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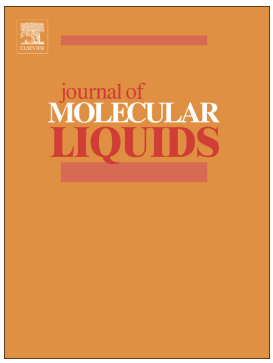

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PII: S0167-7322(19)30982-1
DOI: https://doi.org/10.1016/j.molliq.2019.111040
Article Number: 111040
Reference: MOLLIQ 111040

To appear in: *Journal of Molecular Liquids*

Received date: 19 February 2019
Revised date: 16 May 2019
Accepted date: 23 May 2019

Please cite this article as: N. Wang, Q. Wang, W. Lu, et al., Extraction and stripping of platinum (IV) from acidic chloride media using guanidinium ionic liquid, Journal of Molecular Liquids, https://doi.org/10.1016/j.molliq.2019.111040

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Extraction and Stripping of Platinum (Ⅳ) from Acidic Chloride Media Using Guanidinium Ionic Liquid

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ABSTRACT: The extraction and stripping behaviors of Pt(IV) from acidic chloride media by 2,2-diheptyl-1,1,3,3-tetramethylguanidinium bromide were investigated. The extraction of Pt(IV) was carried out by modulating various parameters such as concentration of the extractant, temperature, and concentration of HCl solution. Based on the characterization of experimental results such as Job's method data, UV-vis spectra and fourier transform infrared spectra analysis, the anion exchange mechanism was confirmed. Quantum chemical calculations were performed to provide theoretical support for the mechanism. The ionic liquid showed outstanding selectivity for Pt(IV) over the base metals. Furthermore, the organic phase could be easily used for four extraction-stripping cycles by reductive stripping process using 0.5 M $CS(NH_2)_2$/0.5 M HCl. The numbers of theoretical stages needed for the effective extraction and stripping of Pt(IV) has been determined by McCabe Thiele's diagram. Under the selected counter-current extraction and stripping stages, the extraction efficiency and stripping efficiency could reach 99.5% and 99.0%, respectively. Therefore, the system is highly effective, selective and recyclable to extract Pt(IV). On the basis of the extraction protocol, the system may be a promising candidate for highly selective extraction of Pt(IV).

Keywords: Guanidinium ionic liquid; Platinum(Ⅳ); Selective extraction; Electrostatic potential map; Theoretical counter-current stages.

1.INTRODUCTION

The platinum group metals (PGMs) include ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt). In recent years, the PGMs are increasingly used in aviation, electronic devices, jewelry, catalysts and many other applications.[1, 2] Among them, Pt and Pd are the most widely used metals, so their consumption is much higher than other PGMs. However, there is less research on the extraction of Pt compared with Pd, whether in mineral ores or secondary resources.

Liquid-liquid extraction is considered one of the most powerful and efficient techniques to recover Pt, offering many advantages such as operation in a continuous mode and simple equipment at both laboratory and industrial scales, but it still needs to be improved to reduce environmental pollution.[3-5] Therefore, it is necessary to explore better extractants to replace traditional organic extractants for the sustainability of liquid-liquid extraction.

Ionic liquids (ILs) are defined as organic salts which can melt below 100 °C. The common cations of ILs include phosphonium, ammonium and N-heterocycle (imidazolium, and pyridinium etc.); anions include halide anion, $(CF_3SO_2)_2N^-$, PF_6^-, CH_3COO^- and CF_3COO^-.[6] They exhibit unique physical and chemical properties, for example, nonvolatility, nonflammability, high conductivity, and ion structure adjustability.[7] Thanks to these properties, ILs have been applied in all fields of chemistry in the last two decades, including extraction of metal ions from aqueous phases.[8-16] Hence, there are more possibilities to improve ILs for better extraction efficiency and selectivity.

Guanidinium ionic liquids (GILs) are new members of ILs family. Owing to the high dispersive degree of the cationic parts, the adjustability of the three nitrogen-atoms and higher thermal and chemical stability, GILs have attracted more and more attention.[17, 18] Moreover, GILs are more environmental friendly than commercial imidazolium ionic liquids, so they are broadly used in bio-scientific research.[19-21] However, no one has explored the possibility and efficiency of GILs in extracting PGMs.

In this paper, we report systematic studies on the liquid-liquid extraction process for the recovery of Pt (IV) from a chloride medium using a 2,2-diheptyl-1,1,3,3-tetramethylguanidinium bromide ([diHTMG]Br). The stoichiometry has

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been confirmed by Job's method. The extracted species were analyzed by fourier transform infrared (FT-IR) and UV-vis spectra. The electrostatic potential (ESP) map of $[diHTMG]^+$ was calculated to support the anion exchange mechanism theoretically. Thermodynamic and dynamic parameters were estimated, providing useful insights into the liquid-liquid extraction system. Extraction-stripping cycles and selective extraction were investigated to verify the performance of the extractant. Theoretical stages of extraction and stripping were confirmed by McCabe−Thiele Diagram.

2. EXPERIMENTAL SECTION

2.1 Reagents and Materials.

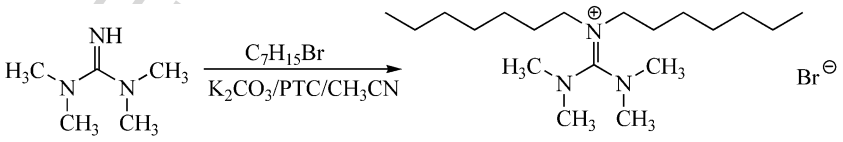
1-bromoheptane $H_2PtCl_6 \cdot 6H_2O$ and 1,1,3,3-Tetramethylguanidine (TMG) were purchased from Aladdin Co., Ltd (Shanghai, China). $MnCl_2 \cdot 4H_2O$, $SnCl_4 \cdot 5H_2O$, $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ were provided by Aladdin Co., Ltd (Shanghai, China). The mixed solutions were prepared by dissolving these metal chlorides in hydrochloric acid solutions. All the other reagents in this study were obtained from Sinopharm Chemical Reagent Co. Ltd (China). All the reagents were of analytical grade and used as received without additional purification.

2.2 Analytical Techniques.

The ^1H NMR spectra of the ionic liquid were obtained in D_2O with a Bruker AV300 spectrometer. The concentrations of Pt(IV), Pt(II) and multi-metal ions (Mn(II), Sn(IV), Fe(III), Co(II), Mg(II),Cu(II)) were determined by a flame atomic absorption spectrometer (3150, Precision & Scientific Instrument, Shanghai, China) and an ICP-OES (iCAP-7000, Thermo Fisher Scientific, Boston, US) respectively. The UV-vis spectra (UV-9000, Metash, Shanghai, China) and FT-IR (Tensor27, Bruker corporation, Karlsruhe, Germany) were used to analyze the [diHTMG]Br and the extracted species.

2.3 Synthesis of Ionic Liquid.

The synthesis of [diHTMG]Br was carried out according to a literature with some modification.[20] The synthesis method is shown in Scheme 1. A mixture of tetramethylguanidine (2.30 g; 20 mmol), tetrabutylammonium bromide (0.128 g; 0.4 mmol), potassium carbonate (8.29 g; 60 mmol) and 1-bromoheptane (7.88 g; 44 mmol) was refluxed in acetonitrile (50 ml) at 60 ℃ for 12 hours with stirring. The cooled reaction mixture was filtered, 80 ml of water was added to the filtrate, and the residue was treated with 5 ml of 30% sodium hydroxide. The resulting aqueous mixture was extracted with 80 ml of petroleum ether to remove any pentaalkylguanidine and unreacted alkylating agent. Then the petroleum ether phase was back-extracted with 30 ml of water. 20 ml of saturated sodium bromide solution was added to the combined aqueous phase. The saturated aqueous phase was extracted with 50 ml of dichloromethane three times to extract the hexaalkylguanidinium salt product. The combined dichloromethane phases were filtered and thereafter evaporated under vacuum to yield the product. ^1H NMR (D_2O,400 MHz): δ 0.90 (t, 6 H), 1.32-1.66 (m, 20 H), 2.98 (d,12 H), 3.10-3.31 (m, 4 H).



Scheme 1. Synthesis of [diHTMG]Br

2.4 Extraction Studies.

Batch Extraction experiments were carried out at room temperature(298±1 K) unless otherwise stated. A certain amount of [diHTMG]Br was dissolved in chloroform as the organic phase and a solution containing the desired concentration of Pt(IV) or mixed metal ions in hydrochloric acid media was employed as the aqueous phase. The two phases were mixed in vials and shaken for 10min by an orbital shaker, then centrifuged for 3min to achieve complete separation. The extraction efficiency (*E%*) and distribution ratio (*D*) were calculated using Eq.(1) and (2):

$$E\% = \frac{C_{in} - C_{eq}}{C_{in}} \times 10 \qquad (1)$$

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$$D = \frac{E}{1-E} \times \frac{V_{aq}}{V_{org}} \qquad (2)$$

Where C_{in} and C_{eq} are the initial and equilibrium concentration of Pt(IV), respectively. $V_{org}$and V_{aq} refer to the volumes of organic and aqueous phase.

The stripping experiments were performed by mixing the loaded organic phase and the stripping solutions, using a similar step of extraction. All experiments were repeated three times and the relative standard deviation was less than 5%.

2.5 Computational details.

We employed the Gaussian 09 program package[22] with the 6-311++g (d, p) basis set to perform all the calculations. The geometry was in ground state and was optimized by density functional theory (DFT) with the exchange-correlation functional Coulomb-attenuating method applied to B3LYP (CAM-B3LYP).[23] The electrostatic potential map was generated by Multiwfn.[24, 25] During the analyses of ESP on van der Waals (vdW) surface, followed by Bader et al.[26] the vdW surface referred here denotes the isosurface of ρ = 0.001 e/bohr^3.

3. RESULTS AND DISCUSSION

3.1 Optimization of Extraction Conditions.

3.1.1 Effect of Contact Time.

A feed solution of 188 mg·L^{-1} Pt(IV) in 1 mol·L^{-1} HCl solution was contacted with 5 g·L^{-1} [diHTMG]Br in chloroform at A/O phase volume ratio of 5. The contact time ranged from 1 to 60 min. The results showed that the *E%* reached up to 80% after the two phases were mixed for 1 min, and remained almost constant afterwards. Therefore, 10 min was selected in further experiments to ensure complete extraction equilibrium.

3.1.2 Effect of Extractant Concentration.

In order to investigate the effect of extractant dosages on the extraction efficiency, the [diHTMG]Br concentration was varied between 1 and 25 g·L^{-1},while other factors kept constant. In addition, a 188 mg·L^{-1} aqueous solution of Pt(IV) was employed as the aqueous phase. Figure 1 shows that *E%* rises sharply with the increase of the concentration of [diHTMG]Br, then it reaches a plateau at 7.5 g·L^{-1} [diHTMG]Br and the maximum *E%* is close to 100%. At the same time, *D* rapidly from 2.98 to 356.67 as expected. Finally 5 g·L^{-1} [diHTMG]Br was employed for further studies of Pt(IV) extraction. Neither third phase nor emulsion was observed in all experiments.

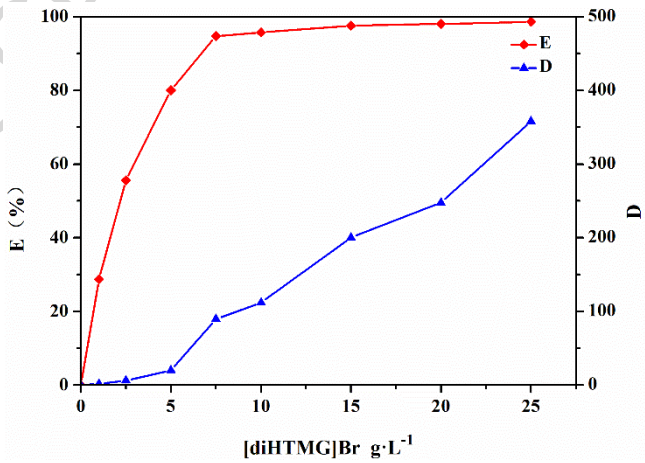

Figure 1. Effect of [diHTMG]Br concentration on Pt(IV) extraction. Conditions: the concentration of extractants varied between 1 and 25 g·L^{-1}, aqueous phase = 188 mg·L^{-1} Pt(IV) in 1 mol·L^{-1} HCl solution, t = 10 min, A/O = 5, T = 298 K.

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3.1.3 Effect of HCl concentration.

Acidity durability is an important parameter in the extraction process, therefore the influence of HCl aqueous solution concentration ranged from 0.5 to 5.0 mol·L^{-1} on *E%* and *D* was investigated. The results are displayed in Figure 2. It shows that *E%* decreases as the concentration of HCl solution increases. The *E%* of Pt(IV) was 91.0% at 0.5 mol·L^{-1} HCl solution, but it gradually decreased to 59.1% at 5.0 mol·L^{-1} HCl solution. As a result, *D* decreased from 50.6 to 7.2. Therefore, it reveals that HCl concentration should be as low as possible for Pt(IV) extraction. Then 0.5 M of HCl solution was selected taking hydrolysis of $PtCl_6^{2-}$ into consideration.

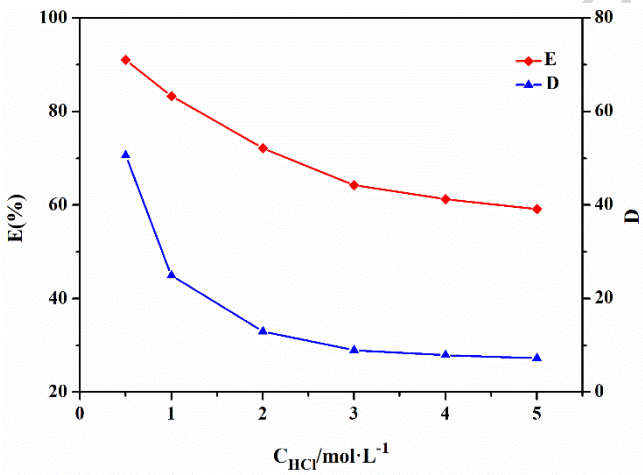

Figure 2. Effect of HCl concentration on Pt(IV) extraction. Conditions: organic phase = 5 g·L^{-1} [diHTMG]Br, aqueous phase = 188 mg·L^{-1} Pt(IV) in 0.5-5 mol·L^{-1} HCl solution, t = 10 min, A/O = 5, T = 298 K.

3.1.4 Effect of H^+ and Cl^- Concentration.

To discern the influence of H^+ concentration on the extraction process of Pt(IV), the experiments were performed by varying H^+ concentration from 0.5 to 5.0 M with HCl. Here we kept the [Cl^-] constant all through by using NaCl. The corresponding data are plotted in Figure 3a. The result reveals that the increase of H^+ concentration had influence neither on the *E%* nor on the *D* with the 5 g·L^{-1} of extractant in chloroform. Then the effect of Cl^- concentration on the extraction of Pt(IV) was studied with aqueous phase containing a constant H^+ concentration of 0.5 M. The Cl^- concentration was varied from 0.5 to 5.0 M adjusted by NaCl (Figure 3b). With the increase of Cl^- concentration, the *E%* decreased continuously, and the situation basically coincided with the influence of hydrochloric acid. The negative effect of Cl^- concentration is certainly due to the limited distribution ratio of Br^- into the aqueous phase when Cl^- concentration is high.

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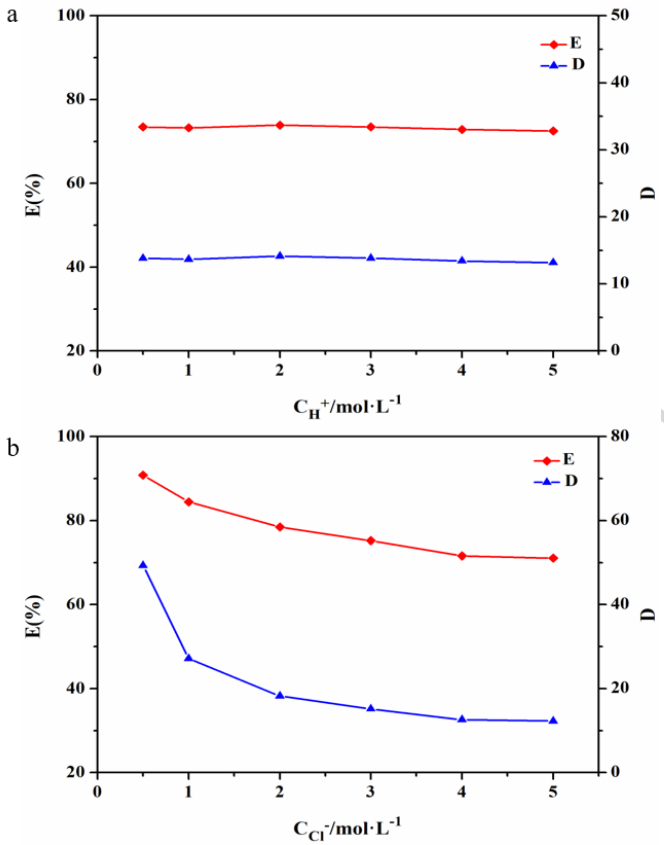

Figure 3. Effect of H^+ and Cl^- concentrations on the Pt(IV) extraction. Conditions: organic phase = 5 g·L^{-1} [diHTMG]Br; aqueous phase = 188 mg·L^{-1} Pt(IV). (a) 0.5–5.0 mol·L^{-1} [H^+], 5.0 mol·L^{-1} [Cl^-]. (b) 0.5 mol·L^{-1} [H^+], 0.5–5.0 mol·L^{-1} [Cl^-]. A/O = 5; t = 10 min; T = 298 K.

3.1.5 Effect of NaBr Concentration and Extraction Mechanism of Pt(IV).

Because the anion of the ionic liquid is Br^-, the effect of NaBr concentration on Pt(IV) extraction was determined. Figure 4 shows an almost linear decrease for *E%* from 84.7 to 35.3% as the NaBr concentration was increased over the range 0.1-1.0 M. Therefore, the extraction mechanism is presumed to be an anion exchange mechanism. As the concentration of bromide ions increases, the equilibrium point shifts to the left side, resulting in a significant decrease in *E%* and *D*.

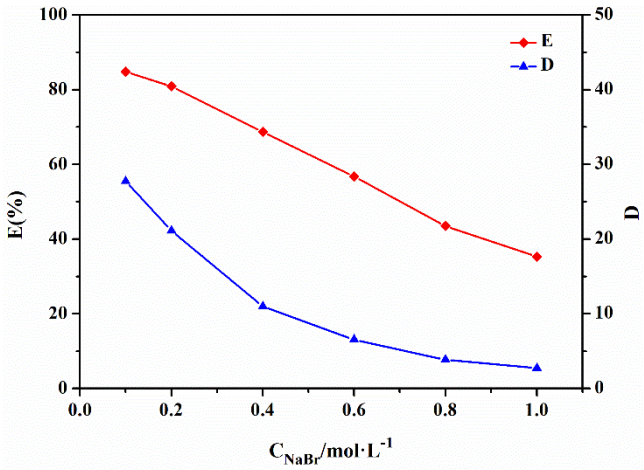

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Figure 4. Effect of NaBr concentration on Pt(IV) extraction. Conditions: organic phase = 5 g·L^{-1} [diHTMG]Br, aqueous phase = 188 mg·L^{-1} Pt(IV) in 0.5 M HCl solution, [NaBr] = 0.1-1.0 mol·L^{-1}, t = 10 min, A/O = 5, T = 298 K.

The coordination number of the extracted species was studied by the Job's method. The total amount of Pt(IV) and [diHTMG]Br was maintained at 3×10^{-6} mol. Pt(IV) and [diHTMG]Br varied from 0.6 to 2.0 mM and 2.4 to 1.0 mM, respectively. Figure 5 illustrates these two fitting curves intersect to an acme when the molar ratio of [diHTMG]Br to Pt(IV) is 2. According to the principle of conservation of charge, the stoichiometry of the extracted species further confirms the anion exchange mechanism we supposed.

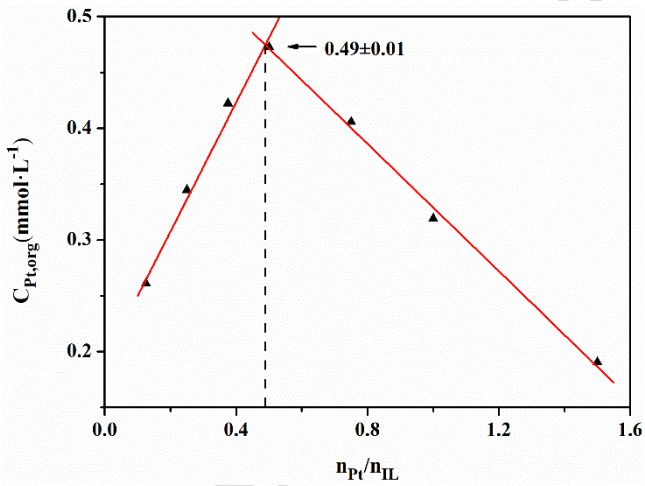

Figure 5. Job's plot for the Pt−[diHTMG]Br system. The molar fraction of Pt(IV) was varied from 0.2 to 0.8, [HCl] = 0.5 mol·L^{-1}, A/O = 5, t = 10 min, T = 298 K.

The UV−vis absorption spectra of $PtCl_6^{2-}$, [diHTMG]Br and the extracted species in chloroform were characterized. Here we can see (Figure 6), the maximum absorbance wavelength center at 262.0 nm for $PtCl_6^{2-}$ and 243.7 nm for [diHTMG]Br, while the blue colored curve corresponding to complex (Pt−[diHTMG]Br) also shows absorption bands in these two regions. The slight difference in the maximum absorbance wavelength is due to the change of solvent. Hence, the results confirm that the structures of extractant and $PtCl_6^{2-}$ did not changed before and after extraction.

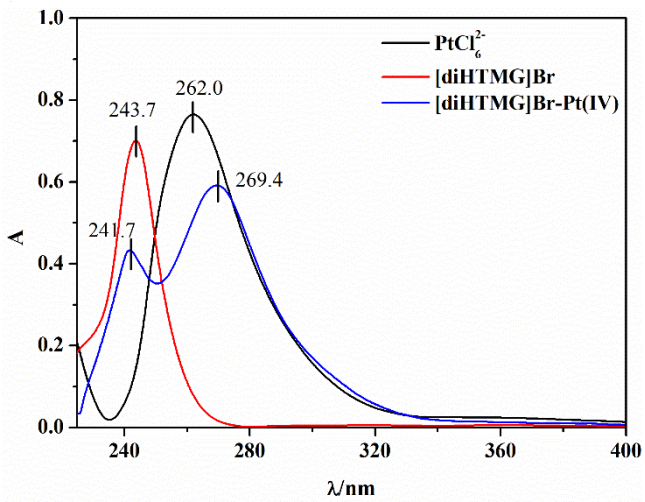

Figure 6. UV-vis spectra of $PtCl_6^{2-}$, [diHTMG]Br and [diHTMG]Br-Pt complex.

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The extractants and the extracted species were further characterized by FT-IR spectroscopy. The spectra of the organic phases before and after saturated extraction are shown in Figure 7. Due to the conjugation of the three nitrogen atoms, the positive charges are dispersed on the three nitrogen atoms and the central carbon atom, which makes the GILs have good thermal stability. This means that positively charged region will show more obvious changes in the FT-IR spectra if the anion exchange mechanism is supported. As we expected, more distinct displacement is obtained from the peaks of C-N stretching vibration which shifted from 1241.86 cm^{-1} to 1262.89 cm^{-1}. As a result, FT-IR spectra also confirm our conjecture of anion exchange mechanism. Finally, according to the evidence above, the reaction is presented as follows:

$$[diHTMG]Br + PtCl_6^{2-} \rightleftharpoons \overline{[diHTMG^+]_2[PtCl_6^{2-}]} + 2Br^-$$

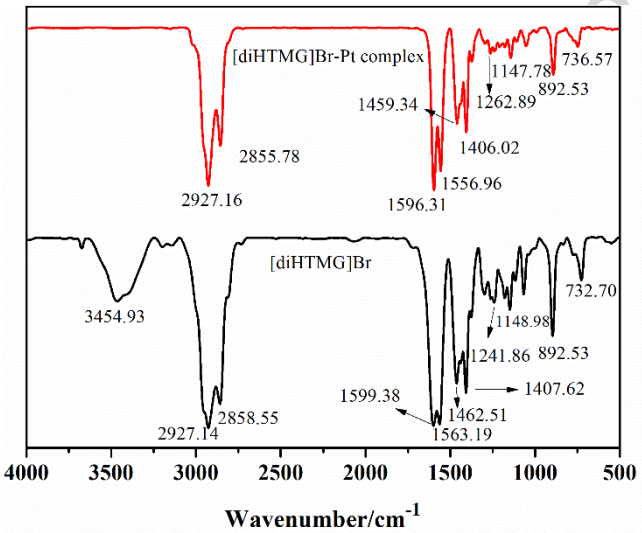

Figure 7. FT-IR spectra of the organic phase before and after saturated extraction.

In order to support the mechanism mentioned above from the quantum chemistry point of view, the ESP map of $[diHTMG]^+$ was calculated. As Figure. 8 shown, the most electron-poor regions, where the values of extrema are larger, are mainly around the three conjugated nitrogen atoms, which would prefer to interact with $PtCl_6^{2-}$.

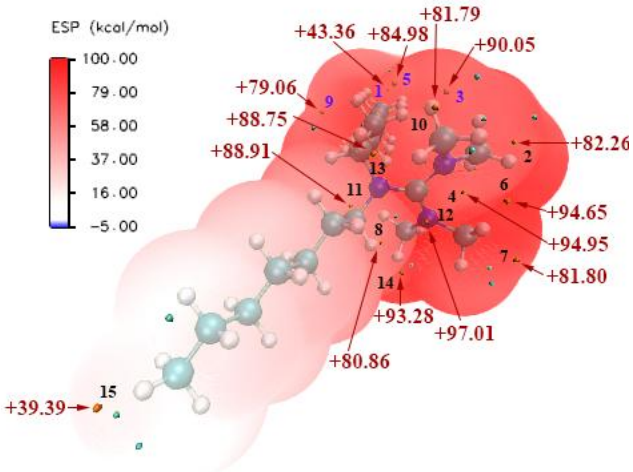

Figure 8. Electrostatic potential (ESP) map of $[diHTMG]^+$. The unit is in kcal/mol. (Surface local minima and maxima of ESP are symbolized as green and orange spheres, respectively. The transparent / opaque ones with blue / black labels correspond to the extrema at backside / front side of graph.)

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3.2 Thermodynamic and Kinetic Studies.

To further study the temperature effect on the extraction of Pt(IV), a series of experiments were carried out by varying the temperature from 298 K to 338 K while other parameters were kept constant. The results show that higher temperature has a negative effect on the extraction.

The extraction equilibrium constant K_{ex} is following Eq.(3):

$$K_{ex} = \frac{[2diHTMG \cdot PtCl_6^{2-}] \cdot [Br^-]^2}{\{[diHTMG]Br\}^2 \cdot [PtCl_6^{2-}]} \quad (3)$$

Taking logarithm and rearranging Eq.(4):

$$\log K_{ex} = logD + 2\log[Br^-] - \log[[diHTMG]Br] \quad (4)$$

Eq.(5) was obtained from Van't Hoff equation:

$$\log K_{ex} = \frac{-\Delta H^\theta}{2.303RT} + C \quad (5)$$

The plots of $logD\ vs$ 1/T are displayed in Figure 9. Therefore, the extraction is exothermic with $\Delta H^\theta = -6.242$ kJ·mol^{-1}.

The standard Gibbs free energy (ΔG^θ) and entropy (ΔS^θ) are obtained from Eq.(6) and (7):

$$\Delta G^\theta = -2.303RTlogK_{ex} \quad (6)$$

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta \quad (7)$$

The value of ΔG^θ and ΔH^θ is negative, suggesting that the extraction is spontaneous and the process is exothermic. Meanwhile, the value of ΔS^θ (−11.0 J·K^{-1}·mol^{-1}) indicates the formation of highly ordered complexes during the extraction process. From the above equations, the equilibrium constants and thermodynamic parameters for the Pt(IV) extraction at different temperatures are shown in Table 1.

Table 1. Equilibrium constants and thermodynamic parameters for the Pt(IV) extraction at different temperatures.

T/K	*Kex(T)*	*ΔG/kJ·mol^{-1}*	*TΔS/kJ·mol^{-1}*	*ΔH/kJ·mol^{-1}*
298	3.615	-3.184	-3.059	
308	3.431	-3.157	-3.085	
318	2.933	-2.845	-3.397	-6.242
328	2.479	-2.476	-3.766	
338	2.304	-2.345	-3.897	

Extraction kinetics data of Pt(IV) were analyzed through pseudo-first-order and pseudo-second-order model. These two models equations follow Eq.(8) and (9). Figure 10 shows that the experiment data conforms to the pseudo-second-order model. The plot of $\ln(q_e - q_t)\ vs\ t$ is not shown because R^2 is low. The pseudo-second-order model means that chemical reaction through anion exchange is the rate-controlling step. The pseudo-second-order equation can also be explained by ''surface reaction'' model, assuming that the chemical reaction on the surface of the ionic liquid droplets is the slowest step during the whole extraction process.[27]

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

Where k_1(min^{-1}) and k_2(mol·min^{-1}) represent the constant of the first-order equation and the constant of the second-order equation, respectively. q_e and q_t represent the equilibrium capacity and the capacity of different times (min), respectively.

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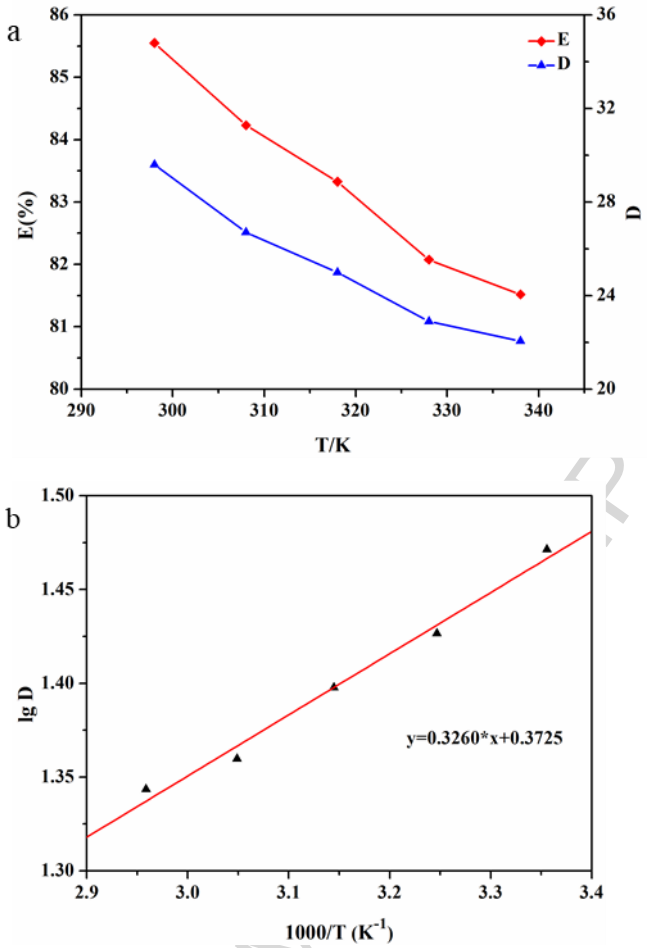

Figure 9. (a) Effect of temperature on the Pt(IV) extraction; (b) plot of *lg D vs 1000/T.* Conditions: organic phase = 5 g·L^{-1} [diHTMG]Br, aqueous phase = 188 mg·L^{-1} Pt(IV) in 0.5 M HCl solution, t = 10 min, A/O = 5, T = 298-338 K.

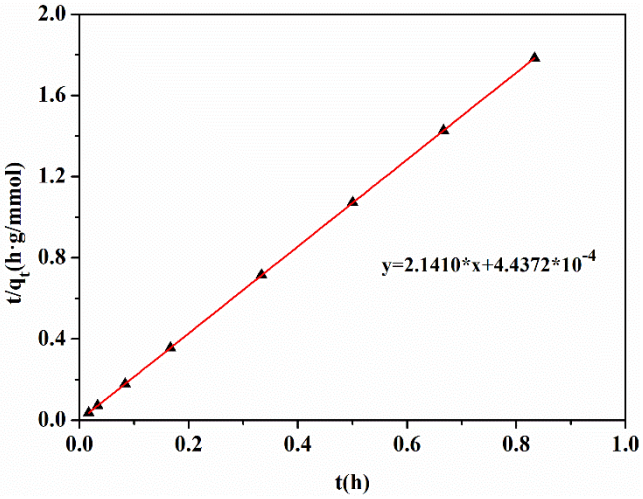

Figure 10. Pseudo-second-order kinetics plot for the extraction of Pt(IV) on [diHTMG]Br.

3.3 Stripping and Reusability.

The stripping step is a crucial step for recycling the organic phase. Hence, a loaded organic phase (188 mg·L^{-1} Pt(IV))

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was used for testing various stripping solutions such as DI water, 6 M HCl, sodium sulfide, sodium sulfite, oxalic acid, thiourea and acidic thiourea. Under acidic conditions (0.5 M HCl solution), thiourea led to an efficient stripping of Pt(IV). The acidity of the solution was kept constant to prevent hydrolysis of the Pt(IV). As shown in Figure 11, 0.5 M $CS(NH_2)_2$ /0.5 M HCl solution was applied. Thiourea is a complexing agent which could reduce Pt(IV) to Pt(II) with the formation of formamidine as the oxidation product, meanwhile, it can form strong cationic complex with Pt(II). As we know, the electron configuration of the ligand is highly related to the formation of stable complexes. The soft electron donor ligands like thiourea prefer low-valent metal ions like Pt(II), while hard electron donor ligands such as chloride ion prefer high-valent metal ions like Pt(IV).[11, 28]

When Pt(IV) in the complexes were reduced to Pt (II), Cl^- in $PtCl_6^{2-}$ will dissociate and then combine to $[diHTMG]^+$. Therefore, [diHTMG]Br was converted to [diHTMG]Cl. As shown below, this conversion did not affect the extraction capacity of [diHTMG]Br for the subsequent cycles.

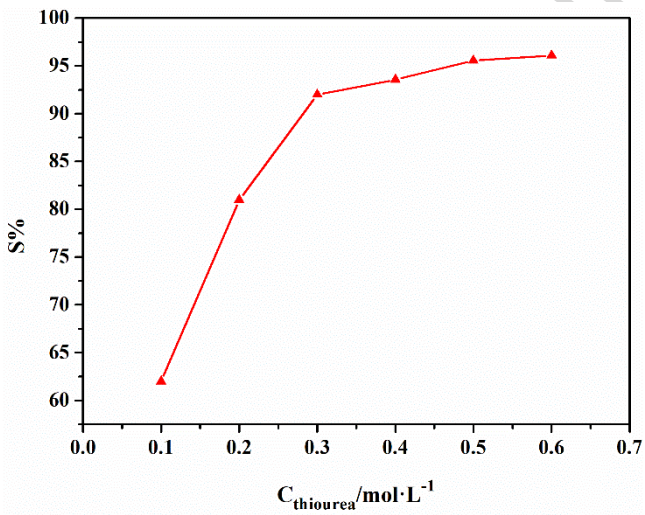

Figure 11. Effect of stripping reagent concentrations on the stripping of Pt(IV). Loaded organic phase = 188 $mg \cdot L^{-1}$ Pt(IV), aqueous phase = thiourea concentration from 0.1−0.6 $mol \cdot L^{-1}$, [HCl] = 0.5 M, A/O = 3, t = 60 min, T = 298 K.

A series of extraction-stripping experiments were performed to test the recyclability of organic phases. A fresh solution of [diHTMG]Br was mixed with Pt(IV) feed solution at the A/O ratio of 5. After separation the organic phase was stripped with 0.5 M $CS(NH_2)_2$ in 0.5 M HCl at the A/O ratio of 5. The stripped organic phase was reused for next extraction-stripping cycle. Figure 12 shows that the extraction efficiency did not decrease significantly during the four cycles, which suggests that the conversion of [diHTMG]Br into [diHTMG]Cl has no negative effect on the extraction behaviors and the organic phase could be easily recycled. The decline of *E%* should be caused by the slight loss of ionic liquids in the operating process or in the aqueous phase.

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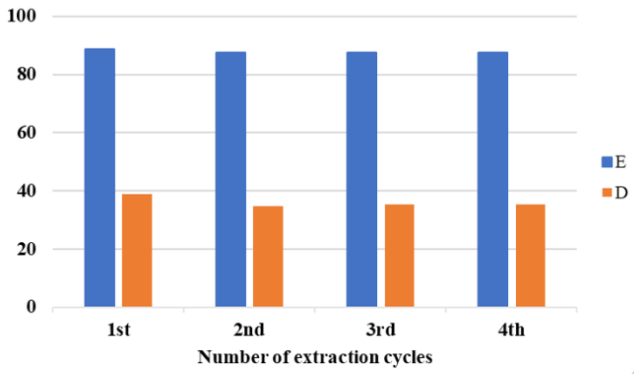

Figure 12. Extraction of Pt(IV) with regenerated [diHTMG]Br. Organic phase = 5 g·L^{-1} [diHTMG]Br, aqueous phase = 188 mg·L^{-1} Pt(IV) in 0.5 M HCl solution, A/O = 5, t = 10 min, T = 298 K.

3.4 Extraction Selectivity of Pt(IV) from Other Metal salt Solutions.

To investigate the extraction selectivity of the [diHTMG]Br/chloroform system for Pt(IV), an aqueous multi-metal ions solution was prepared by dissolving 1.0 mM of each metal chloride salt in 0.5 M HCl solution. The obtained data are plotted in Figure 13. It demonstrates that [diHTMG]Br showed excellent selectivity toward Pt(IV) which was extracted up to 98.2%, and low selectivity of 4.2% for Mn(II), 2.0% for Al(III), 2.28% for Cu(III), 4.7% for Co(II), 4.3% for Mg(II), 7.8% for Sn(IV) and <1.0% for Fe(III). The simplicity of separation and recovery of Pt(IV) shown by [diHTMG]Br demonstrates its potential application in selective separation of Pt(IV).

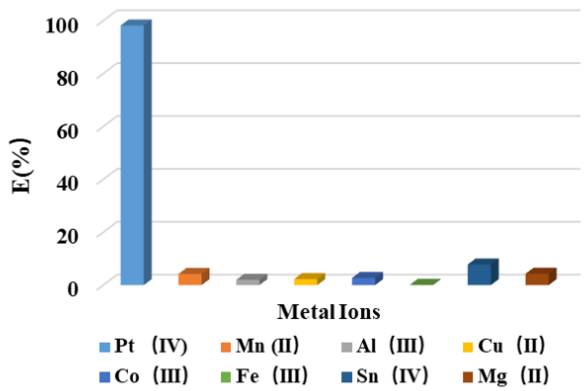

Figure 13. Selective extraction of Pt(IV) with [diHTMG]Br from simulated mixed-metal solutions. Conditions: organic phase = 10 g·L^{-1} [diHTMG]Br in chloroform, [metal ions] = 1 mM in 0.5 M HCl solution, t = 10 min, A/O = 5, T = 298 K.

3.5 McCabe−Thiele Diagrams

3.5.1 Extraction Isotherm and McCabe−Thiele Diagram.

The Pt(IV) extraction isotherm and the McCabe−Thiele diagram are shown in Figure 14. The feed solution containing 188 mg·L^{-1} Pt(IV) in 0.5 M HCl solution was mixed with the organic phase (12.7 mmol·L^{-1} [diHTMG]X in chloroform (initially 5 g·L^{-1} [diHTMG]Br) X = Br^{-} with fresh organic phase and X^{-} = Cl^{-} with recycled organic phase) at different A/O

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phase ratios from 13/1 to 1/7 while keeping the total volume of phases constant. Figure 14 indicates that two theoretical stages were needed for quantitative extraction of Pt(IV) using 12.7 mmol·L^{-1} [diHTMG]X at the O/A ratio of 1/5 and leaving a tiny amount of Pt(IV) in feed solution.

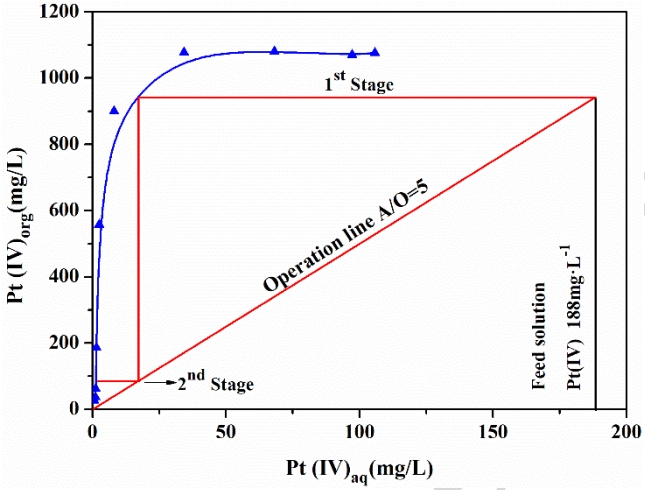

Figure 14. McCabe−Thiele diagram for Pt(IV) extraction. Organic phase = 5 g·L^{-1} [diHTMG]Br, aqueous phase = 188 mg·L^{-1} Pt(IV) in 0.5 M HCl solution, A/O = 13/1-1/7, t = 10 min, T = 298 K.

A two-stage counter-current extraction simulation experiment was carried out using 5 g·L^{-1} [diHTMG]Br at A/O ratio of 5/1 to confirm the prediction of McCabe−Thiele diagram. All data are measured at the steady state which was attained within five complete operation cycles. Figure 15 shows the profile of Pt(IV) concentration in the aqueous and organic phases. The final raffinate containing less than 1.0 mg·L^{-1} Pt(IV) corresponds to over 99.0% extraction of Pt(IV) into the ionic liquid phase and the concentration of Pt(IV) in the loaded organic phase also confirms the mass balance during the extraction stage. The E% of Pt(IV) in the first and second stage were found to be 69.1% and 99.5%, respectively, matched well with the predicted data of the McCabe−Thiele diagram.

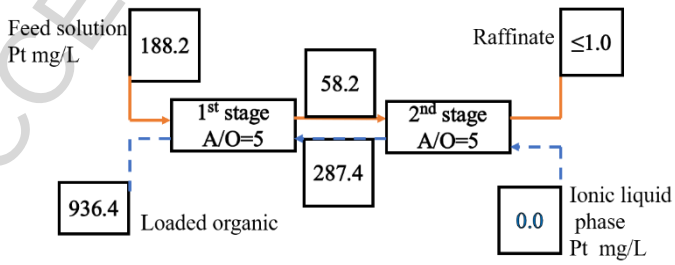

Figure 15. Counter-current experiment with two stages for Pt(IV) extraction. Organic phase = 5 g·L^{-1} [diHTMG]Br, aqueous phase = 188 mg·L^{-1} Pt(IV) in 0.5 M HCl, A/O = 5, t = 10 min, T = 298 K.

3.5.2 Stripping Isotherm and McCabe−Thiele Diagram.

To investigate the effect of O/A ratios on the stripping efficiency of Pt(IV) from the scrubbed loaded organic phases using a strip solution of 0.5 M HCl/0.5 M thiourea, a series of stripping experiments were performed at different O/A ratios from 1/9 to 7/1, keeping the total volume constant. Figure 16 implies that two theoretical counter-current stripping stages

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are needed for quantitative stripping of Pt(IV) at O/A ratio of 1/1, while three theoretical stages are required at O/A ratio of 3/2. Considering the O/A ratio and the number of theoretical stages, the O/A ratio of 1/1 was selected.

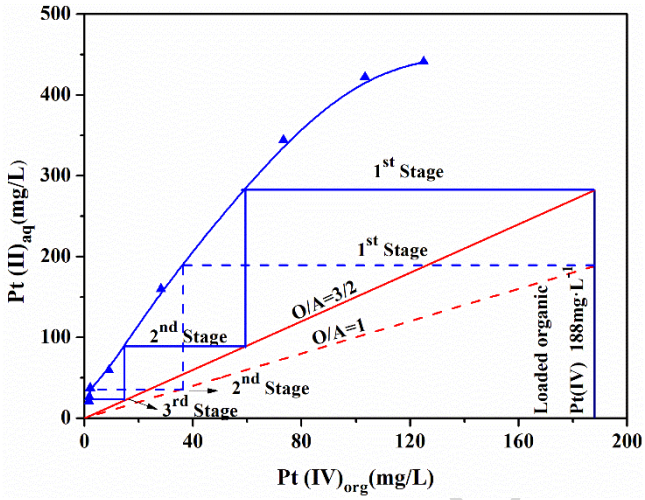

Figure 16. McCabe−Thiele diagram for the stripping of Pt(IV). Loaded organic phase = 188 mg·L^{-1} Pt(IV), aqueous phase = 0.5 M HCl/0.5 M thiourea, O/A = 1/9 to 7/1, t = 60 min, T = 298 K.

Similarly, two-stage counter-current stripping simulation experiments were performed to confirm the McCabe−Thiele diagram prediction using 0.5 M HCl/0.5 M thiourea at A/O ratio of 1/1. The obtained data are shown in Figure 17. The results match well with the prediction of the McCabe-Thiele diagram. The final strip liquor contained over 186.5 mg·L^{-1} Pt(II), which indicated more than 99% stripping efficiency. The Pt(IV) concentration in the loaded organic was less than 2.0 mg·L^{-1}, so the organic phase could be used for next cycle of Pt(IV) extraction.

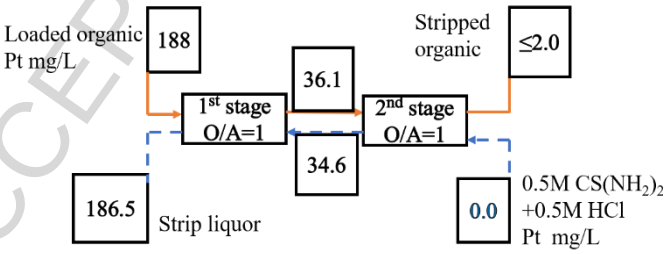

Figure 17. Counter-current experiment with two stages for Pt(IV) stripping from loaded organic. Loaded organic phase = 188 mg·L^{-1} Pt(IV), aqueous phase = 0.5 M HCl/0.5 M thiourea, O/A = 1, t = 60 min, T = 298 K.

4. CONCLUSIONS

A new guanidinium ionic liquid([diHTMG]Br) extraction system was designed for the separation of Pt(IV) from hydrochloric acid solution. Under the optimum conditions, the system shows high extractability and selectivity for Pt(IV) over base metals (Mn(II), Al(III), Cu(II), Co(II), Fe(III) and Mg(II)). According to the analysis of experiment results, the IL−Pt complexes were deemed as $[diHTMG]^{+}_{2}\cdot[PtCl_6]^{2-}$. ESP map of $[diHTMG]^{+}$ was calculated to support the anion exchange mechanism theoretically. Furthermore, the stripping process and the recovery of the organic phase could be achieved by the reduction using 0.5 M $CS(NH_2)_2$/0.5 M HCl. To further understand the nature of the extraction reaction and

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the rate-controlling step, the thermodynamic and kinetic properties of the extraction process were studied. Pt(IV) could be quantitatively extracted from 0.5 mol·L^{-1} HCl solution initially containing 188 mg·L^{-1} Pt(IV) with 5 g·L^{-1} [diHTMG]Br with two counter-current stages at A/O = 5, whereas its total stripping as Pt(II) with 0.5 M $CS(NH_2)_2$/0.5 M HCl also required two counter-current stages at O/A = 1.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This work was supported by Shandong Provincial Natural Science Foundation, China (ZR2019MB060) and Natural Science Foundation of China (21476129 and 21606147).

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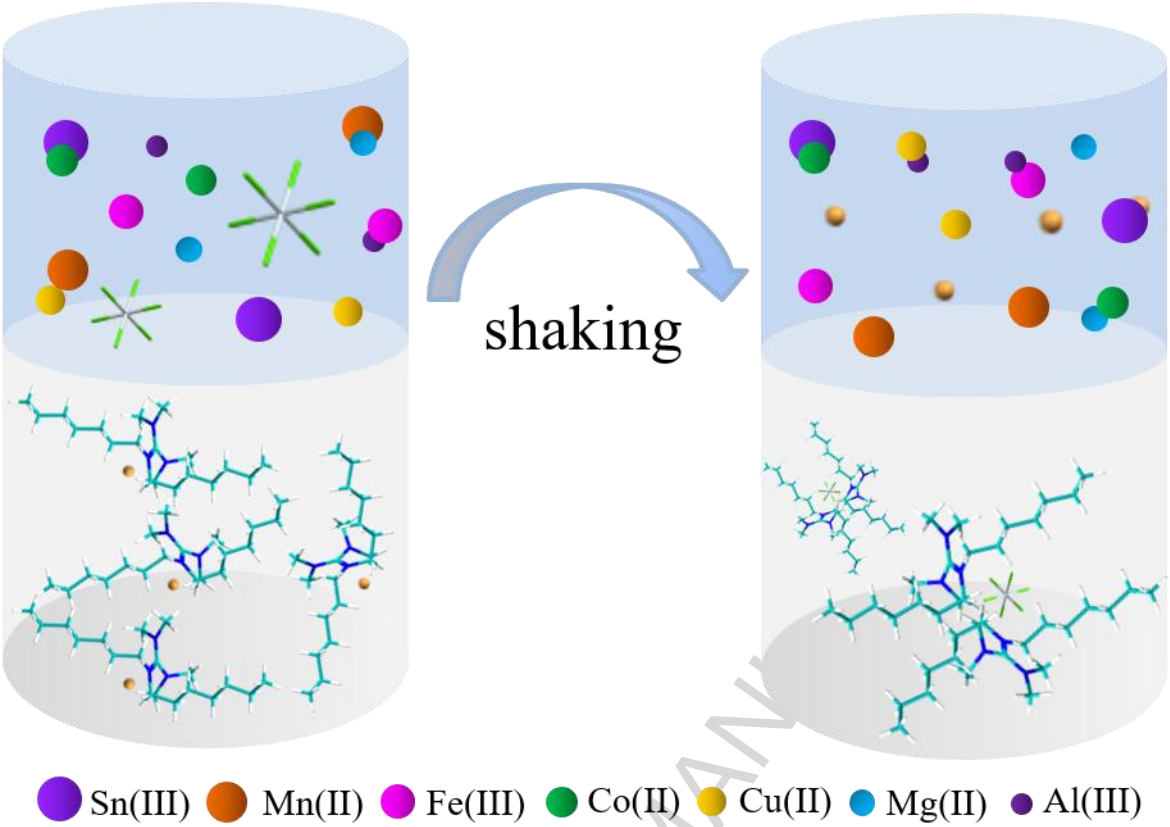

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Highlights

1. A guanidinium ionic liquid was synthesized and used to extract Pt(IV).
2. Optimum conditions for extraction of Pt(IV) were established.
3. Extraction mechanism was proved combining theoretical study with spectral analysis.
4. The ionic liquid exhibited outstanding selectivity and recycling utilization.
5. Two theoretical counter-current stages were enough to fully extract and strip Pt(IV).

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