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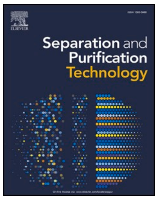

Separation of rhodium from iridium through synergistic solvent extraction

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ABSTRACT

There are currently few effective processes for the solvent extraction of rhodium from hydrochloric acid streams, and none that allow rhodium to be selectively extracted over iridium. Realizing this goal could allow rhodium to be recovered earlier in a typical platinum group metal (PGM) refining flowsheet and reduce the environmental impact of PGM refining. In this work, we show that a synergistic combination of a *tert*-alkyl primary amine L^A and various inner-sphere ligands L can be used to recover rhodium via the complex $[RhCl_5L].HL^A_2$. Although we show that rhodium is extracted by several extractant combinations, it is only readily stripped from the amine/amide synergistic mixture. As this extraction relies on the inner-sphere coordination of the amide to the metal, this process also demonstrates a route to obtain preferential extraction of rhodium over more inert iridium chloridometalates under industrially relevant conditions.

1. Introduction

Rhodium is a rare platinum group metal (PGM) with a range of uses in chemical catalysis, electronics and in jewelry. Its primary industrial application is found in automotive catalytic converters which reduce nitrous oxide emissions.[1] In both virgin ores and secondary sources rhodium is typically found alongside other PGMs such as iridium, from which it must be separated and purified for active use. Here the workflow typically starts with a pyrometallurgical step to concentrate the metals present, before employing hydrometallurgy for metal separation. This typically involves the oxidative leaching of the PGMs into hydrochloric acid, followed by a sequence of solvent extraction (SX), distillation or precipitation methods for selective metal recovery.[2].

In a SX process the aqueous feed solution is contacted with an immiscible organic phase that contains extractant molecules designed to transport a specific metal into the organic phase.[3] The two phases are separated and the metal-loaded organic phase contacted with a fresh aqueous solution to strip the metal ions and regenerate the organic phase. The ability to reuse this organic phase with a fresh batch of feed solution is a key advantage of SX processes, as the organic phase is effectively recycled in a closed loop. However, developing a viable SX process for the recovery of rhodium from hydrochloric acid has proven particularly challenging for a number of reasons.

The first challenge for a rhodium SX process stems from the fact that this element forms a range of chloridometalates of the type $[RhCl_n(H_2O)_{6-n}]^{(n-3)-}$ in dilute HCl, with $[RhCl_6]^{3-}$ and $[RhCl_5(H_2O)]^{2-}$ the dominant complexes at industrially relevant HCl concentrations. The exact composition of chloridometalates present varies with HCl and rhodium concentration, as well as with temperature, pH and the age of the solution.[4–11] This variable speciation affects ligand design, as more than one target ion exists in solution, which in turn affects extraction efficiency. Secondly, the nature of the rhodium metalates themselves present further challenges for SX: $[RhCl_6]^{3-}$ is a relatively small, charge-dense anion that has a high energy of hydration[12] which disfavors its extraction into a non-polar organic phase in accordance with the Hofmeister bias, [13,14] while $[RhCl_5(H_2O)]^{2-}$ is difficult to extract into an organic phase due to its hydrophilicity.[4].

A further challenge for a rhodium SX process is to achieve selectivity over iridium, which has similar chemical and physical properties to rhodium.[15] Iridium is substitutionally inert compared with rhodium and forms $[IrCl_6]^{3-}$ under normal refinery conditions. Separation from rhodium is typically achieved by oxidizing Ir(III) to Ir(IV), forming the dianion $[IrCl_6]^{2-}$ which is more readily extracted into an organic phase than $[RhCl_6]^{3-}$.[16,17] Achieving selectivity for rhodium over iridium would avoid this additional oxidation step, and would also allow for recovery of the more valuable rhodium earlier in the refining process. Previous reports on the preferential extraction of rhodium over iridium used tin chloride as a reducing and labilising agent, to form a more

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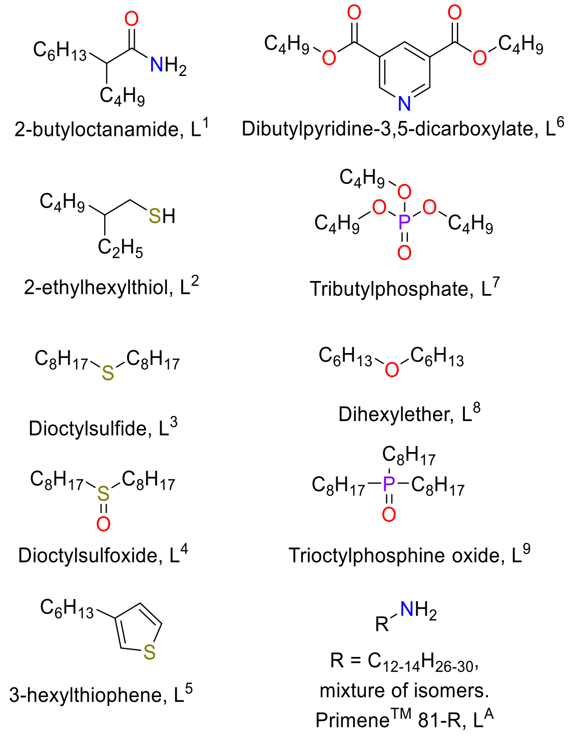

Chart 1. Structures of the inner-sphere extractants L^{1-9} and Primene^{TM} extractant L^A used in this work.

readily extractable rhodium-tin complex, [18–20] however rhodium and tin must subsequently be separated. Other reports have achieved selectivity under very low acid concentrations [21] or rely on the use of additives such as thiocyanate, [22] both of which are undesirable routes for industrial processes. The lack of a commercially viable SX process means rhodium is often recovered using single-use precipitants at the end of the metal refining flowsheet, which contributes to rhodium having the highest global warming potential per kilogram produced of any metal.[23].

We have previously reported that the combination of a primary amine (2-ethylhexylamine) and a primary amide (3,5,5-trimethylhexanamide) synergistically extracts rhodium from HCl.[24] Two different complexes were extracted into the loaded organic phase: the $[RhCl_6]^{3-}$ metalate, which is extracted by protonated amines via outer-sphere interactions, and $[RhCl_5(L)]^{2-}$, which contains an inner-sphere amide ligand and is also charge-balanced by protonated amines. The inner-sphere complex was predominately extracted at low [HCl], whereas the outer-sphere complex was extracted from higher [HCl]. While this system is capable of extracting a high percentage of rhodium, no selectivity over other PGMs such as iridium was seen. Moreover, the protonated extractants were readily lost from the organic phase to the acidic aqueous phase, preventing reuse of the organic phase in further extraction steps.

In this work we have sought to improve upon our original synergistic system, to minimize ligand loss into the aqueous phase and to develop a system which is selective for rhodium over iridium. As the primary amine appeared to be the most important component of the previous synergistic system, we continued using primary amines but looked to increase the length of the hydrocarbon chain to address the solubility problem. This led us to consider the industrial reagent Primene^{TM} 81-R, which is a mixture of *tert*-alkyl primary amines with long alkyl chains. When considering replacements for our original primary amide ligand, we noted that a range of SX systems using different ligands that bind to rhodium in the inner-sphere have previously been investigated.[25–27] However, they suffer from slow kinetics or low levels of extraction due to the number of inner-sphere chloride ligands that must be substituted to form a charge-neutral complex that can be transported into the organic phase. These issues could potentially be overcome if inner-sphere ligands were employed alongside a primary amine synergist, as this offers a route that requires only one inner-sphere substitution to form $[RhCl_5(L)]^{2-}$, which could then be charge-balanced by the protonated amines, as observed in our original work. This approach was previously taken by Narita and co-workers, [28] who used a combination of tertiary amines and sulfides to extract rhodium. This inspired us to investigate a variety of compounds with different functional groups as potential synergists for a new rhodium SX process.

Herein we evaluate the combination of a broad range of inner-sphere ligands (L^{1-9}) alongside the primary amine Primene^{TM} 81-R (hereafter L^A, see Chart 1) as potential synergistic extractants for rhodium. We use computational modelling in a screening capacity to rank the binding energies of the inner-sphere ligands and to assess their lability under high acid concentrations to predict their ease of stripping. We have also undertaken a full experimental study, to assess both rhodium extraction and subsequent stripping of the organic phase. Specifically, we look to address the aqueous phase solubility issues associated with the previously reported rhodium extractants and to develop a system that is selective for rhodium over iridium.

2. Experimental

2.1. Chemicals

Synthetic procedures and characterization data for L^1, L^4 and L^6 are provided in the SI. All other solvents and reagents were used as received from Sigma-Aldrich, Fisher Scientific UK, Alfa Aesar, Acros Organics, VWR International or Dow. Precious metal salts were provided by Johnson Matthey. Ultra-pure (UP) water was sourced from a Milli-Q purification system.

2.2. Solvent extraction experiments

Na_3RhCl_6 (0.01 M) and/or Na_3IrCl_6 (0.01 M) were dissolved in aq. HCl (1-11 M, 2mL). The feed solution was aged for 1 day and contacted with an organic solution (2 mL) containing the extractant(s) in toluene or 1-octanol. Samples were stirred at RT for 1-72 h before phase separation. These procedures were carried out in duplicate.

2.3. Stripping of loaded organic phases

The metal-loaded organic phase was contacted with an equal volume of 10 M HCl as the strip solution. Samples were stirred at RT for 1 h before phase separation. These procedures were carried out in duplicate.

2.4. ICP-OES/MS

Following phase separation, an yttrium internal standard (1000 ppm, 0.1 mL) and 1-methoxy-2-propanol or 2 % aq. HNO_3 (9.8 mL) were added to the organic or aqueous phase samples (0.1 mL). Analyses were repeated in duplicate using either a Perkin Elmer Optima 8300 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) or an Agilent 7900 Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

2.5. Uv–vis spectrophotometry

The neat organic phase solutions from the SX experiments were analyzed against a solvent blank over the range 300 – 800 nm on a Shimadzu UV-1900 spectrometer.

2.6. NMR spectroscopy

NMR spectra were recorded on Bruker AVA500 or AVA600 spectrometers at 300 K at 500 or 600 MHz for ^1H and 126 or 151 MHz for

Table 1
ΔG exchange energies for the replacement of the water ligand in $[RhCl_5(H_2O)]^{2-}$ with an inner-sphere organic ligand.

Ligand	Donor atom	ΔG_{ee} /kJ/mol
L^6	N	−66
L^2	S	−34
L^3	S	−33
L^4	S	−32
L^1	N	−11
L^5	S	5
L^7	O	8
L^8	O	14
L^9	O	33

^{13}C, referenced internally to residual non-deuterated solvent. Chemical shifts are reported in δ (ppm).

2.7. ESI FT-ICR mass spectrometry

Measurements were recorded in positive-ion or negative-ion mode using the standard Bruker electrospray ionization (ESI) sprayer operated in infusion mode coupled to a SolariX Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer. All mass spectra were analyzed using Bruker Compass DataAnalysis 5.0 software. Ion peaks were assigned manually.

2.8. Computational modelling

Hybrid density functional theory (DFT) (M06) geometry optimization calculations were carried out using Gaussian16.[29,30] The LANL2DZ pseudopotential basis set [31] was used for rhodium, and the 6–31+G* basis set [32] for all other atoms. In some cases alkyl chains on the ligands were truncated to reduce the computational demand of the calculations. Structures were optimized to standard convergence criteria and confirmed as minima through subsequent vibrational frequency calculation (all eigenvectors real numbers). The vibrational frequency calculations also provided the required thermodynamic corrections to recast the optimization energies as free energy (ΔG) values. Local (mass-independent) vibrational force constants were determined using the LModeA-nano plugin [33] in Pymol.[34].

3. Results and discussion

DFT calculations were used to screen the inner-sphere ligands ($L^{1\text{-}9}$) that could potentially bind to the rhodium center. The calculations sought only to rank the ligands in order of their binding strengths, via computed water/ligand exchange energies according to Equation 1.

$$[RhCl_5(H_2O)]^{2-} + L \rightarrow [RhCl_5(L)]^{2-} + H_2O \qquad (1)$$

The resulting energies are presented in Table 1, with the ligands arranged from the most favorable (top) to least favorable (bottom). Coordinates and energies for the optimized structures (Tables S2, S3 and S4), alongside images illustrating the lowest energy binding motifs, are provided in the SI. In general, the compounds containing sulfur or nitrogen donor atoms are predicted to bind more strongly to rhodium, and therefore might be expected to be more effective extractants than those ligands that bind through oxygen donor atoms. L^5, L^7, L^8 and L^9 present with positive exchange energies, suggesting that ligand/water exchange is unfavourable for these inner-sphere ligands on thermodynamic grounds.

Following the computational screening, an experimental study was undertaken to assess $L^{1\text{-}9}$ as single-component extractants for rhodium. No loss of extractants to the aqueous phase was observed by ^1H NMR when C_6D_6 organic phases were contacted with 4 M HCl. Metal extraction experiments were carried out using a toluene organic phase (also containing 5 % v/v 1-octanol as a modifier/ligand solubiliser), however no rhodium was extracted from 4 M HCl by 0.1 M solutions of any of the ligands, either after 1 or 72 h (Table S1). Likewise, L^A does not extract rhodium when used alone. This is in contrast to other primary amines such as 2-ethylhexylamine which can extract rhodium when used as a single extractant.[24] The most obvious structural reason for this difference in behavior is the presence of alkyl branching at the α-position in L^A, a feature that is absent in 2-ethylhexylamine. Further investigation into how exactly this impacts on rhodium extraction is currently underway in our group.

Table 2
Synergistic extraction of rhodium using amines and inner-sphere ligands, ordered according to the results from the computational screening study.[a]

Ligand	Donor atom	% extraction into organic phase	
		1 h contact	72 h contact
L^6	N	0	44
L^2	S	3	81
L^3	S	0	44
L^4	S	8	97
L^1	N	30	52
L^5	S	0	0
L^7	O	2	1
L^8	O	0	1
L^9	O	0	1

[a] Conditions: Rh (0.01 M) in HCl (4 M, 2 mL) aged for 1 day, contacted with $L^{1\text{-}9}$ (0.1 M) and L^A (2.25 % v/v, approx. 0.1 M) in an organic phase (2 mL) comprised of toluene and 1-octanol (5 % v/v). Stirred for 1 or 72 h at RT.

Combining the inner-sphere ligands $L^{1\text{-}9}$ with L^A produced a pronounced synergistic effect in some cases (Table 2), with near quantitative extraction after 72 h using L^4. Fig. 1 shows a typical extraction experiment (for L^1/L^A) before phase separation, with the loaded organic layer on the top dominated by peach color of the $[RhCl_5]^{2-}$ complex, while the pink color in the lower aqueous layer is indicative of the $[RhCl_6]^{3-}$ metalate. The extraction of $[RhCl_5]^{2-}$ is confirmed by the presence of UV–vis absorption bands at 372 and 466 nm, while the ^1H NMR (see Figure S1) provides further evidence that the amide ligand L^1 is bound in the inner-sphere in the tautomerized form. The UV–vis spectrum also confirms that negligible amounts of the $[RhCl_6]^{3-}$ metalate are co-extracted. The inner-sphere substitution and re-equilibration (to regenerate $[RhCl_5]^{2-}$ from $[RhCl_6]^{3-}$) means that the rate of extraction is relatively slow.

Significant levels of extraction are observed for all of the ligands previously highlighted in the computational screening study that show favourable inner sphere binding to $[RhCl_5]^{2-}$ through H_2O displacement. In general terms this suggests that ligands with nitrogen and sulfur donor ligands make better extractants for rhodium than those that contain oxygen. The one exception is L^5, which is a poorer extractant than the other sulfur donor ligands from both a theoretical and experimental standpoint. This result is unsurprising given that thiophene has previously been reported as coordinating weakly, or not at all, to many transition metal complexes.[35].

Although the computational screen provides a good approximation as to which extractants are likely to work, it fails to predict the order of the ligands in terms of the extraction efficiency. For instance, the exchange energy calculated for L^6, which is significantly more negative than any other ligand, is not reflected in its efficacy as an extractant. This is likely a consequence of the simplicity of the computational model, which does not capture the impact of important factors such as acid concentration, solvation effects, the interfacial activity of the ligands or the interactions with the outer-sphere amine in the organic phase. That said, the top ranked ligands from the computational study did prove to be the better extractants experimentally, and so the screening process based purely on the thermodynamics of swapping H_2O for an organic ligand was successful in guiding ligand design.

While some of the synergistic combinations achieve near quantitative extraction, it is obvious that the rates of extraction vary

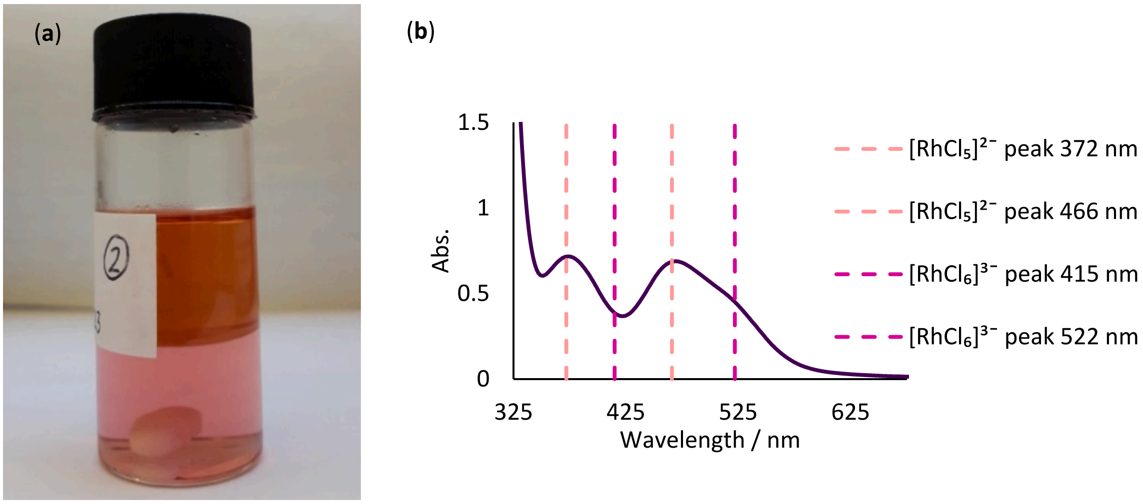

Fig. 1. (**a**) Image of rhodium SX using the synergistic combination of L^A and L^1. Image shows the biphasic sample before phase separation, with the organic layer on top. (**b**) UV–Vis spectra of the upper loaded organic phase confirms the presence of $[RhCl_5(L^1)]^{2-}$ (peach color) and absence of $[RhCl_6]^{3-}$ (pink color) which remains in the lower aqueous phase. Conditions: Rh (0.01 M) in HCl (4 M, 2.5 mL) aged for 1 day, contacted with L^A (4.5 % v/v, approx. 0.2 M) and L^1 (0.1 M) in an organic phase (2.5 mL) comprised of toluene and 1-octanol (5 % v/v). Stirred for 3 h at RT. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3
Rh-X local force constants for the inner-sphere ligands that successfully extract rhodium.

Ligand	Donor atom X	$[RhCl_5(L)]^{2-}$		$[RhCl_5(LH)]^{-}$	
		Rh-X force constants / mdyn $Å^{-1}$	Rh-X bond lengths / Å	Rh-X force constants / mdyn $Å^{-1}$	Rh-X bond lengths / Å
L^6	N	1.60	2.081	1.57	2.068
L^2	S	0.86	2.416	1.31	2.264
L^3	S	0.93	2.406	1.40	2.276
L^4	S	0.78	2.417	1.07	2.316
L^1	N	1.63	2.068	0.28	2.439
H_2O	O	0.60	2.244	N/A	N/A

significantly, which most likely reflects the variable kinetics of ligand inner-sphere binding. Thus, while other ligands extract more rhodium after 72 h, the higher level of extraction observed with the primary amide L^1 after 1 h means this is the best inner sphere ligand to combine with L^A for synergistic extraction.

Another factor to consider when assessing extractant performance is how readily the rhodium may be stripped from the loaded organic phase into a fresh aqueous phase, thereby allowing the organic phase to be reused. For the inner-sphere extractants $L^{1\text{-}9}$ the strength of the Rh-X bonds formed between the metal and the respective donor atoms (where X = O, N or S) directs how easily the ligand will be displaced by chloride under the high HCl concentrations used in the strip solution. Here we first considered computational modelling to predict which ligands could be most readily displaced. This was done through local force constant analysis, [36] which provides a direct measure of the variation in the Rh-X bond strengths. As the calculated force constants are mass-independent values, the results can be compared regardless of the identity of X. The modelling data shows that Rh-N bonds, formed with L^1 and L^6 (Table 3, Column 3, see Chart S1 for representative structures), are the strongest bonds, followed by Rh-S (L^2-L^4) which are

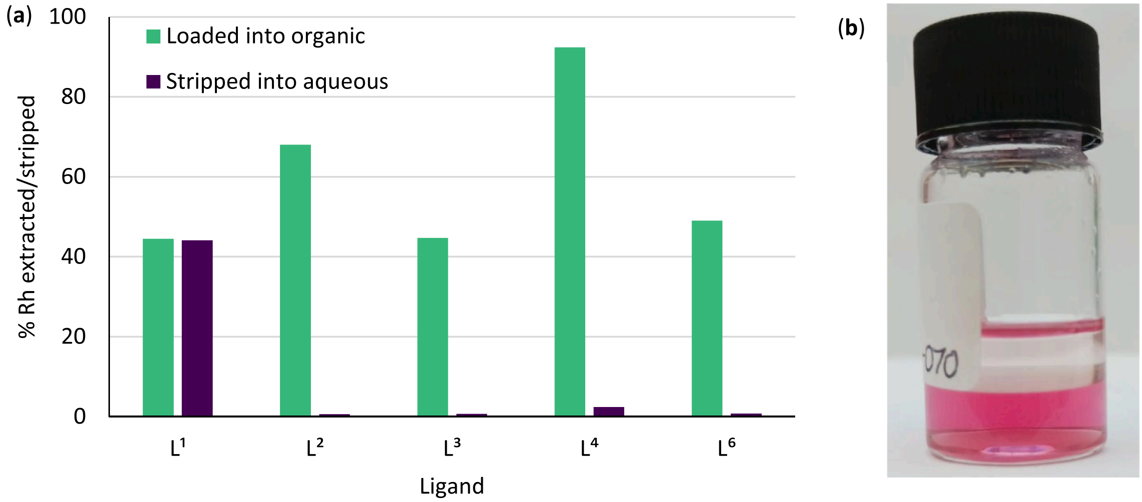

Fig. 2. (**a**) Stripping of Rh-loaded organic phases with 10 M HCl. Extraction conditions: Rh (0.01 M) in HCl (4 M, 2 mL) aged for 1 day, contacted with an organic phase (2 mL) containing $L^{1/2/3/4/6}$ (0.1 M) and L^A (2.25 % v/v, approx. 0.1 M) in toluene and 1-octanol (5 % v/v). Stirred for 72 h at RT. Stripping conditions: HCl (10 M, 1.5 mL), contacted with the loaded organic phase (1.5 mL). Stirred for 1 h at RT. (**b**) Image of Rh stripping from a L^1/L^A organic phase with 10 M HCl. Image shows the biphasic sample before phase separation, with the organic layer on top.

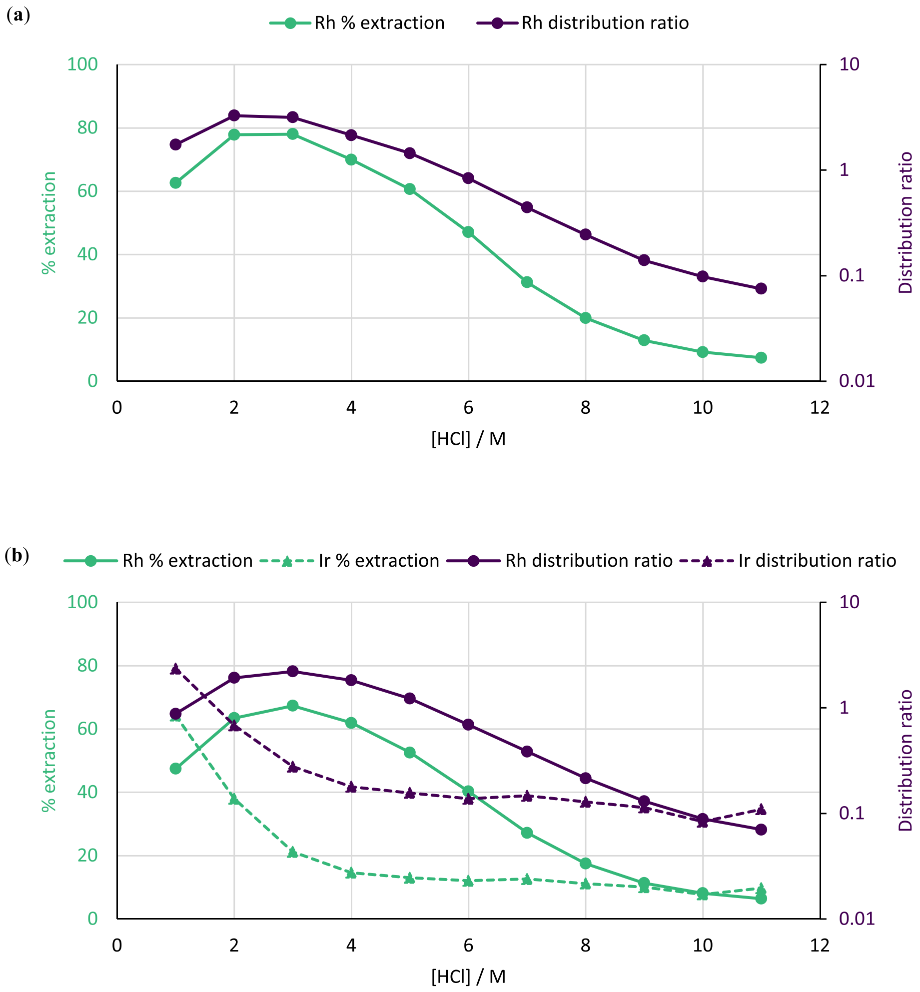

Fig. 3. Extraction of Rh and Ir from feed solutions of varying [HCl] by the mixture of L^A and L^1. Conditions: Rh (0.01 M) (a), or Rh (0.01 M) and Ir (0.01 M) (b) in HCl (1-11 M, 2mL) aged for 1 day, contacted with L^A (4.5 % v/v, approx. 0.2 M) and L^1 (0.1 M) in an organic phase (2 mL) comprised of toluene and 1-octanol (5 % v/v). Stirred for 3 h at RT.

approximately half the strength. All of the ligands that extract rhodium when used synergistically with L^A form stronger Rh-X bonds than the water ligand in $[RhCl_5(H_2O)]^{2-}$, further rationalizing the extraction observed with these ligands.

The modelling work can be taken a step further to show how ligand binding is affected upon protonation (see Chart S2 for representative structures), which is likely to occur under the highly acidic conditions of the 10 M HCl strip solution. The modeling work shows that the Rh-X bonds strengthen upon ligand protonation for the majority of ligands with the exception of the Rh-N bond formed by L^1 (Table 3, Column 5). This would indicate that replacing the inner-sphere organic ligand with a chloride to form $[RhCl_6]^{3-}$ may occur more readily for this ligand at high HCl concentrations, and therefore stripping the rhodium from this loaded organic phase is more likely.

The loaded organic phases obtained for the successful extractants were separated from the original aqueous phases and contacted with a 10 M HCl strip solution. The combination of L^1/L^A is the only extractant system that exhibits quantitative stripping (Fig. 2a). Fig. 2(b) shows the resulting biphasic solution for the L^1/L^A system, with the pink phase on the bottom of the vial confirming transport of $[RhCl_6]^{3-}$ into the aqueous phase.

Given the L^1/L^A system is selective for $[RhCl_5]^{2-}$ over $[RhCl_6]^{3-}$, this suggests that this synergistic system may offer selectivity for rhodium over iridium. The latter presents as the hexachloridometalate only, and as iridium complexes are typically considered more inert than rhodium complexes, it would be expected that substitution of the chloride ligands by amides, and hence extraction into the organic phase, would be significantly reduced. To test this hypothesis, extractions from single metal rhodium solutions and mixed-metal solutions containing equimolar amounts of rhodium and iridium were carried out across a range of HCl concentrations (Fig. 3). Contact times were increased to 3 h to maximize metal loading (Figure S2).

Rhodium extraction is observed to increase as the HCl concentration is increased from 1 M up to a peak at 3 M HCl, before gradually decreasing at higher HCl concentrations due to the large excess of chloride present. The slightly lower extraction at 1 M HCl is likely due to the presence of more aquated complexes (i.e. $RhCl_4(H_2O)]^-$) in the feed solution. In contrast, iridium extraction decreases from a peak at 1 M HCl. This is almost certainly due to the lower lability of chloride ligands on iridium chloridometalates.

A common metric for measuring the selectivity of SX processes for one metal over another is to calculate the separation factor (SF). To determine this, the distribution ratio, or *D* value, describing the partitioning between the two phases is first calculated for each metal according to Equation (2). These values are plotted in Fig. 3. SF is then defined as the ratio of the respective *D* values for the two metals, according to Equation (3).

$$D_M = [M]_{(org)}/[M]_{(aq)} \quad (2)$$

$$SF_{M1/M2} = D_{M1}/D_{M2} \quad (3)$$

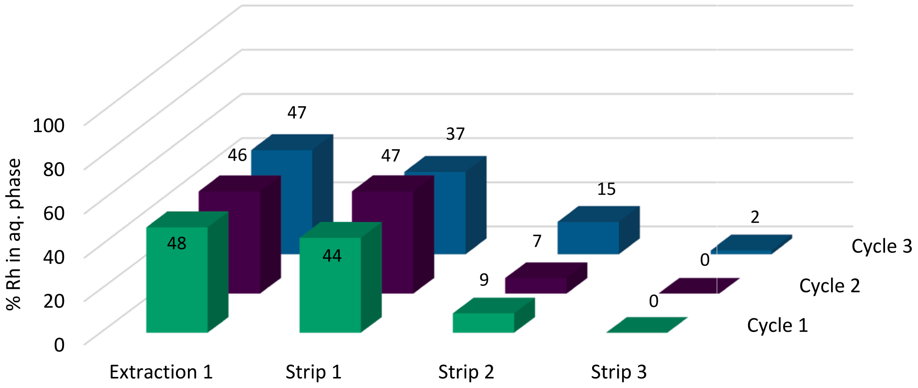

Fig. 4. Repeat extraction and stripping of Rh using the synergistic mixture of L^A and L^1. Extraction conditions: Rh (0.01 M) in HCl (4 M) aged for 1 day, contacted with an organic phase of equal volume containing L^A (4.5 % v/v, approx. 0.2 M) and L^1 (0.1 M) in toluene and 1-octanol (5 % v/v). Stirred for 3 h at RT. Stripping conditions: Rh-loaded organic phase contacted with a fresh HCl solution (10 M) of equal volume. Stirred for 1 h at RT. Stripping process was repeated 3 times. Overall process repeated 3 times using recycled organic phase.

The distribution ratios shown in Fig. 3 show that the L^1/L^A synergistic system is selective for Rh over Ir at almost all concentrations of HCl, with a maximum SF of 10.2 achieved at 4 M HCl. This represents the first example of a SX system that can preferentially extract rhodium over iridium from industrially relevant HCl concentrations without the prior addition of tin chloride to form a rhodium-tin complex.[15] Extraction decreases significantly at higher [HCl], which allows the loaded organic phase to be stripped through contact with a fresh solution of 10 M HCl, as the large excess of chloride displaces the inner sphere amide ligands. This forms the $[RhCl_6]^{3-}$ metalate, which is stripped into the fresh aqueous phase (shown in Fig. 2(b)).

Finally, we have demonstrated that the L^1/L^A synergistic system is recyclable, due to the successful retention of both extractants in the organic phase. Fig. 4 shows three repeat extraction cycles of the organic phase, demonstrating that similar quantities of rhodium are recovered in each cycle. Although the maximum extraction with this system is lower than that previously reported, [24] due to the lack of $[RhCl_6]^{3-}$ co-extraction, changing the amine to prevent extraction of this complex does allow for the differences in ligand lability between rhodium and iridium to be exploited. This results in the first example of a reusable SX system that can selectively extract rhodium over iridium from industrially relevant feedstocks.

4. Conclusions

Although neither component transports rhodium into an organic phase when used in isolation, combining *tert*-alkyl primary amines such as L^A with the inner-sphere ligands $L^{1\text{-}9}$ can result in the synergistic extraction of rhodium from an HCl solution. A computational screen suggested that compounds containing sulfur or nitrogen donor atoms are more effective synergists than oxygen-donors, which was confirmed experimentally. Local force constant analysis highlighted that protonating sulfur donor ligands, as would likely occur when stripping with concentrated acid, actually strengthens the Rh-S bonds, making it difficult to remove these inner-sphere organic ligands. In contrast, the Rh-N bond to an enolised amide ligand L^1 is weakened upon protonation, allowing the rhodium to be stripped more easily and the organic phase recycled.

Rhodium is transported into the organic phase as $[RhCl_5(L^1)]^{2-}$, with protonated amines charge-balancing this complex. As the *tert*-alkyl amine L^A does not readily extract $[MCl_6]^{3-}$, this species is left behind in the aqueous phase. Although this lowers the overall extraction compared to our previous synergistic system, which could transport both metalates, this new synergistic system displays a high degree of selectivity for rhodium over the more inert iridium chloridometalates while overcoming the solubility issues faced in our original study. To date this separation has not been reported under industrially relevant conditions. Moreover, the loaded rhodium organic phase may be stripped using more concentrated HCl solutions, and the extractant reused in multiple cycles. This allows for the recovery of rhodium with a reusable solvent extraction system rather than the current approach of single-use precipitants, and thus has the potential to reduce the environmental impact of metal separations.

Associated content

The following files are available free of charge: Rh SX with individual extractants, time dependence of L^1/L^A extraction, NMR of Rh-loaded L^1/L^A organic phase, synthesis of extractants and energies and coordinates of DFT-optimized structures (PDF).

Notes

The research contained in this manuscript forms the basis of patent application 2211199, reference P101832GB01 and P101832WO01. The authors declare no other competing financial interest.

CRediT authorship contribution statement

Andrew I. Carrick: Formal analysis, Investigation, Methodology, Writing – original draft. **Jane Patrick:** Conceptualization, Funding acquisition, Project administration, Writing – review & editing, Formal analysis, Validation. **Emma R. Schofield:** Conceptualization, Writing – review & editing. **Paul O'Shaughnessy:** Conceptualization, Formal analysis, Writing – review & editing, Validation. **Barbara Breeze:** Formal analysis, Writing – review & editing, Validation. **Jason B. Love:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Project administration, Writing – review & editing, Validation. **Carole A. Morrison:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Validation, Writing – review & editing, Data curation, Software, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

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