



## Liquid–liquid extraction/separation of platinum(IV) and rhodium(III) from acidic chloride solutions using tri-iso-octylamine

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### ABSTRACT

Liquid–liquid extraction/separation of platinum(IV) and rhodium(III) from acidic chloride solutions was carried out using tri-iso-octylamine (Alamine 308) as an extractant diluted in kerosene. The percentage extraction of platinum(IV) and rhodium(III) increased with increase in acid concentration up to 8 mol L<sup>-1</sup>. However, at 10 mol L<sup>-1</sup> HCl concentration, the extraction behavior was reversed, indicating the solvation type mechanism during extraction. The quantitative extraction of ~98% platinum(IV) and 36% rhodium(III) was achieved with 0.01 mol L<sup>-1</sup> Alamine 308. The highest separation factor (S.F. = 184.7) of platinum(IV) and rhodium(III) was achieved with 0.01 mol L<sup>-1</sup> Alamine 308 at 1.0 mol L<sup>-1</sup> of hydrochloric acid concentration. Alkaline metal salts like sodium chloride, sodium nitrate, sodium thiocyanate, lithium chloride, lithium nitrate, potassium chloride and potassium thiocyanate used for the salting-out effect. LiCl proved as best salt for the extraction of platinum(IV). Temperature effect demonstrates that the extraction process is exothermic. Hydrochloric acid and thiourea mixture proved to be better stripping reagents when compared with other mineral acids and bases.

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### 1. Introduction

Liquid–liquid extraction (LLE), also called solvent extraction (SX), is a process that allows the separation of two or more components due to their unequal solubilities in two immiscible liquid phases. The liquid–liquid dispersion created during the mixing is then separated by gravity or by centrifugal force depending upon the type of extractor selected. The mixing and separation steps constitute one stage of extraction [1]. The solvent is chosen to selectively extract certain components from the feed solution. Depending upon the selectivity of the solvent and the amount of mass transfer required to achieve the desired solute recovery, several stages of extraction may be required. In this case, counter-current contact is the most efficient extraction method. In LLE processes, there are many cases both in analytical and industrial chemistry where the main objective of separation is achieved by extraction using a chemical extractant. It is well reported that the extractive separation of platinum group metals (PGMs) is difficult

due to their similar chemical and physical properties [2]. LLE behavior of these metal ions with commercially available extractants and synthetic complexing reagents is worth exploring [2].

The PGMs namely platinum, palladium, rhodium, iridium, osmium and ruthenium together with silver, and gold generally occur in nature with the major base metals like iron, copper, nickel and cobalt and wide range of minor elements such as lead, tellurium, selenium and arsenic and both technical and commercial considerations demand that the individual PGMs be separated from the other metals and each other to high purity, with high yield and with a high percentage recovery [2].

The high prices of precious metals like PGMs have ensured that there is continued interest in the development of new extractants for the commercial concentration and separation of these metals. The extraction and separation of metals from source materials such as ores or spent catalysts or industrial waste need several multi-step procedures [3]. The final refining stage is often based on hydrometallurgical treatments, which can be achieved by use of ion-exchange/LLE.

The low concentrations of PGMs in mineral deposits and the effort required to separate and purify them from the significantly higher concentrations of the transition metal host ores accounts for their high commercial value, considering the demand for their unique properties in a wide range of markets. The availability, therefore, of a process technique that could selectively and rapidly recover PGMs from mining/refining operations or the recovery and

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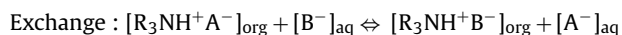
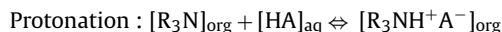
**Table 1**  
Typical analysis of Alamine 308.

Content	Amount (%)
Tertiary amine content	95.0–100.0
Tertiary amine value	151–159
Secondary amine content	≤5.0
Color (ALPA)	≤500
Clarity	Clear

recycling of PGMs from manufactured products such as pharmaceutical, industrial or automobile catalysts would be of real economic benefit.

The separation factor of palladium(II) and platinum(IV) mixed solutions is  $10^6$  using 1,3,4-thiodiazole-2-nonylmercapto-5-thiol as extractant [3]. The synergistic extraction of platinum from hydrochloric acid solutions was investigated by isoamylalcohol + methylisobutylketone [4]. At optimum conditions, the platinum extraction is over 99%; Al, Ca, Mg, Mn, Ni, Cr are quantitatively retained in the aqueous phase [4]. An effective separation of palladium(II) from an excess of platinum(IV) can be achieved by the idoformazan (extraction time: 24 h, stirring time: 48 h) [5]. The separation factor in between platinum and palladium with the protonated trioctylphosphine oxide (TOPO) is a little higher than protonated tri-*n*-octyl amine (TOA) [6]. A novel sulfur containing extractant, 3,3-diethylthietane (DETE) was extracted platinum and complexed as  $\text{PtCl}_4 \cdot 2\text{DETE}$  was found to have no interfacial activity and the aqueous partition coefficient as high as  $8.17 \times 10^{-4}$  [7]. The distribution behavior of ion associates of  $\text{PtCl}_6^{2-}$  with quaternary ammonium cations ( $\text{Q}^+$ ) between aqueous phase and two organic phases ( $\text{CHCl}_3$  and  $\text{CCl}_4$ ) was examined and the extraction constants ( $\log K_{\text{ex}}$ ) were determined [8]. The results indicate that amine Alamine 304 in chloride form extracts Pt(IV) in chloride media. The extraction mechanism corresponds to an anion exchange, in which a complex of stoichiometric formula  $(\text{R}_3\text{NH}^+)_2 \text{PtCl}_6^{2-}$  is formed in the organic phase liberating at the same time  $\text{Cl}^-$  ions in the aqueous phase [9]. Some extractants are reported for extraction separation of platinum from palladium [10–20] but very less number of extractants is utilized for separation of platinum from rhodium [21,22]. The LLE literatures reviewed showed that, despite a large number of studies, no system has been identified as yet to yield quantitative extraction of rhodium from concentrated solutions [23–27].

Alamine 308 is water-insoluble, tri-*n*-octyl amine which is capable of forming oil soluble salts of anionic species at low pH. It contains a basic nitrogen atom, typically can react with a variety of inorganic and organic acids to form amine salts, which are capable of undergoing ion exchange reactions with a host of other anions. The general reactions which are shown below in two steps, protonation and ion exchange, describe this behavior.



The extent to which extent to which  $\text{B}^-$  will exchange for  $\text{A}^-$  is a function of the relative affinity of the two anions for the organic cation and the relative solvation energy of the anions by the aqueous phase. Typical analysis data of Alamine 308 was presented in Table 1.

Saturated aliphatic tertiary amines like Alamine 308 and 336 dissolved in organic solvents are effective extractants for carboxylic acids [28]. Limited studies are reported on Alamine 308 as extractant for acids and transition metals [29–32].

For PGMs extraction and separation no systematic attempt is reported till now. The reported literature says that very less number of extractants were used for the separation and extraction studies of

**Table 2**  
Inductively coupled plasma optical emission spectrometer (ICP-OES) parameters.

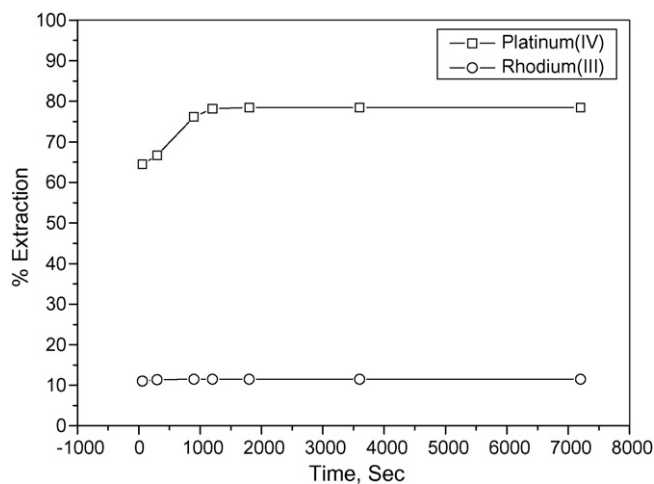
Parameter	Range
Forward power	800–1200
Sample gas flow (1/min)	0.20–0.90
Plasma gas flow (1/min)	10.00–13.00
Aux. gas flow (1/min)	0.50–1.00
Pump speed (%)	5.0–50.0
Torch height (mm)	3.0–15.0
Torch mono Posn (mm)	–3.0 to 3.0
Torch poly Posn (9 mm)	–3.0 to 3.0
Platinum	
Wave length	214.423
Detection limit	10 ppb
Rhodium	
Wave length	233.477
Detection limit	7 ppb

platinum(IV) and rhodium(III). The present investigations focused on to develop experimental parameters for extraction of platinum and possible separation from rhodium. A good separation factor for platinum(IV) and rhodium(III) using Alamine 308 as an extractant is reported.

## 2. Experimental

### 2.1. Reagents

Stock solutions of  $\text{PtCl}_4$  (Aldrich) of 98% purity,  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (Kojima Chemicals Co. Ltd.) were prepared in distilled water with addition of concentrated sulphuric acid to prevent hydrolysis of metal ions. 0.3369 g of platinum chloride [ $\text{PtCl}_4$ ] and 0.26331 g of rhodium chloride [ $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ] were weighed, dissolved in double distilled water containing a few drops of concentrated sulphuric acid and made up to 100 mL. The required dilute solutions of platinum(IV) and rhodium(III) were prepared suitably by diluting the stock solution ( $0.01 \text{ mol L}^{-1}$ ) with double distilled water. The commercial grade extractant Alamine 308 was supplied by Cognis Corporation USA and used as it is without purification. Alamine 308 is amine based commercial extractant. It is effective for cobalt recovery from chloride leach solutions and tungsten extraction. All other reagents used were analytical reagent grade.



**Fig. 1.** Effect of phase contact time on extraction of platinum(IV) and rhodium(III) using Alamine 308 as extractant. Platinum(IV) and rhodium(III):  $0.0005 \text{ mol L}^{-1}$ ; HCl:  $1.0 \text{ mol L}^{-1}$ ; Alamine 308:  $0.005 \text{ mol L}^{-1}$ .

## 2.2. Apparatus

Analysis of platinum(IV) and rhodium(III) was obtained using inductively coupled plasma optimal emission spectrometer (ICP-OES) PerkinElmer Model Optima 2000 Dr. The optimum parameters of ICP-OES was given in Table 2.

## 2.3. Liquid–liquid extraction procedure

Equal volumes (30 mL) of the aqueous phase containing desired concentrations of platinum(IV) and rhodium(III) and organic phase containing the extractant, Alamine 308 was equilibrated for 3600 s in glass stopped separating funnels using a mechanical shaker. After phase disengagement, the aqueous phase was separated and its metal concentrations were analyzed by ICP-OES. The concentration of the metal in the organic phase was calculated from the mass balance. All the experiments were conducted at  $25 \pm 1$  °C excepting that involving temperature effect and the general agreement with distribution values obtained was within  $\pm 5\%$ .

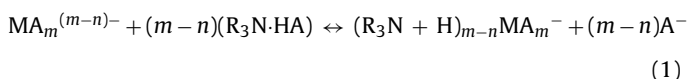
## 3. Results and discussion

### 3.1. Influence of time on extraction of platinum(IV) and rhodium(III)

The effect of phase contact time on the distribution ratio for the extraction of platinum(IV) and rhodium(III) ( $0.0005 \text{ mol L}^{-1}$ ) from  $1.0 \text{ mol L}^{-1}$  hydrochloric acid solutions for platinum,  $5.0 \text{ mol L}^{-1}$  hydrochloric acid solutions for rhodium using  $0.005 \text{ mol L}^{-1}$  Alamine 308 has been studied. Distribution ratio increases with increasing phase contact time up to 3600 s and thereafter the curve levels off for platinum (Fig. 1) where as there is no change for rhodium (30–7200 s). It is clear from the results that the time required for attaining the extraction equilibrium for platinum system is about 3600 s and rhodium is 30 s.

### 3.2. Effect of hydrochloric acid concentration on extraction of platinum(IV) and rhodium(III)

The effect of the hydrochloric acid concentration in the range  $0.005$ – $10 \text{ mol L}^{-1}$  on the extraction of platinum(IV) and rhodium(III) was carried out using  $0.005 \text{ mol L}^{-1}$  Alamine 308. The concentration of platinum(IV) and rhodium(III) taken is  $0.0005 \text{ mol L}^{-1}$  and aqueous–organic (A:O) volume ratio of 1:1 was maintained. With in the acid concentration  $0.005$ – $5.0 \text{ mol L}^{-1}$ , the percentage extraction of platinum(IV) increased from 43.8 to 93.2% with  $0.005 \text{ mol L}^{-1}$  Alamine 308 and from 52.1 to 97.3% with  $0.01 \text{ mol L}^{-1}$  with Alamine 308 (Fig. 2). At  $8.0$ – $10.0 \text{ mol L}^{-1}$  the extraction was reversed (70.3 with  $0.005 \text{ mol L}^{-1}$  extractant and 88.6% with  $0.01 \text{ mol L}^{-1}$  extractant). The high acid concentration showing that reverse phenomena of the present study, basically amine-based extractants having the nitrogen ion as donor atom in higher acidic conditions extraction of a metal  $M^{n+}$ , which forms anionic complexes with an anion  $A^-$  in the aqueous phase, by an amine salt  $R_3N \cdot HA$  can be represented as an anion exchange process such as [33]:



In case of rhodium(III) also similar behavior was observed (Fig. 2). The maximum extraction of rhodium(III) with  $0.01 \text{ mol L}^{-1}$  Alamine was reached to 36.3%. The extraction of metal increases substantially indicating the use of HCl in favoring the extractable species.

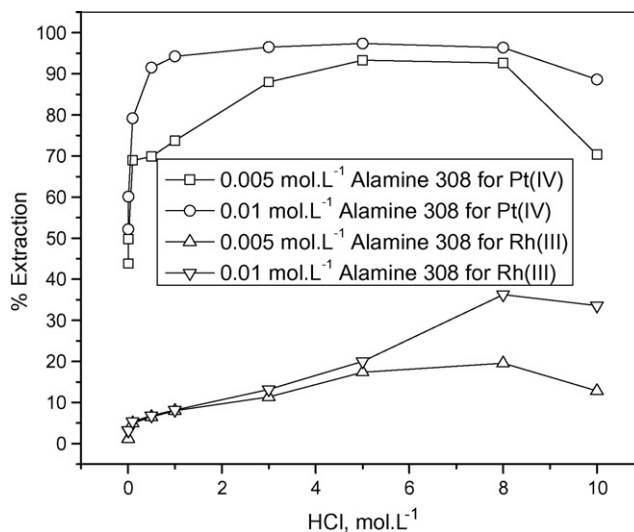


Fig. 2. Effect of hydrochloric acid concentration on platinum(IV) and rhodium(III) extraction. Platinum(IV) and rhodium(III):  $0.0005 \text{ mol L}^{-1}$ .

### 3.3. Effect of hydrochloric acid concentration on the separation factor

The separation factor is the ratio of distribution ratio's of two metals divided by another, it is a measure of the ability of the system to separate two metals. In the present system we are measuring the separation factor in between platinum(IV) and rhodium(III) by using following equation:

$$\text{separation factor (S.F.) } \beta = \frac{D_{Pt(IV)}}{D_{Rh(III)}} \quad (2)$$

where  $D_{Pt(IV)}$  = distribution coefficient of platinum(IV);  $D_{Rh(III)}$  = distribution coefficient of rhodium(III).

The effect of hydrochloric acid concentration on separation factor's (S.F.'s) of platinum and rhodium using  $0.005$  and  $0.01 \text{ mol L}^{-1}$  Alamine 308 is illustrated in Fig. 3. The S.F.'s of platinum and rhodium was increased with increase in hydrochloric acid concentration up to  $5 \text{ mol L}^{-1}$  for  $0.005 \text{ mol L}^{-1}$  Alamine 308 and up to  $1 \text{ mol L}^{-1}$  for  $0.01 \text{ mol L}^{-1}$  Alamine 308. Thereafter the S.F. values decreased with increase in acid concentration (Fig. 3). The highest

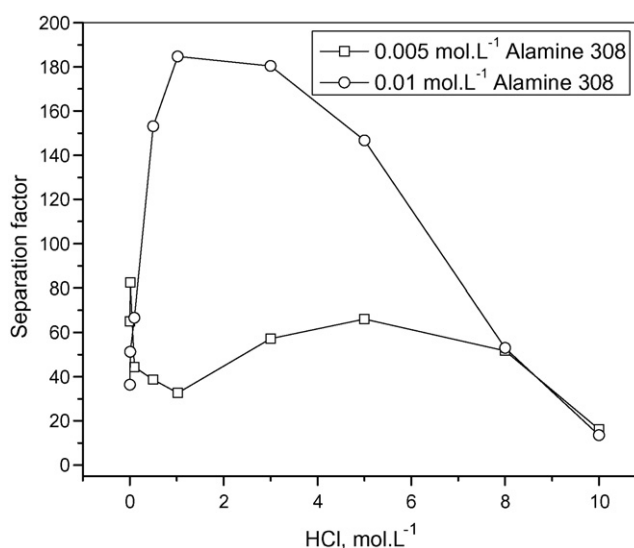


Fig. 3. Effect of hydrochloric acid concentration on separation factor of platinum(IV) and rhodium(III). Platinum(IV) and rhodium(III):  $0.0005 \text{ mol L}^{-1}$ .

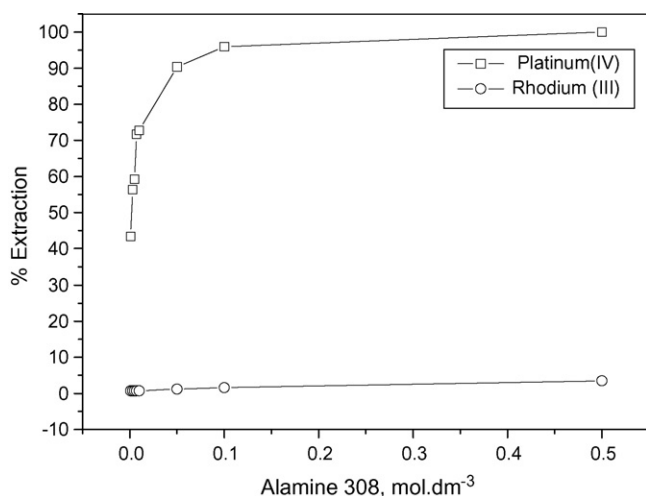


Fig. 4. Effect of Alamine 308 (extractant) on platinum(IV) and rhodium(III) extraction. Platinum(IV) and rhodium(III): 0.0005 mol L<sup>-1</sup>; HCl: 1.0 mol L<sup>-1</sup>.

S.F. value was observed at 5.0 and 1.0 mol L<sup>-1</sup> HCl concentrations for 0.005 and 0.01 mol L<sup>-1</sup> Alamine 308, respectively (S.F. = 66.1, 184.7).

### 3.4. Effect of extractant concentration on extraction of platinum(IV) and rhodium(III)

The effect of extractant concentration in the range 0.001–0.5 mol L<sup>-1</sup> of Alamine 308 was studied on the extraction of 0.0005 mol L<sup>-1</sup> platinum(IV) and rhodium(III) from 1.0 mol L<sup>-1</sup> acid concentration (HCl). Extraction of metal increased with increase in extractant concentration and reached quantitative extraction with 0.5 mol L<sup>-1</sup> extractant for platinum(IV) (Fig. 4). Whereas in case of rhodium(III), the percentage of extraction was reached >5% with 0.5 mol L<sup>-1</sup> extractant (Alamine 308) (Fig. 4).

### 3.5. Effect of salts on extraction of platinum(IV)

The influence of various salts such as sodium chloride (NaCl), sodium nitrate (NaNO<sub>3</sub>), sodium thiocyanate (NaSCN), lithium chloride (LiCl), lithium nitrate (LiNO<sub>3</sub>), potassium chloride (KCl) and potassium thiocyanate (KSCN) (0.1 mol L<sup>-1</sup> each salt) was used as salting-out reagents on extraction of 0.0005 mol L<sup>-1</sup> platinum(IV) from 1.0 mol L<sup>-1</sup> hydrochloric acid solutions using 0.001 mol L<sup>-1</sup> Alamine 308. At a given concentration of metal, extractant and acid, the percentage extraction follows in the decreasing order (% extraction): LiCl (81.1) > KSCN (79.7) > NaCl (70.1) > NaSCN (68.2) > KCl (60.0) > LiNO<sub>3</sub> (57.4) > NaNO<sub>3</sub> (49.5). Present study demonstrated that LiCl is better salting-out reagent for platinum(IV) extraction when compared to other alkaline metal salts. Maximum separation factor ( $\beta = 72.0$ ) could be achieved in the presence of 0.1 mol L<sup>-1</sup> LiCl. Separation efficiency of these salts at 0.1 mol L<sup>-1</sup> concentration could be followed in the order LiCl (72.0) > KSCN (65.9) > NaCl (39.5) > NaSCN (35.9) > KCl (25.4) > LiNO<sub>3</sub> (22.7) > NaNO<sub>3</sub> (16.6). Based on above results we expecting the good extraction and separation efficiency of lithium metal: it is a very active metal when compared with other metals in the alkaline group, may be due to this activity Li compounds giving the good extraction than the other metals in the group.

### 3.6. Effect of temperature on extraction of platinum(IV)

Temperature is perhaps the most complex factor affecting the equilibrium in LLE processes. Increase in temperature could increase the extraction of the complex due to the increased dehy-

Table 3  
Thermodynamic parameters for extraction of platinum(IV).

Slope	-1.818
Intercept	12.4118
$\Delta H$ (kJ mol <sup>-1</sup> )	34.809
$\Delta S$ (kJ mol <sup>-1</sup> )	103.191

dration of the species. On the other hand, increase in temperature could decrease the extraction due to the decreased stability of the complex at higher temperatures. In the present systems, the former effect is found to be predominant.

Effect of temperature in the range of 298–328 K ( $\pm 1^\circ$ ) on the extraction of metal from an aqueous solution containing 0.0005 mol L<sup>-1</sup> platinum(IV) and 1.0 mol L<sup>-1</sup> HCl using 0.005 mol L<sup>-1</sup> Alamine 308 was studied by contacting the phases for 3600 s in a thermostat fitted mechanical shaker.

At constant extractant concentration and at low metal concentrations, the relationship between the temperature and distribution

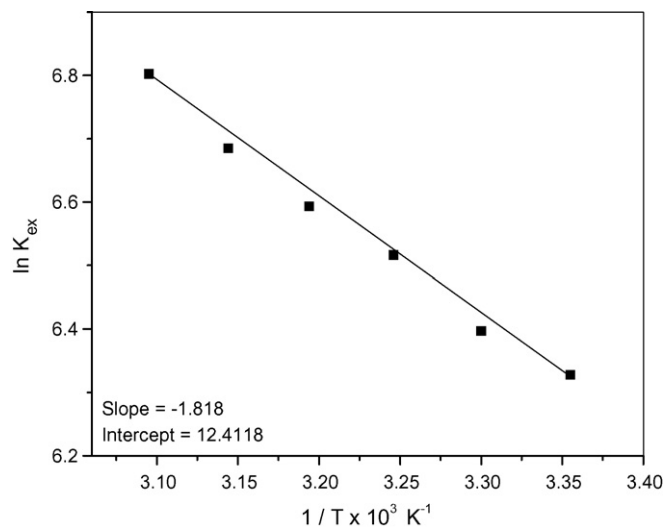


Fig. 5. Effect of temperature on the extraction of platinum(IV). Platinum(IV): 0.0005 mol L<sup>-1</sup>; HCl: 1.0 mol L<sup>-1</sup>; Alamine 308: 0.005 mol L<sup>-1</sup>.

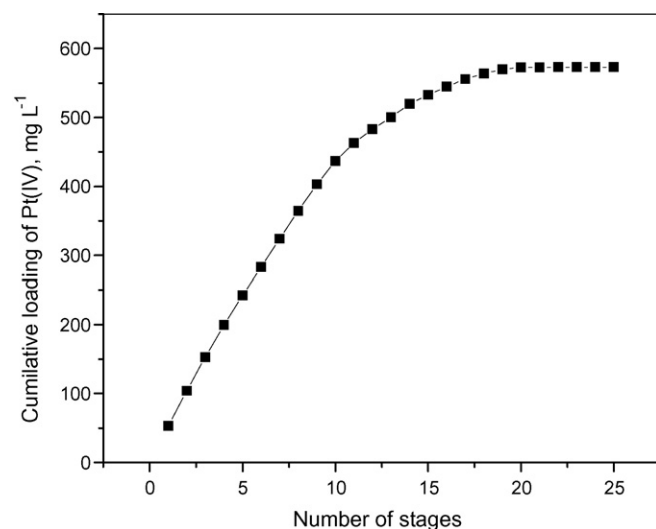


Fig. 6. Loading capacity of the extractant. Platinum(IV): 0.0005 mol L<sup>-1</sup>; Alamine 308: 0.005 mol L<sup>-1</sup>; HCl: 1.0 mol L<sup>-1</sup>.



**Table 4**  
Stripping of platinum(IV) from a loaded organic phase.

Name of the stripping reagent	Stage number and % stripping				
	1st stage	2nd stage	3rd stage	4th stage	5th stage
1.0 mol L <sup>-1</sup> HCl	16	24	33	42	53
5.0 mol L <sup>-1</sup> HCl	16	27	37	46	56
1.0 mol L <sup>-1</sup> HCl + 0.5 mol L <sup>-1</sup> thiourea	45	51	64	71	79
5.0 mol L <sup>-1</sup> HCl + 0.75 mol L <sup>-1</sup> thiourea	54	68	84	92	100
1.0 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>	9	14	21	24	28
5.0 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>	6	9	12	15	17
1.0 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub> + 0.5 mol L <sup>-1</sup> thiourea	36	40	44	47	52
1.0 mol L <sup>-1</sup> HNO <sub>3</sub>	37	43	47	50	54
5.0 mol L <sup>-1</sup> HNO <sub>3</sub>	43	46	49	52	57
1.0 mol L <sup>-1</sup> Thiourea	52	59	64	68	70
1.0 mol L <sup>-1</sup> Sodiumthiosulphate	34	39	41	42	43
5% H <sub>2</sub> O <sub>2</sub>	14	21	28	33	37
5% NH <sub>3</sub>	38	52	54	55	57
1.0 mol L <sup>-1</sup> NaOH	28	42	47	52	54

coefficient may be expressed as

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (3)$$

The above Eq. (3) represents the Gibbs free energy in terms of enthalpy and entropy. Where  $K$ =constant;  $\Delta H$ =absolute enthalpy;  $\Delta S$ =absolute entropy;  $R$ =gas constant (8.314 kJ mol<sup>-1</sup>);  $T$ =absolute temperature (K).

Thus by plotting  $\ln K$  against reciprocal of absolute temperature, the slope value yields  $-\Delta H/2.303R$  [34] and intercept =  $\Delta S/R$ , from which  $\Delta H$  and  $\Delta S$  are calculated (Table 3). In the present study, percentage of extraction was increased from 73.4 to 90.1% extraction with rise in temperature (Fig. 5), indicating exothermic type of extraction process.

### 3.7. Loading capacity of the Alamine 308

Loading capacity of 0.005 mol L<sup>-1</sup> Alamine 308 was determined by contacting 30 mL of organic phase for 3600 s repeatedly with the same volume of aqueous phase containing 0.0005 mol L<sup>-1</sup> of platinum(IV) and 1.0 mol L<sup>-1</sup> of HCl. After equilibrium and phase separation, the aqueous phase was analysed for metal content. The amount of platinum(IV) transferred into the organic phase in each contact was determined by the difference of metal in the aqueous phase after each contact and the cumulative increase in the concentration of metal in the organic phase after each stage of contact. The plot of cumulative [Pt(IV)]<sub>org</sub> vs. contact number is given in Fig. 6. The experimental results demonstrate that transfer of metal from aqueous phase to extractant phase occurs after each contact and complete loading of the extractant is possible after third stage of contact and by the analysis of loaded organic (L.O.) contained 0.573 g L<sup>-1</sup> of platinum(IV).

### 3.8. Stripping studies

In any commercial extraction process it becomes necessary to back extract the metal from the loaded organic phase. Platinum stripping from a single stage loaded organic solvent system, Alamine 308 (0.005 mol L<sup>-1</sup>) containing 54 mg L<sup>-1</sup> platinum(IV) has been investigated using various acids and bases (Table 4). Present results demonstrated that 5.0 mol L<sup>-1</sup> HCl + 0.75 mol L<sup>-1</sup> thiourea system is better system for the platinum stripping.

### 3.9. Recycling capacity of Alamine 308

The recycling capacity of Alamine 308 was tested with 12 successive extractions and stripping cycles, simultaneously. Studies on the recycling capacity of 0.005 mol L<sup>-1</sup> Alamine 308 for the extrac-

tion of platinum(IV) was carried out by first loading the extractant with an aqueous phase containing 0.0005 mol L<sup>-1</sup> platinum(IV) and 1.0 mol L<sup>-1</sup> HCl solutions. The loaded organic was stripped with 5.0 mol L<sup>-1</sup> HCl + 0.75 mol L<sup>-1</sup> thiourea for the back extraction of the metal. The recovery of each step was calculated from the amount of platinum that was extracted in the organic phase in that particular cycle. A negligible change in the percent extraction and recovery was observed up to 12 cycles.

## 4. Conclusions

The following conclusions are drawn from the present systematic liquid–liquid extraction/separation of platinum(IV) and rhodium(III) process:

1. Effect of time concluded that 3600 s for platinum and 30 s for rhodium is enough to get quantitatively of title metals.
2. We report in this paper, a highest separation of platinum(IV) and rhodium(III) from chloride solutions using Alamine 308 diluted in kerosene.
3. Salts addition revealed that the LiCl is a better salting-out reagent with high separation factor when compared to other alkaline earth metal salts.
4. From the temperature data given the absolute enthalpy and entropy. The present study concluded that extraction phenomena follows the exothermic type process.
5. Present experimental results conclude good loading of the platinum to Alamine 308 and better stripping with HCl and thiourea mixed combination.
6. Recycling and reusing capacity of Alamine 308 was performed at ~100% for 12 consecutive cycles of extraction and stripping.
7. The reported approach can be applied to the separation of platinum(IV) and rhodium(III) from chloride leach solutions of spent matrices/or any other related solutions.

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