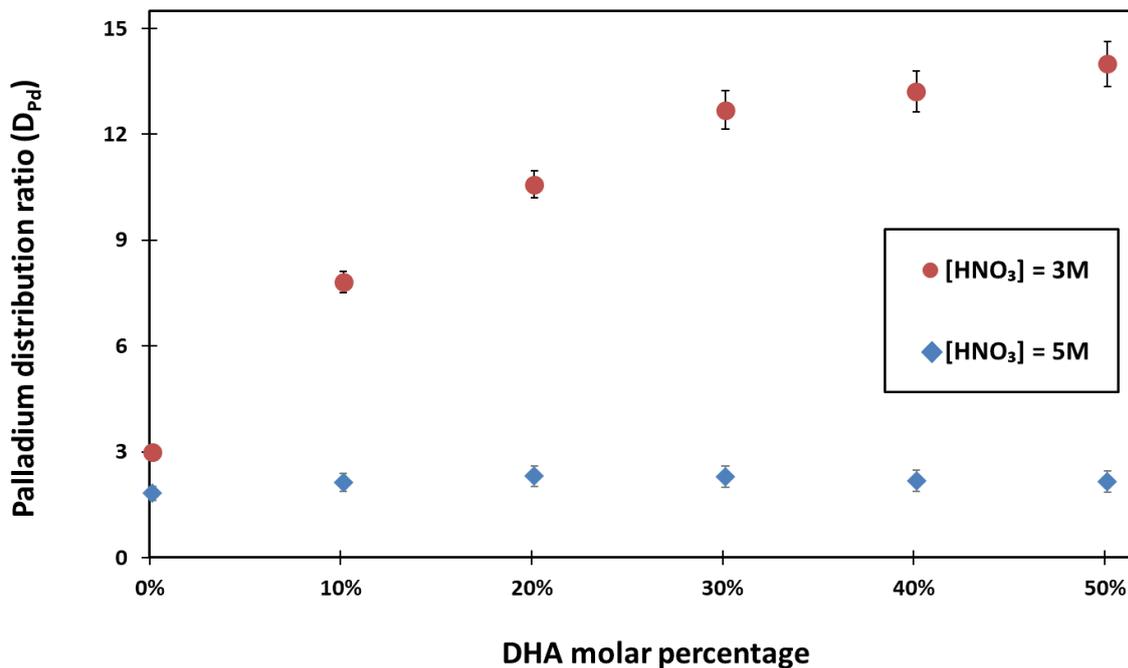
3

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

$$k_{DHA} = 0.87 [DHA] \quad (7)$$

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

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



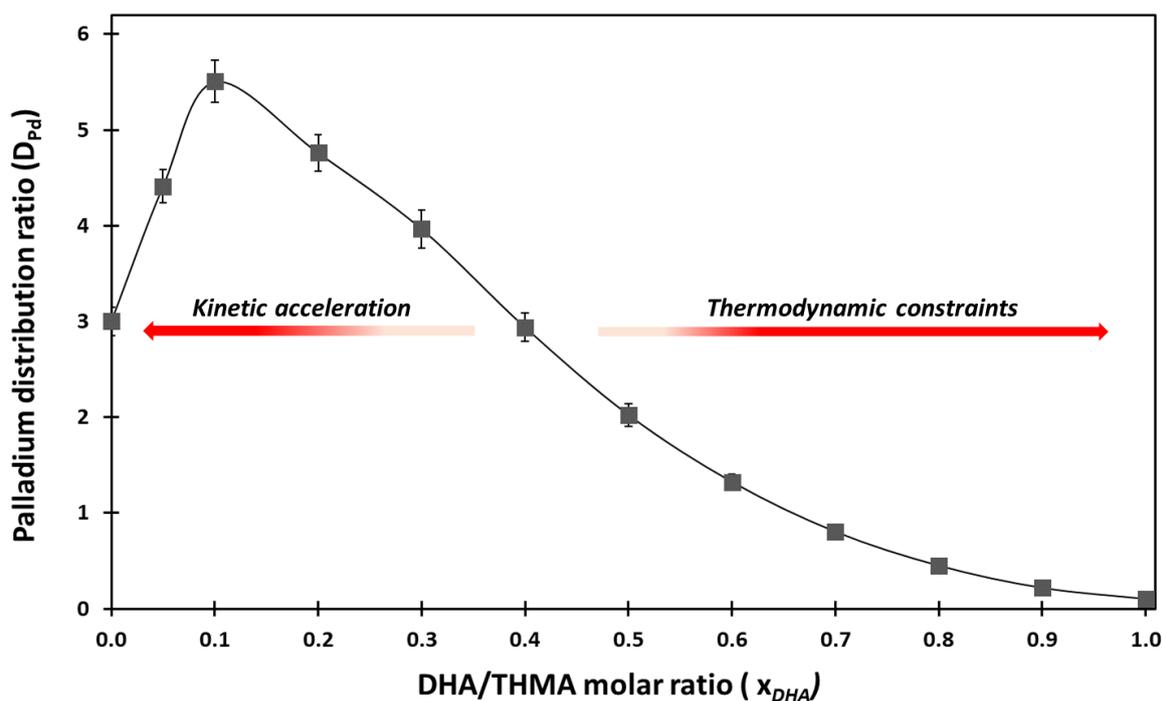
1

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

5

6 **3.4. Extraction solvent formulation: optimization of added DHA quantity**

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



1
 2 **Figure 6.** Pd(II) distribution ratio after extraction with THMA/DHA mixtures.
 3 [THMA]+[DHA] = 0.2M in toluene, initial [Pd]_{aq} 500 mg/L, [HNO₃]_{aq} 3M, 1 h extraction,
 4 stirring speed 1200 rpm.

5
 6 Palladium distribution ratios rapidly rose as the molar ratio of DHA in the organic
 7 phase increased, and maximum of $D_{Pd} = 5.5$ was reached for $x_{DHA} = 0.1$. Conversely, by
 8 exceeding this limit, palladium distribution ratios decreased continuously, and reached $D_{Pd} =$
 9 0.14 for pure DHA. As expected, the Pd(II) extraction strongly relies on sufficient THMA
 10 concentration in the organic phase. As long as the THMA content in the solvent is sufficient
 11 to enable the extraction of Pd(II), the contributory effect of DHA is visible. At the maximum
 12 point ($x_{DHA} = 0.1$), the THMA concentration is still close to 0.2M (0.18M precisely), and the
 13 DHA concentration is 0.02M, very close to 10 mol% respective to THMA. Afterwards, Pd(II)
 14 extraction efficiency decreases, as the THMA content in the organic phase decreases. Thus, it
 15 can be concluded that the benefit of DHA addition is optimum at 10 mol%. Further addition
 16 of DHA does increase the kinetics, but the increase is insufficient to counterbalance loss of
 17 efficiency due to lower amount of THMA. Extraction half-time is lowered from 13 min to
 18 10 min upon doubling of the DHA quantity from 10 mol% to 20 mol%. Thus, unless kinetics
 19 are the most important parameter, we think that it is not worth adding more than 10 mol%
 20 DHA. It is worth mentioning here again that these results have been gathered in conditions
 21 voluntarily chosen in order to **reduce** mass transfer during the liquid-liquid extraction process.

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

21

22 **3.5. Extraction of Pd with crude THMA**

23 As DHA proved to have a beneficial effect on the extraction of Pd(II) with THMA
24 from nitric acid media, we investigated the possibility to employ unpurified THMA to prepare
25 the extraction solvent. When DHA is employed in excess (more than 2.0 equiv.) respective to
26 diethyl malonate in the synthesis of THMA, the crude reaction mixture only contains residual
27 DHA in addition to THMA. Thus, a batch of crude (unpurified) THMA was evaluated for
28 Pd(II) extraction. This THMA batch was prepared using excess DHA (10 mol%), with the
29 same synthetic procedure, except that all purification stages (dilution in diethyl ether, HCl
30 washing, drying over magnesium sulfate and distillation of diethyl ether) were not performed:
31 The synthesis was run solvent free by heating at 180°C, and the crude mixture was employed
32 directly, after cooling, through dilution of the viscous yellow liquid obtained in toluene.
33 Determination of the molar ratio of residual DHA was performed through integration of

1 corresponding signal areas in ^1H NMR spectrum (see SI, Figure S11). Other diluents can be
 2 employed, such as aromatic cuts, eg. SolvessoTM 150 (*vide infra*). Comparison of the results
 3 obtained during Pd(II) extraction between purified THMA and crude THMA in toluene are
 4 presented in Table 2:

5 **Table 2.** Extraction of Pd(II) with purified THMA and crude THMA synthesized with an
 6 excess of DHA (10 mol%). THMA concentration 0.2M in toluene, initial $[\text{Pd}]_{\text{aq}}$ 500mg/L,
 7 $[\text{HNO}_3]_{\text{aq}}$ 3M, stirring speed 2000 rpm, A/O = 1.

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

8

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

18

19 3.6. Extraction of Pd(II) and Pt(IV) from chloride media

20 THMA has proven to be a performing extractant for Pd(II) from nitric acid media. The
 21 investigation was further extended to assess the efficiency of THMA in the extraction of
 22 Pd(II) from chloride media. From an industrial application perspective, toluene was replaced
 23 by SolvessoTM 150 as diluent. These experiments were carried out with crude THMA using
 24 the batch and the procedure described above. THMA concentration was set at 0.2M. THMA
 25 showed an efficient extraction of Pd(II) (Table 3). So far, results obtained on Pd(II) extraction
 26 with malonamides were mitigated: The best results were obtained in 1,2-dichloroethane at 8M
 27 HCl,⁵⁷ with specific malonamides, with distribution ratios close to 4. In our hands, extraction
 28 of Pd(II) with DBMA from chloride media was very low, so that we employed a sodium

1 chloride solution as stripping reagent in the Pd purification process we developed. The
 2 possibility to extract Pd(II) with excellent efficiency from chloride media ($D_{Pd} = 35.4$ at $[HCl]$
 3 $= 1M$) is particularly striking, as only the hydrophobic part of the molecule was modified, the
 4 coordinating head is still the same diamide moiety. Using same conditions, Pd(II) extraction
 5 yield with DBMA (0.6M in toluene) was only 2%. Also, extraction of Pt(IV) was evaluated
 6 and gave successful results (Table 3). Distribution ratios of both metals strongly depend on
 7 the aqueous hydrochloric acid concentration. The distribution ratio of Pd(II) decreased from
 8 35.4 to 1 with HCl concentration increasing from 1M to 6M, whereas that of Pt(IV) increased
 9 from 10.3 to 27.4. The separation of Pt(IV) from Pd(II) is efficient at 6M aqueous
 10 hydrochloric acid concentration, where the separation factor $S_{Pt/Pd}$ was 27.4.

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

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

15
 16 Altogether, these preliminary results on platinum group metals (PGM) extraction from
 17 chloride media demonstrate the potential interest of THMA for the extraction and purification
 18 of these metals. Significant distribution ratios could be obtained in classical conditions, ie.
 19 after 1 h, with crude THMA. As a comparison, the extraction of PGM with alkyl sulfides from
 20 chloride media require the addition of a fatty amine to obtain acceptable kinetics. It could be
 21 worth envisioning the study of the optimum DHA quantity before adapting the technology to
 22 PGM separation from chloride media.⁵⁸

23 It is finally interesting to take into consideration the cost of reagents: DHA is the
 24 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 ($g \cdot mol^{-1}$)	Density	Cost ($€ \cdot mol^{-1}$)	Equi v.	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 €

1

2 Thus, each 10 mol% added DHA will increase the cost of prepared THMA by 4.5 %
3 (2.6 €). This cost analysis is preliminary, only based on reagents costs. The results are
4 indicative, they should only be considered in comparison with other reagents available from
5 the same supplier in same packaging. For instance, tributyl phosphate (TBP) can be purchased
6 in 2.5 L packaging for 137 € from Sigma-Aldrich (France), thus at a 56 €/kg price, to be
7 compared with the 134 €/kg price for THMA based on reagents employed. In other words, the
8 cost for THMA is expected to be in the same order of magnitude as that of TBP. From same
9 supplier, and based on same packaging, dioctyl sulfide (DOS) is 10-20 times as expensive as
10 TBP. Thus, THMA is one order of magnitude cheaper than DOS, an extracting molecule than
11 can be employed at industrial scale for PGM refining. Altogether, this analysis and the
12 obtained results suggest that THMA should be investigated with careful attention for PGM
13 refining.

14

15 4. Conclusion

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

1 The kinetics study was performed *via* simple experimental models. By deliberately
2 lowering the stirring speed, we demonstrated that relevant data can be acquired. A deeper
3 understanding of the kinetics phenomena involved, and the determination of precise absolute
4 mass transfer rate constants require more complex devices (single drop technique, rotating
5 membrane, cell with controlled interface) that cannot be employed for intensive screening.
6 Our approach enabled to precise the importance of different parameters (DHA concentration,
7 THMA concentration, aqueous HNO₃ and Pd(II) concentrations...) so that dimensioning of
8 adapted kinetics studies will be straightforward. More generally, the proposed method is
9 worth considering when kinetics limitations are suspected. Finally, we would like to point
10 attention to possible artefacts and pitfalls related to misinterpretation of solvent extraction
11 results when kinetics are not properly checked: Although the results obtained on THMA/DHA
12 mixtures sound like synergism, they should not be interpreted this way.

13

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17

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1 **Supporting information**

2

3

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

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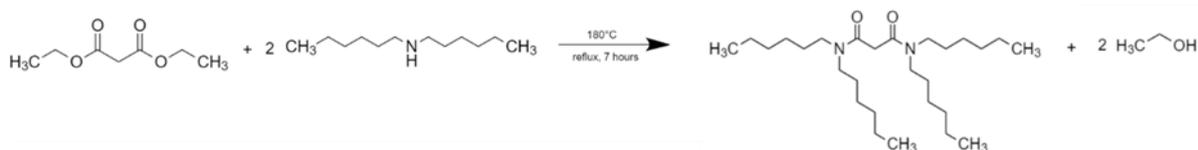
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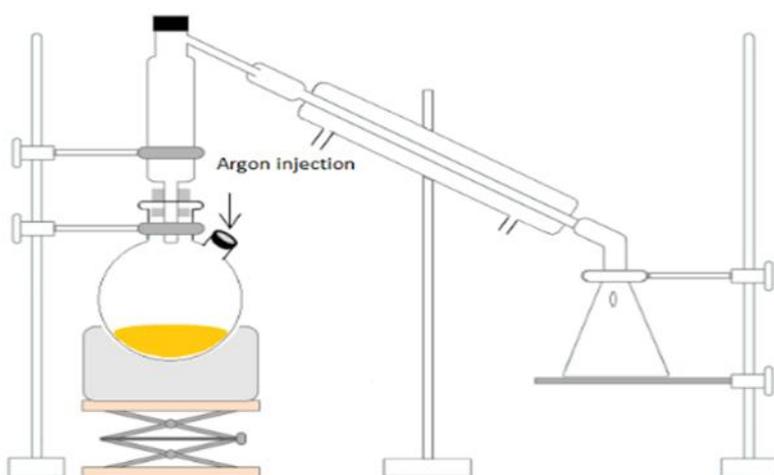
1 **Figure S1:** Experimental set-up for the synthesis of *N,N,N',N'*-
2 tetrahexylmalonamide.

3 Reaction:



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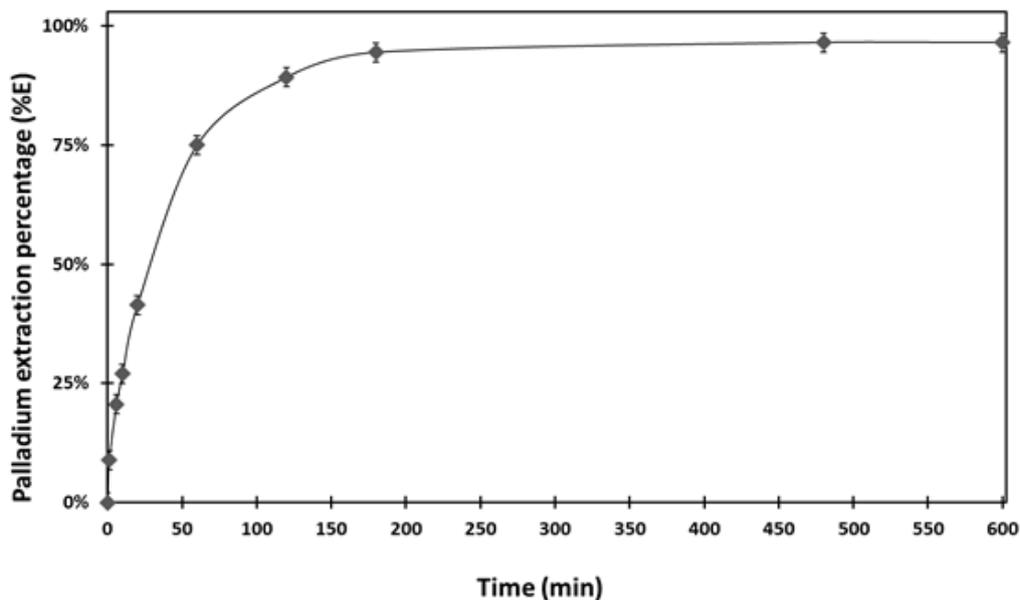
5 Set-up:



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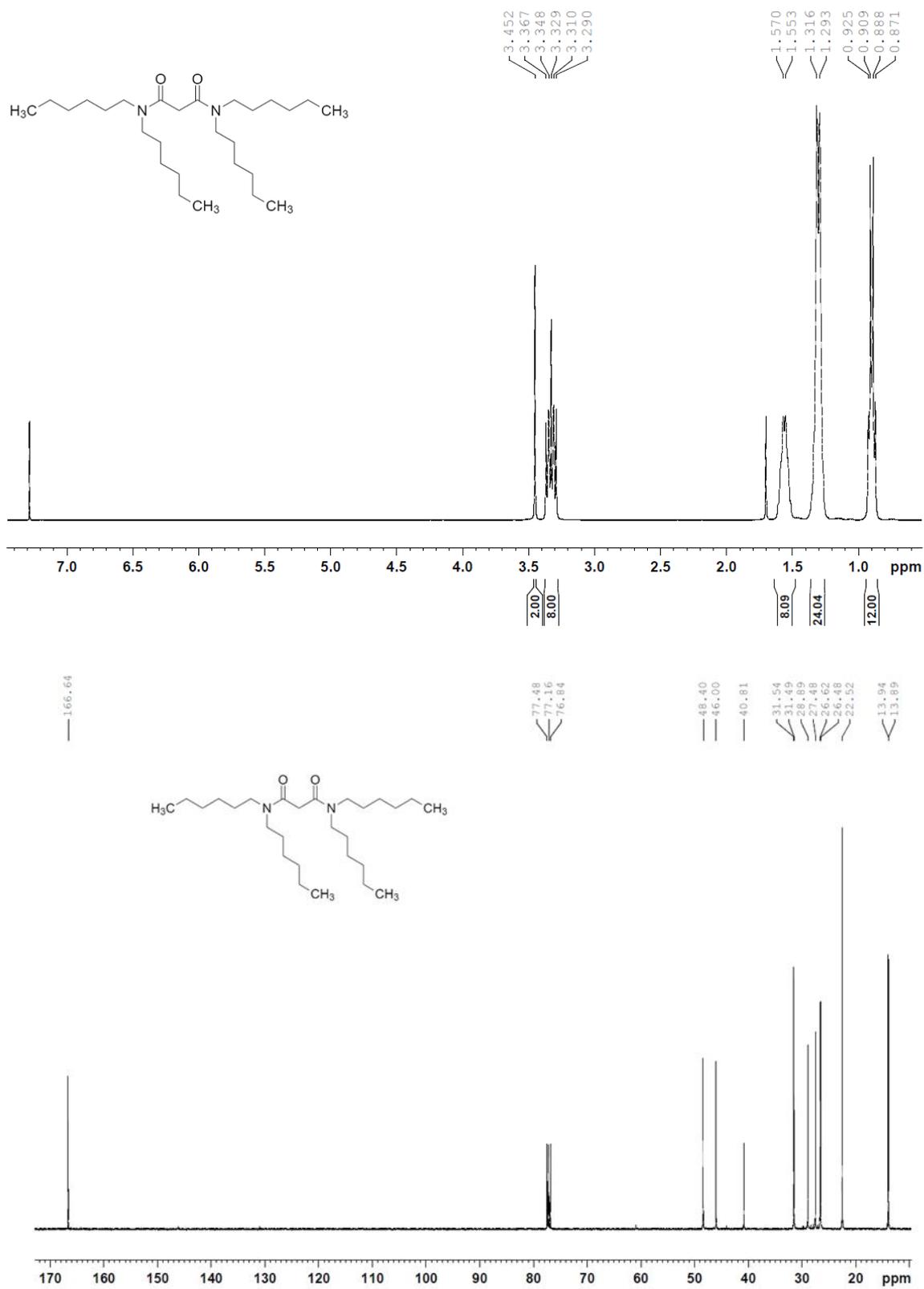
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8 **Figure S2:** Progress of Pd(II) extraction with 0.2M THMA in toluene as a
9 function of time. $[HNO_3]_{aq}$ 3M, initial $[Pd]_{aq}$ 500mg/L, A/O=1, stirring speed
10 1200 rpm.



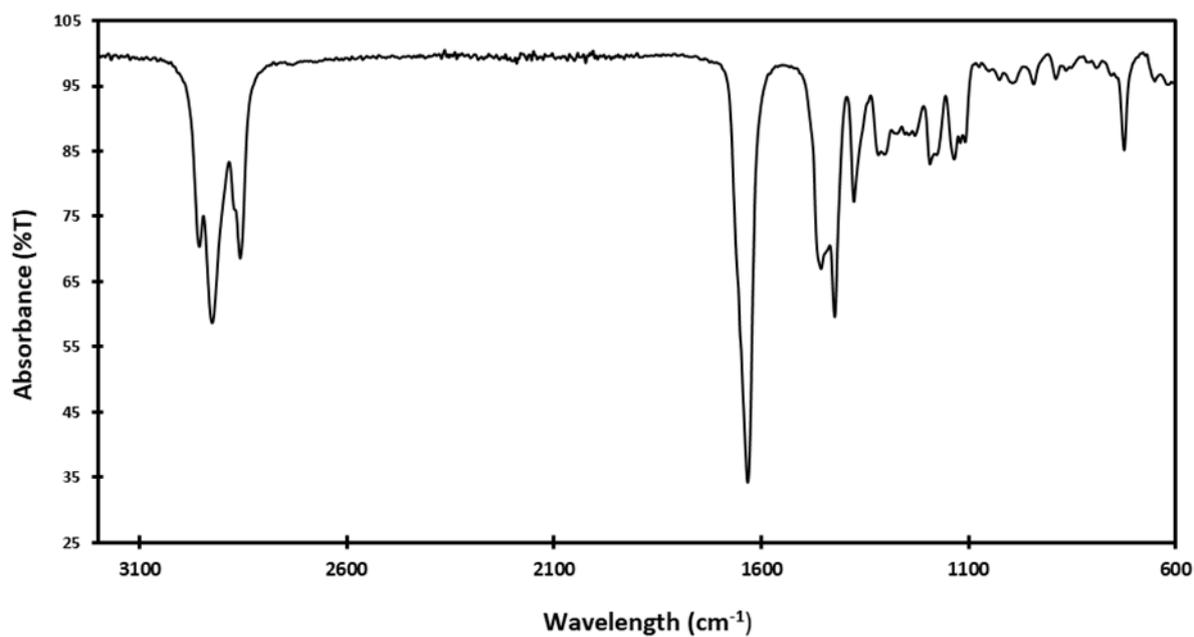
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1 **Figure S3:** ^1H NMR and ^{13}C NMR spectra of THMA (400 MHz, 100 MHz, solvent CDCl_3).



3

1 **Figure S4:** FT-IR spectrum of THMA.



4 **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)

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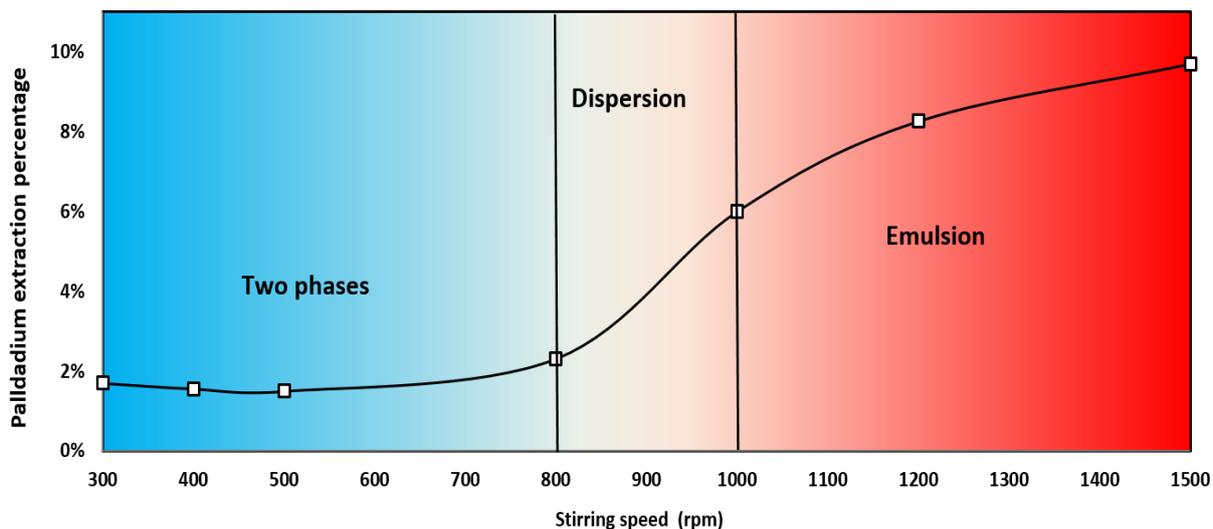
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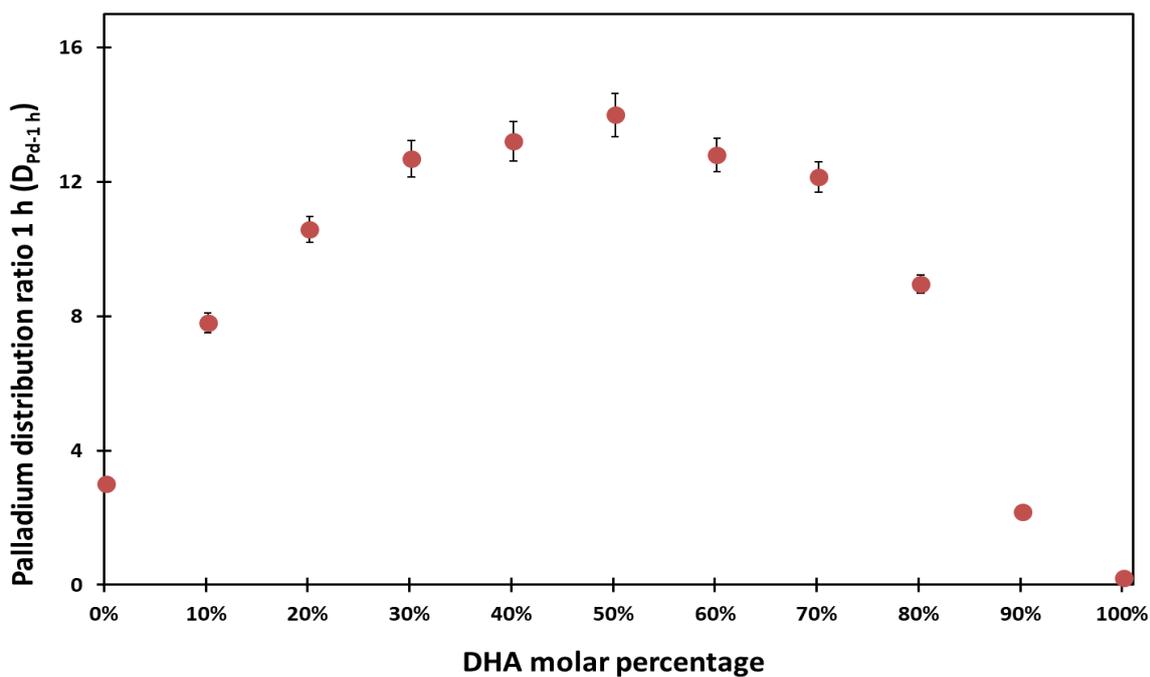
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1 **Figure S5:** Effect of stirring speed on the Pd(II) extraction with 0.2M THMA in
2 toluene. $[HNO_3]$ 3M, initial $[Pd]_{aq}$ 500 mg/L, 1 min of extraction.



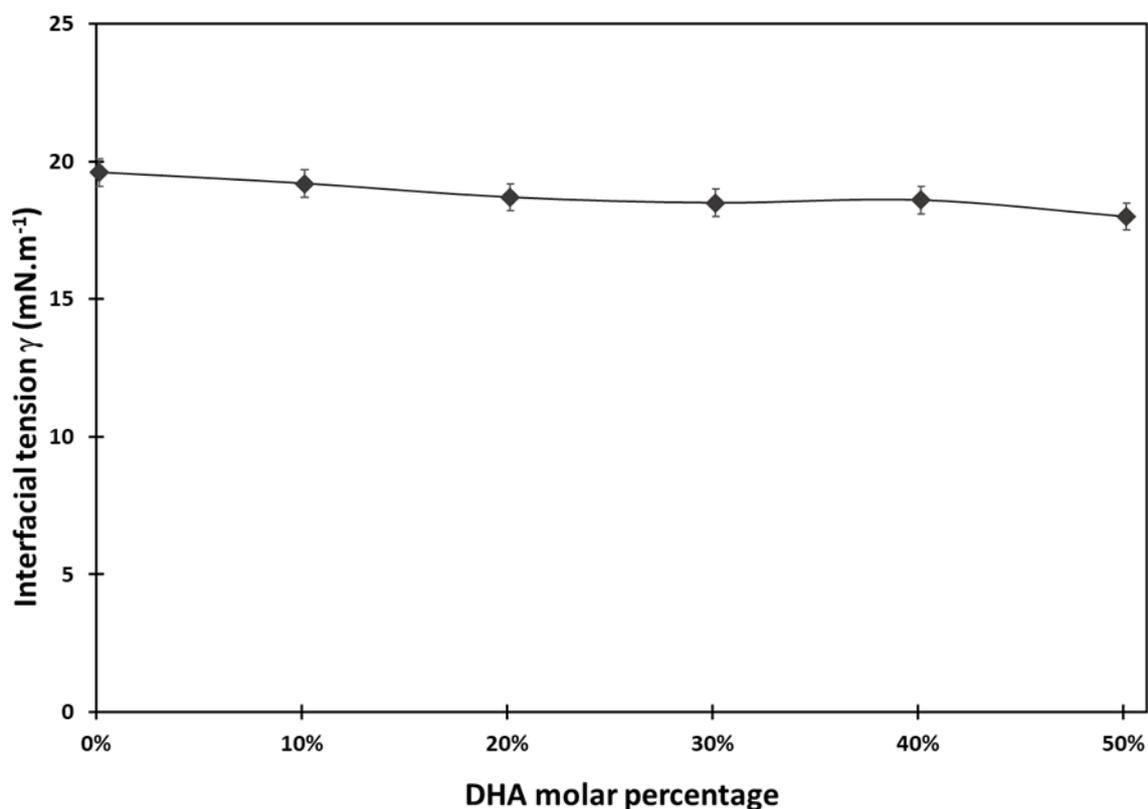
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7 **Figure S6:** Pd(II) distribution ratio with 0.2M THMA in toluene with added
8 DHA after 1 h of extraction. DHA molar percentage 0 mol% to 100 mol%
9 respective to THMA, initial $[Pd]_{aq}$ 500mg/L, $[HNO_3]_{aq}$ 3M, A/O=1, stirring
10 speed 1200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



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12

1 **Figure S7:** Variation of the interfacial tension upon addition of DHA in the
 2 organic phase. 0.2M THMA in toluene, DHA molar percentage 0 mol% to
 3 50 mol% respective to THMA, $[\text{HNO}_3]_{\text{aq}} 3\text{M}$, $T = 23^\circ\text{C}$.



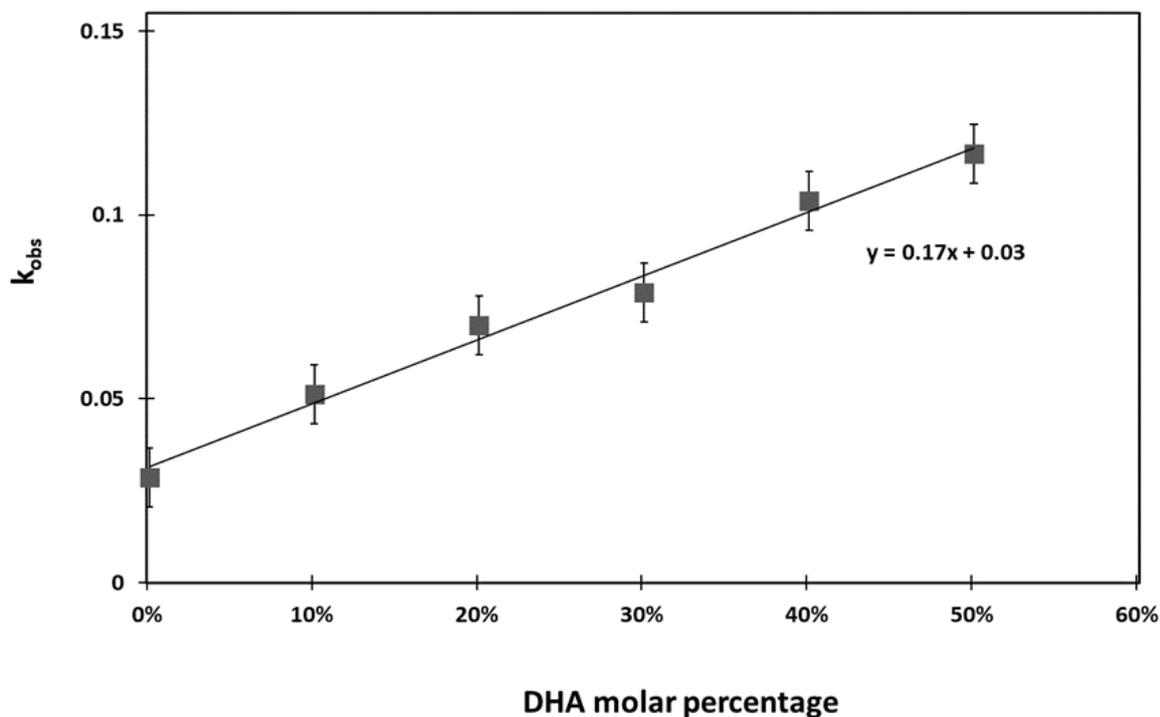
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8 **Table S2:** Variation of the aqueous concentration of Pd(II) at equilibrium (24 h)
 9 after extraction with 0.2M THMA in toluene with added DHA. DHA molar
 10 percentage 0 mol% to 50 mol% respective to THMA.

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

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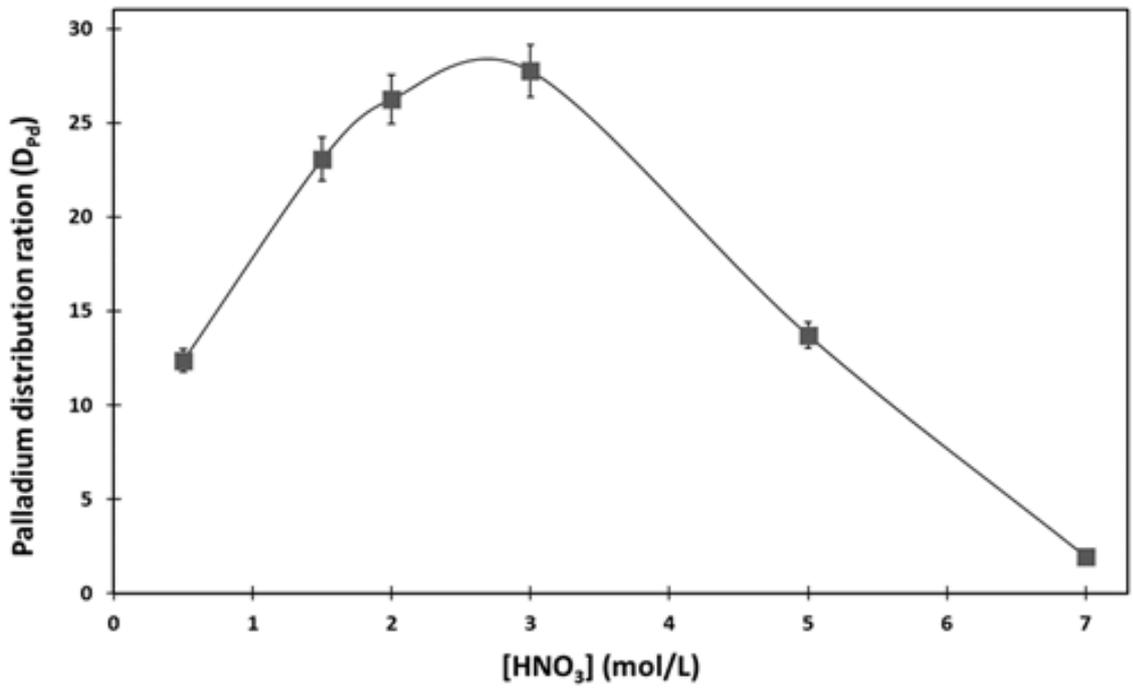
1 **Figure S8:** Evolution of observed rate constant k_{obs} of Pd(II) extraction with
2 0.2M THMA in toluene from aqueous 3M HNO₃ solution according to the
3 added DHA quantity. Initial [Pd]_{aq} 500 mg/L, [HNO₃]_{aq} 3M, stirring speed
4 1200 rpm.



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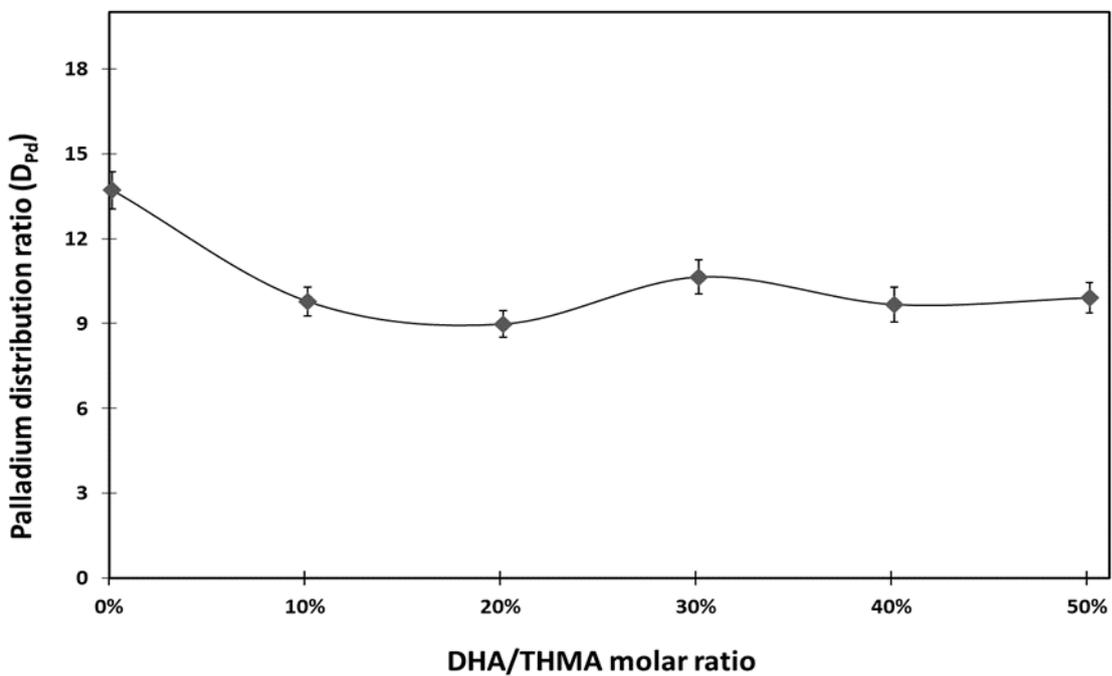
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7 **Figure S9:** Effect of HNO₃ on Pd(II) extraction with 0.2M THMA in toluene at
8 equilibrium (24 h). Initial [Pd]_{aq} 500 mg/L, A/O=1.



1

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



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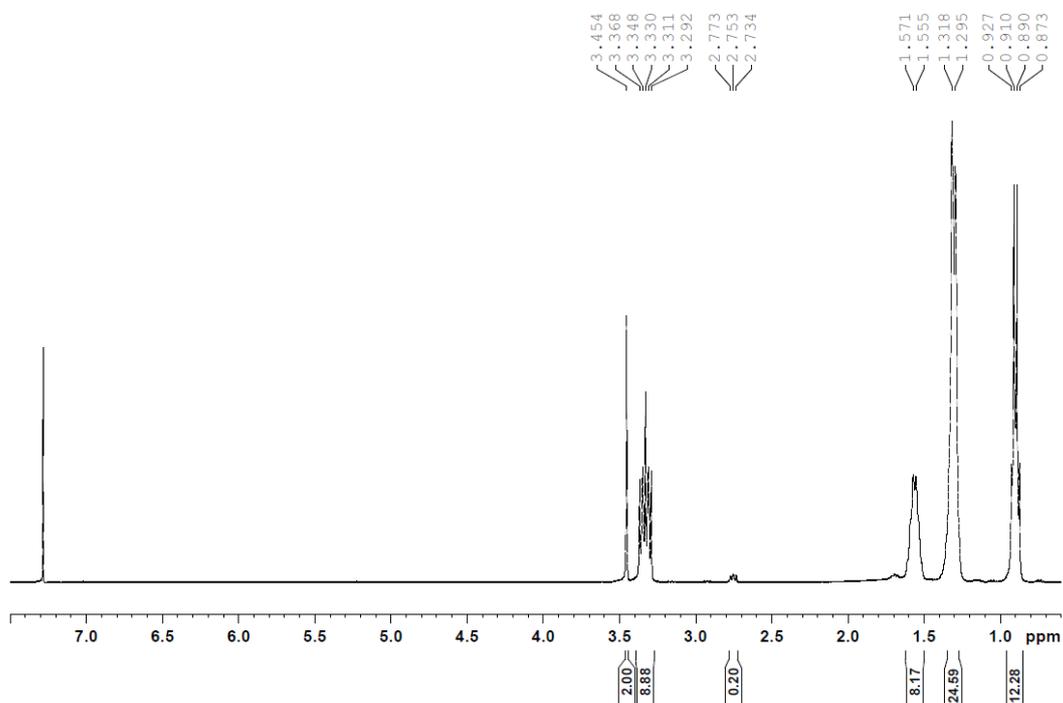
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- 1 **Figure S11:** ^1H NMR spectra (400 MHz, 100 MHz, solvent CDCl_3) of (a) crude
- 2 THMA and (b) Dihexylamine (DHA).



3 **(a)**

4

1 (b)

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