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Abstract

With the rapid development of modern industry, it is necessary to effectively recycle precious metals such as gold and palladium from e-waste. IL (ionic liquid) is an efficient extractant with high boiling points, non-flammability, and high thermal stability. The properties of IL can be improved by modifying the n-substituted groups of their cations, enhancing the separation efficiency of noble metals. Thus, two guanidinium ILs, with the substituents of -R and -OR, were synthesized to extract Au(III) from a hydrochloric acid medium. These ILs exhibited excellent extraction properties, including high selectivities, rapid kinetics, and significant extraction capacities. The maximum extraction capacities of Au(III) by [diMTMG][Tf₂N] and [diPTMG][Tf₂N] were 519.4mg/g and 427.9mg/g, respectively, achieving rapid extraction equilibrium within 30s. The introduction of o-containing functional atoms enhanced extraction capacity and selectivity. The extraction mechanism involving anion exchange was confirmed by slope method, jobs method, as well as ultraviolet and nuclear magnetic resonance analysis.

KEYWORDS

ionic liquids, electronic waste, liquid-liquid extraction, gold, selectivity

1 INTRODUCTION

Gold has earned the moniker "king of metals" since ancient times due to its scarcity and

preciousness. With the development of society, the monetary role of gold is diminishing, while its utilization in various industries and high-tech fields, such as electronics, chemicals, medicine, and aerospace, is gradually expanding.¹⁻³ However, gold reserves in nature are typically low and often occur as semi-ores of other metals, which fail to meet the industry's daily requirements. With the continuous development of the mining industry, the cost of mining gold has also gradually increased with the reduction of the primary mineral grade. The increased use of modern equipment has resulted in a significant generation of electronic waste, also known as e-waste.⁴⁻⁵ E-waste production is rapidly increasing worldwide.⁶ It is estimated that by 2030, the annual generation of e-waste will reach about 75 million tons.⁷ E-waste mainly includes discarded circuit boards, discarded automobile exhaust catalysts and anode slime, etc., and the content of gold is much higher than that of gold in symbiotic ore⁸⁻⁹. Hence, e-waste has become a global concern. Recycling gold from e-waste is one of the effective ways to obtain gold, which is more energy and cost-effective than traditional mineral mining¹⁰⁻¹¹. So far, the primary methods for Au(III) recovery include liquid-liquid extraction (LLE), cementation, adsorption, precipitation, and electrodeposition. LLE is an effective method for the recovery of Au(III) due to its large amount of single recovery, simple device and strong practicability.¹²⁻¹⁵ However, most extractants have low selectivity and some toxicity.¹⁶ Therefore, it is of great significance to develop low-toxicity, green, highly selective and reusable extractants to recover gold from e-waste.

ILs have a unique negative and cationic structure, which make them significantly different from common molecular solvents and traditional salts. ILs have the advantages of extremely low vapor pressure, good stability, easy formation of liquid-liquid two-phase, and

designability, etc., and have shown a good application prospect in the field of metal extraction.¹⁷⁻²² ILs, such as imidazoles, pyrrolidines, morpholines, and quaternary amines, exhibit exceptional extraction performance for Au(III).²³⁻²⁶ Lv et al synthesized a new gemini-type IL, [C6BIM₂][NTf₂]₂, for selective extraction of gold from hydrochloric acid medium with 98.4% extraction rate.²³ Wang et al. synthesized three UCST-type ILs to extract Au(III) from acidic medium, and the maximum extraction capacity of [EtbetmMor][Tf₂N] for Au(III) reached 2.27mmol/g.²⁴ Wang et al. studied the hydrophobic IL [Suc][Tf₂N]₂ for selective extraction of Au(III), showing good selectivity for Au(III) and a maximum extraction capacity of 2.15mmol/g. At the same time, the temperature regulation characteristics of [Suc][Tf₂N]₂ was investigated, and the mass transfer problem of IL without adding diluent was overcome. Comparing the traditional liquid-liquid extraction (TLLE) with the homogeneous liquid-liquid extraction (HLLE), it was found that HLLE is more suitable for the recovery of Au(III).²⁵ Mahandra et al. synthesized two quaternary phosphine ILs to extract recover Au(I) from thiosulfate media. The high phase ratio (A/O=10 and O/A=10) during extraction and stripping cycle proves that it has high industrial potential and can be scaled from the laboratory to the factory scale.²⁶

Guanidinium IL is a new type of nitrogen-containing IL extractant, which has three nitrogen atoms with higher thermal and chemical stability. Compared with commercial imidazolyl ILs, it is more environmentally friendly. And guanidinium IL has higher freedom in structural design, which can be modified by adding functional groups according to the need to achieve the purpose of selective recognition and separation of precious metals. The presence of N-substituents in ILs has been found to have a significant impact on their physical

chemistry properties, ultimately affecting their extraction performance. Specifically, the length of the alkyl chain on the N-substituted group plays a crucial role. The extraction performance will be improved with the increase of alkyl chain. However, when the alkyl chain length is greater than 6 and continues to increase, the ILs viscosity increases, affecting the mass transfer efficiency and resulting in the decline of extraction performance.²⁷ Introduction of -COOR group on N-substituents increases the positive charge of cations and the hydrophobicity of ILs, which improves the extraction performance.²⁸ At present, there are few studies on the extraction of Au(III) by guanidinium ILs, and few systematic studies on the influence of IL structure on the extraction performance and mechanism.

In this work, we synthesized two ILs, 2-dipropoxy-3-oxomethyl-1,1,3,3-tetramethylguanidinium bis(trifluoromethylsulfonyl)imide ([diMTMG][Tf₂N]) and 2,2-dipentyl-1,1,3,3-tetramethylguanidinium bis(trifluoromethylsulfonyl)imide ([diPTMG][Tf₂N]). The viscosities, water solubilities, heat stabilities and acid resistances of the two ILs were investigated, and they were used to recover Au(III) from acidic medium solution by LLE. The effects of aqueous pH, temperature, time and concentrations of hydrochloric acid, hydrogen ion, chloride ion, extractant and Au(III) on the extraction performance of gold were investigated. The stoichiometric ratio of IL to Au(III) was determined using Job's method and the slope method. Additionally, the extraction mechanism was investigated through NMR and UV-vis analysis. Finally, the thermodynamics and kinetics of [diMTMG][Tf₂N] and [diPTMG][Tf₂N] were studied, and they were applied to extract gold from the actual e-waste leaching solution.

2 EXPERIMENTAL SECTION

2.1 Materials

1-Bromo-3-Methoxypropane (97%), 1-Bromopentane (99%), 1,1,3,3-Tetramethylguanidine (99%), lithium bis(trifluoromethanesulphonyl)imide ($\geq 98\%$), CH_3CN ($\geq 99.9\%$), tetrabutylammonium bromide (99.9%), potassium carbonate (99.99%), dichloromethane ($\geq 99.9\%$), petroleum ether, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ($\geq 99.9\%$), $\text{SnCl}_2 \cdot 5\text{H}_2\text{O}$ (98%), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ($>99\%$), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (98%), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ($\geq 99.9\%$), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (98%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), PbCl_2 ($\geq 99.9\%$), AuCl_3 , $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (99.9%) and PdCl_2 were purchased from Titan Scientific Co., Ltd. (Shanghai, China). Other chemical reagents were of analytical grade.

2.2 Analytical instruments

The concentration of metals in aqueous solution was analyzed by flame atomic absorption spectrometer (AA-6880, Shimadzu, Japan) and ICP-MS (ICAP-7850, Agilent, America). The structures, aqueous solubility and purities of ILs were characterized by ^1H NMR and ^{13}C NMR using a NMR spectrometer (Bruker AV 400, Bruker Scientific Instruments, Germany). The UV-vis spectra (UV-2600, Shimadzu, Japan) were used to analyze the ILs and the extracted species. The thermogravimetric analyzer (TGA55, TA INSTRUMENTS, USA) was used to determine the thermal stabilities of ILs. The viscosities of ILs were characterized by a rotary viscometer (DV-II+ Pro, Brookfield, America).

2.3 Synthesis of ILs

40 mmol 1,1,3,3-tetramethylguanidine, 88 mmol 1-bromo-3-methoxypropane, 0.8 mmol anhydrous tetrabutylammonium bromide, and 120 mmol anhydrous potassium carbonate were added to 100 ml of acetonitrile. The mixture was stirred at reflux for 24 hours at $60\text{ }^\circ\text{C}$. After

the system is cooled and filtered, 100 ml water was added to the obtained filtrate. The filtrate was washed by 160 ml of petroleum ether, and 50 ml of water is used to extract the petroleum ether phase. The two water phases were combined, and the aqueous phase was extracted with 150ml of dichloromethane in multiple fractions. An appropriate amount of anhydrous magnesium sulfate was added to dichloromethane phase to remove water, and then the dichloromethane was removed to obtain the intermediate product [diMTMG][Br]. Subsequently, 60 ml water and 44 mmol of lithium ditrifluoromethane sulfonimide were added to the intermediate product, and the reaction was stirred at 35 °C for 24h. After the reaction was completed, the lower IL was removed, washed and dried in vacuum at 80 °C for 48h to obtain the final product [diMTMG][Tf₂N]. The synthesis method of [diPTMG][Tf₂N] is consistent with that of [diMTMG][Tf₂N].

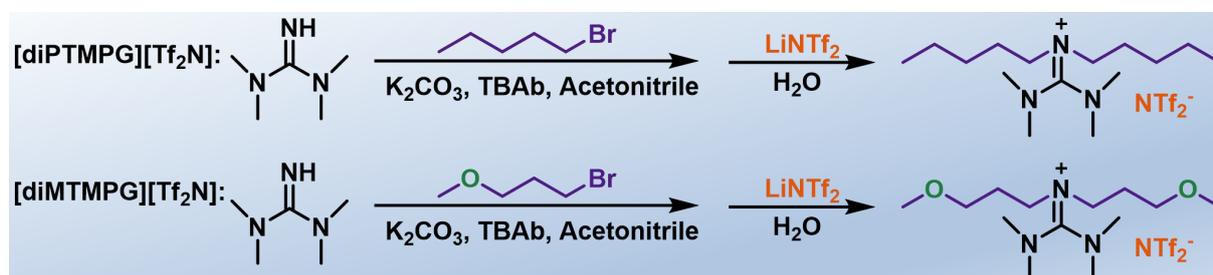


FIGURE 1 Synthetic Routes of two guanidinium ILs.

2.4 Extraction experiments

The organic phase was prepared by dissolving ILs in dichloromethane, and the aqueous phase is prepared by a hydrochloric acid solution with a certain concentration of gold ions or mixed concentration of metal ions. The equal volume (5 mL) of aqueous phase and organic phase were mixed in a 50 ml centrifuge tube and shaken at 25 °C for 2 hours. The concentration of metal ion in the water phase was analyzed by atomic absorption, and the concentration of metal ion in the organic phase was obtained by subtraction method. The following equations

are used to calculate the extraction rate (E%) and the distribution ratio (D):

$$E\% = \frac{C_{in} - C_{eq}}{C_{in}} \times 100\% \quad (1)$$

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

where C_{in} and C_{eq} represent the concentrations of metal ions in the aqueous phase before and after extraction, respectively, V_{aq} and V_{org} represent the volumes of the aqueous phase and organic phase, respectively.

2.5 Stripping and recycling.

To perform stripping, thiourea solution was added to the organic phase containing Au(III). After shaking at 25 °C for 2 hours, the aqueous phase was separated and analyzed for gold ion concentration. The organic phase was utilized in subsequent cycling experiments. The raffinate and organic phase were mixed after stripping and shaken at 25 °C for 2h to regenerate the IL. The organic phase was washed three times with deionized water to remove residual thiourea. Stripping was performed by adding 1mol/L thiourea solution to the loaded Au(III) organic phase. After oscillating at 25 °C for 2h, the water phase was separated, and the gold ion concentration was analyzed. The stripping efficiency (S%) was calculated by Equations (3). The organic phase was regenerated by raffinate phase and washed three times with deionized water for recycling experiment.

$$S\% = \frac{n_{aq}}{n_{org}} \times 100\% \quad (3)$$

where n_{org} and n_{aq} represent the molar amount of metal ions in the organic and aqueous phase

before and after stripping, respectively.

2.6 Determination of aqueous solubilities of ILs

The aqueous solubilities of the two guanidinium ILs were determined using qNMR, as reported in the literature.²⁹ D₂O ($\delta=4.79$ ppm) served as the solvent, and maleic acid ($\delta=6.40$ ppm) served as the internal standard. The experiments were conducted as follows. 0.2 g IL was mixed with D₂O (1.5 ml). The mixture was shaken at 25 °C for 3 hours. Then the mixture was centrifuged at a speed of 8000 rpm for 10 minutes to facilitate the separation of the two phases. Subsequently, maleic acid (10 mg) was added to D₂O (1 ml) and the samples were fully dissolved using sonication. Currently, the solubility of maleic acid in D₂O is 10mg/mL. Finally, the mixed solution mentioned above (0.8 ml) was carefully transferred to the NMR tube. The aqueous solubility was calculated according to the following equation:

$$A = K \cdot N \quad (4)$$

where N represents the count of excited atoms, and K is the spectral constant. In the same tests, the spectral constants are uniform for all atoms, making A directly proportional to N.

2.7 Practical application of gold recovery from electronic waste

0.1 g e-waste was leached in 20 ml of aqua regia for 3 hours. The acid leach solution was filtered to remove solid impurities and diluted 10 times by deionized water. Then the leach solution and organic phase containing 5mmol/L of ILs was mixed and shaken at 25 °C for 2 hours. Finally, the concentrations of metal ions in the aqueous phase were determined to study the extraction performance of the two ILs for gold in e-waste.

3 RESULTS AND DISCUSSION

3.1 Properties of guanidinium ILs

So far, there are few systematic studies on the structure and properties of IL for Au(III) extraction. Moreover, the extraction mechanism primarily involves anion exchange. Therefore, introducing O functional atoms is expected to improve the maximum extraction capacity and improve the selectivity of the ILs. Two kinds of N-substituent tetramethyl guanidinium ILs were synthesized by introducing the substituents of -R and -OR. NTf_2^- was used as anion, which can provide ILs with low viscosity, strong hydrophobicity, and high stability.

The aqueous solubilities of two guanidinium ILs, $[\text{diMTMG}][\text{Tf}_2\text{N}]$ (5.67 g/L) and $[\text{diPTMG}][\text{Tf}_2\text{N}]$ (0.70 g/L), were determined using qNMR, as depicted in (Figure 2A,B). The water solubility of $[\text{diMTMG}][\text{Tf}_2\text{N}]$ is greater than that of $[\text{diPTMG}][\text{Tf}_2\text{N}]$, attributed to -OR hydrophilic group, which can improve the hydrophilicity of ILs. At room temperature, the viscosities of $[\text{diMTMG}][\text{Tf}_2\text{N}]$ and $[\text{diPTMG}][\text{Tf}_2\text{N}]$ determined by a rotary viscometer were 4.8 mPa/s and 81.0 mPa/s, respectively. In general, most ILs tend to have high viscosities. Here, the viscosities of ILs can be reduced significantly by adding hydrophilic group -OR. The low viscosities of ILs help to improve mass transfer and diffusion during extraction, thus improving extraction performance.

Furthermore, as shown in Figure 2C, the thermogravimetric analysis of these two guanidinium ILs shows that $[\text{diMTMG}][\text{Tf}_2\text{N}]$ and $[\text{diPTMG}][\text{Tf}_2\text{N}]$ have excellent thermal stability. Generally speaking, the extraction process of Au(III) is carried out in a strongly acidic environment, so the acid resistance of ILs is very important. After the two guanidinium ILs were immersed in 4mol/L HCl solution for 4h, the hydrochloric acid phase was removed,

then acid the treated ILs were obtained after drying under vacuum at 80°C for 24h. Figure 2D demonstrates that, compared to ILs, the peaks of ^1H NMR for the acid-treated ILs do not exhibit a significant shift. This observation suggests that both ILs remain highly stable after being immersed in strong acidic conditions. In a word, these two ILs have excellent physicochemical properties, including low water solubilities, low viscosities, good thermal stabilities, and good acid resistances.

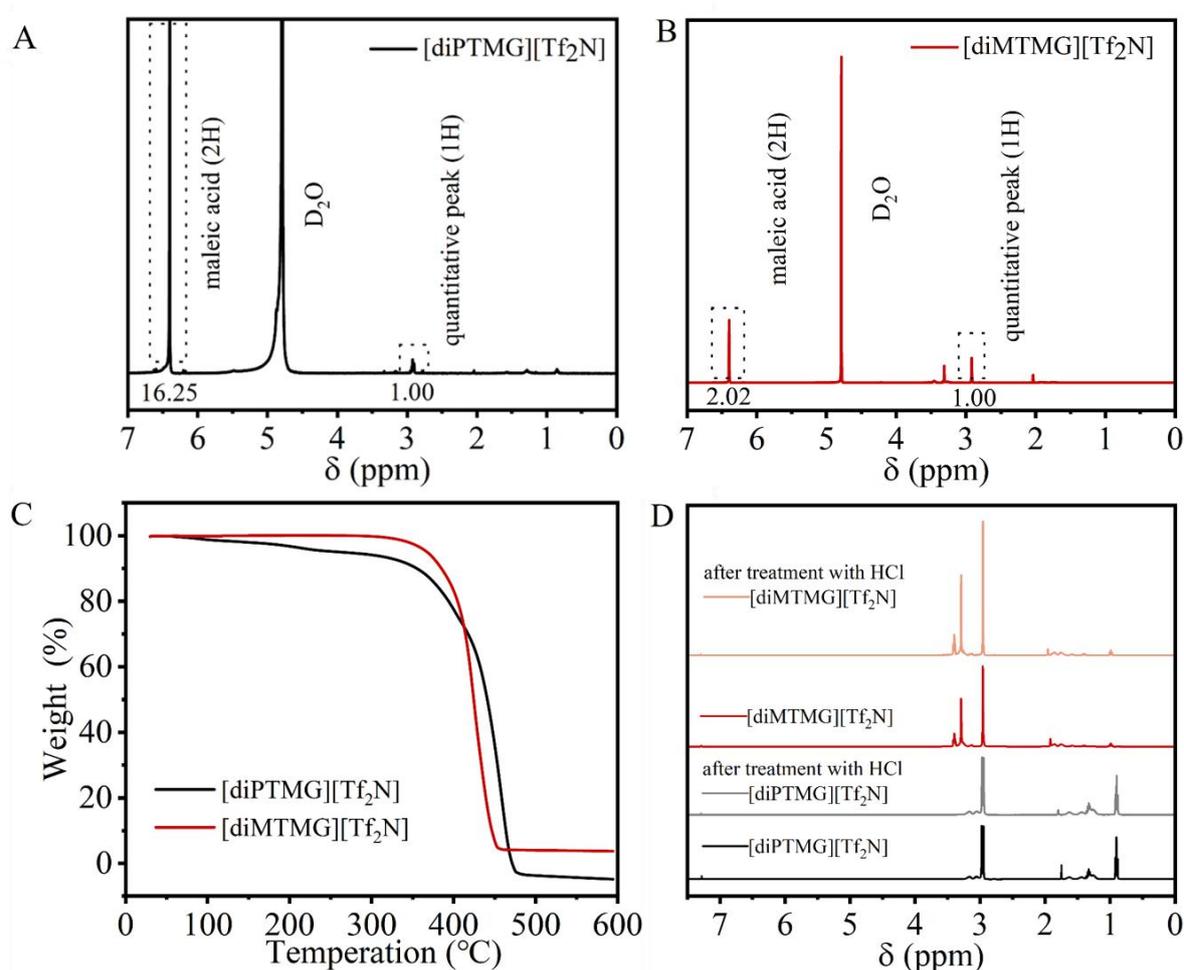


FIGURE 2 (A-B) ^1H NMRs of the two guanidinium ILs. (C) thermal stabilities of the two ILs. (D) acid stabilities of the two ILs after treatment with 4 mol/L HCl for 4 h.

3.2 Extraction efficiency in different diluents

The high viscosity of IL will lead to slow mass transfer, which can be solved by adding

organic solvent. Here, the impact of various polar diluents on the extraction of Au(III) using two guanidinium ILs was investigated. Figure 3 demonstrates the influence of different diluents on the extraction effect. It can be found from Figure 4 that the extraction rate increases continuously as the diluent polarity increases. Notably, when employing non-polar solvents like n-hexane and kerosene as diluents, the extraction efficiencies were only 12.7% and 12.2%, respectively. These two guanidinium ILs have small solubility in non-polar diluents such as kerosene and n-hexane, which are not conducive to extraction of Au(III). The high solubilities of the ILs in polar diluents such as dichloromethane (DCM), 1,2-dichloroethane (DCE) and chloroform, allow them to fully interact with the water phase, enhancing the extraction process. Here, DCM was selected as the suitable diluent for further extraction.

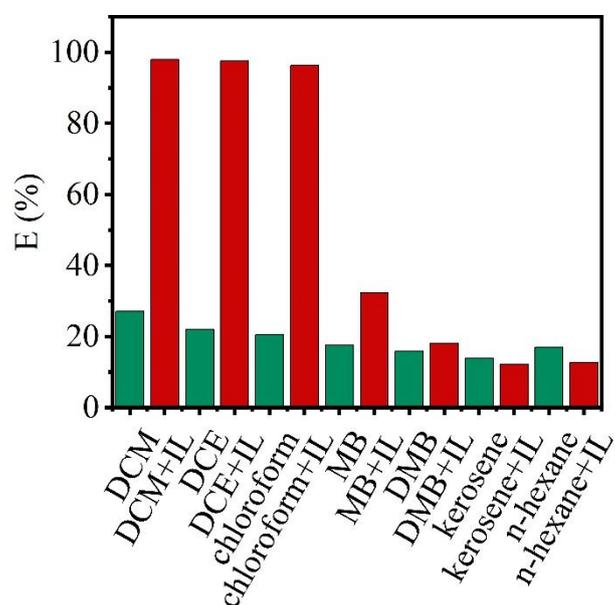


FIGURE 3 The impact of diluents on the extraction of Au(III) by guanidinium ILs ($C_{\text{Au(III)}}=1\text{mmol/L}$, $C_{[\text{diMTMG}][\text{Tf}_2\text{N}]}=5\text{mmol/L}$, $C_{\text{H}^+}=1\text{mmol/L}$, $t=2\text{h}$, $A/O=1$, $T=298\text{K}$)

3.3 Optimization of extraction conditions

In industrial applications of ionic liquids, wastewater presents different pH. The effects of

different pH environments on the extraction of Au(III) were studied (Figure 4A). Figure 4A indicates a notable decline in extraction rate as a result of pH increase. Specifically, at a pH of 7, the E% is merely 9.7%. The majority of gold ions in the solution exist as AuCl_4^- when the pH is below 5. When the pH ranges from 5 to 7, the presence of gold ions becomes more complex, including AuCl_4^- , $\text{AuCl}_3(\text{OH})^-$, $\text{AuCl}_2(\text{OH})_2^-$, $\text{AuCl}(\text{OH})_3^-$ and $\text{Au}(\text{OH})_4^-$. Generally, the extraction of Au(III) by ILs follows the anion exchange mechanism. Therefore, the extraction effect is significantly influenced by the electrostatic interaction between the cations of ILs and gold anions. Once the pH surpasses 5, the electrostatic interaction diminishes, leading to a steep decline in extraction rate.³⁰

The impact of HCl concentration on extraction efficiency was also investigated. As shown in Figure 4B, with the increase of HCl concentration, there was no significant effect on the extraction rate. The effects of concentrations of H^+ and Cl^- in aqueous phase on the extraction of Au(III) were also investigated in order to investigate the specific reasons why the concentration of hydrochloric acid had no effect on the extraction of Au(III). The influence of H^+ concentration on the extraction of Au(III) was determined by controlling the concentration of H^+ in aqueous phase from 0.1 to 3mol/L and adding NaCl to fix the concentration of Cl^- at 3mol/L. As shown in Figure 4C, there is no effect of H^+ concentration on the extraction rate.

Furthermore, keeping H^+ concentration in the aqueous phase at 0.1mol/L, Cl^- concentration in the aqueous phase was varied from 0.1 to 3mol/L by adding NaCl to examine the impact of Cl^- concentration on the extraction rate. Figure 4D indicates that E% remains relatively constant at the tested range of Cl^- concentration. It can be inferred that H^+ and Cl^- are hardly

involved in the reaction between ILs and Au(III).

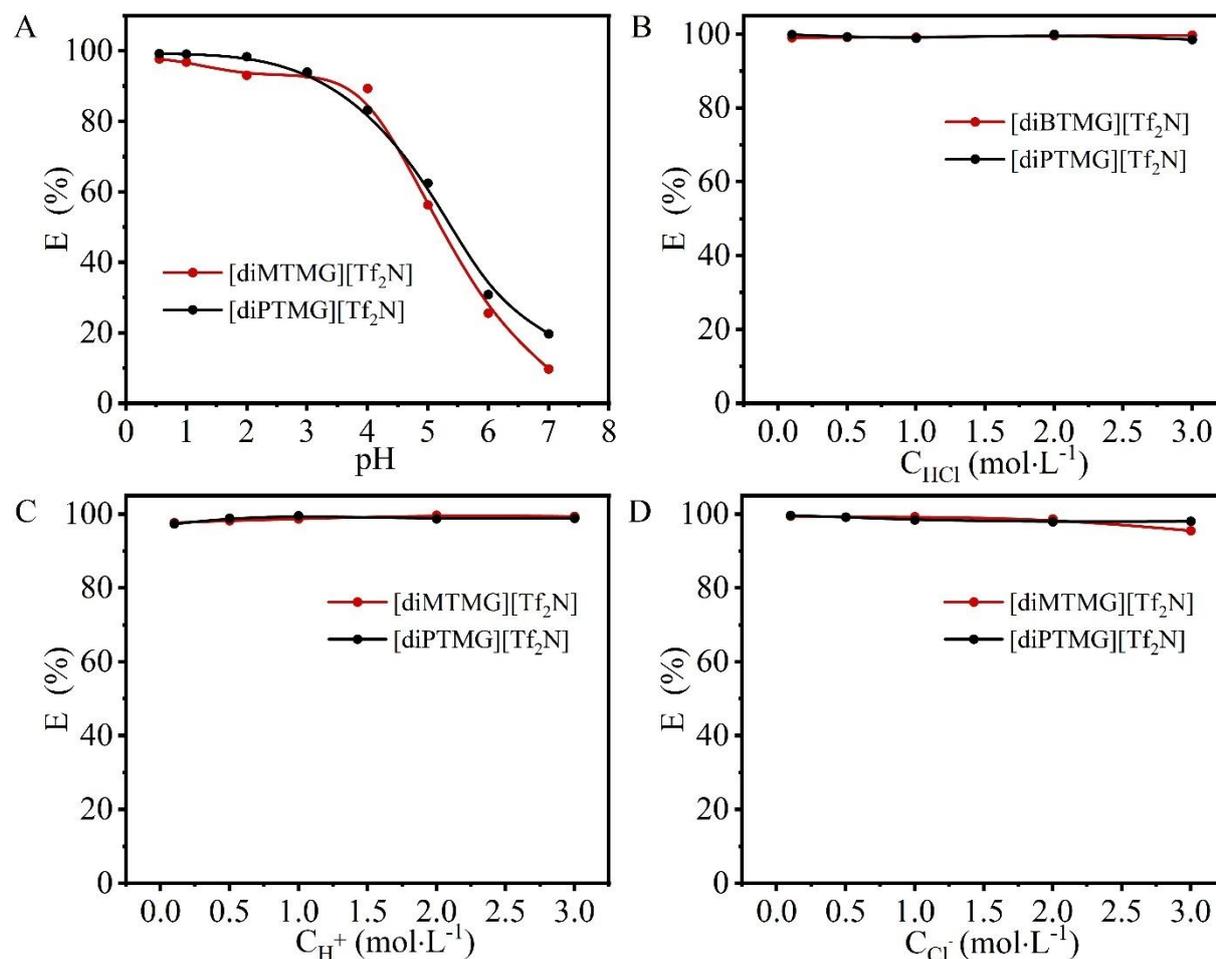


FIGURE 4 Effects of (A) pH, (B) HCl concentration, (C) Cl⁻ concentration, and (D) H⁺ concentration on extraction of Au(III) with the two ILs ($C_{Au(III)}=1\text{mmol/L}$, $C_{IL}=5\text{mmol/L}$, $t=2\text{h}$, $A/O=1$, $T=298\text{K}$).

3.4 Maximum extraction capacity

The maximum extraction capacity is the most direct index to evaluate the extraction performance of the extractant. In order to obtain the maximum extraction capacities (q_e) of Au(III) by [diPTMG][Tf₂N] and [diMTMG][Tf₂N], the amount of IL was fixed, and the amount of Au (III) was gradually increased until $C_{org, Au}$ remained unchanged. q_e (mg/g) can be calculated as follows:

$$q_e = \frac{q_{in} - q_{ep}}{m} \times V \times 196.97 \quad (5)$$

where q_{in} (mmol/L) and q_{ep} represent the initial and equilibrium concentrations of metal ions in the aqueous phase, respectively, m (g) represents the quantity of ILs, V (L) is the volume of the aqueous solution, and the relative atomic mass of Au is 196.97 (mg/mol).

Figure 5 demonstrates that the extraction capacities of the two ILs for Au(III) increase with increasing HAuCl_4 concentration until they reach equilibrium at 2 mmol/L. It can be determined that the maximum extraction capacities of $[\text{diPTMG}][\text{Tf}_2\text{N}]$ and $[\text{diMTMG}][\text{Tf}_2\text{N}]$ for Au(III) are 427.9 mg/g and 519.4 mg/g, respectively. The difference in maximum extraction capacities is attributed to the structural difference in the N-substituents of -R and -OR, which indicates that oxygen atom plays an important role in extraction capacity. In general, substituents have an impact on the physicochemical properties of ILs, including water solubility, density, charge distribution, stability, and viscosity. The extraction performance is significantly influenced by the charge distribution. The addition of O atoms decreases the electron cloud density surrounding N atoms in guanidinium ILs, resulting in increase in the positive charge of cation site of guanidinium ILs. In other words, the electrostatic attraction between $[\text{diMTMG}][\text{Tf}_2\text{N}]$ cations and Au(III) is stronger than that between $[\text{diPTMG}][\text{Tf}_2\text{N}]$ cations and Au(III). Therefore, $[\text{diMTMG}][\text{Tf}_2\text{N}]$ has a greater extraction capacity than $[\text{diPTMG}][\text{Tf}_2\text{N}]$.

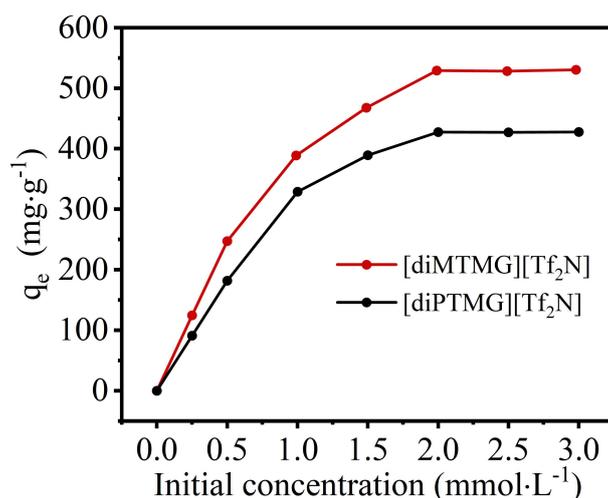


FIGURE 5 Effect of initial concentration of Au(III) on extraction capacities of Au(III) with the two ILs. ($C_{\text{Au(III)}}=0-2.98\text{mmol/L}$, $C_{\text{IL}}=1\text{mmol/L}$, $t=2\text{h}$, $A/O=1$, $T=298\text{K}$).

3.5 Anion exchange extraction of Au(III)

The excellent extraction performance drives us to study the extraction mechanism, and the stoichiometric ratio of ILs to Au(III) can be determined by slope analysis and Job's method. The mechanism of ionic liquid extraction of Au(III) is generally considered as an anion exchange process, in which the negatively charged metal complex $[\text{AuCl}_4]^-$ in the acidic solution is exchanged with the anion (Tf_2N^-) in the ionic liquid phase.

For the extraction systems of two guanidinium ILs, the initial concentration of $[\text{AuCl}_4]^-$ in the aqueous phase was fixed, while the initial concentration of the extractant was varied from 0.5 to 4. mmol/L. The logarithm of D was plotted against the logarithm of IL concentrations. The number of moles of ILs in the extractive complex was calculated from the slope of the line.³¹⁻³² It can be seen from Figure 6A that the slopes of the two lines are 1.31 and 1.12, respectively, confirming the complexation ratio of the extractant to gold. That is to say, each AuCl_4^- in the extract binds to a cation of guanidinium ILs during extraction.

To further confirm the complexation ratio of ILs to Au(III), the extraction mechanism

was studied by Job's method. Job's plot was plotted by varying the molar ratio of Au(III) to extractant from 0.25 to 3, while maintaining a constant total molar concentration of Au(III) and ILs at 6 mmol/L. As shown in Figure 6B, when the molar ratio is 0.98, the two fitting lines intersect, indicating that the extraction amounts reach a peak. This further proves that AuCl_4^- and the ILs are combined at a ratio of 1:1, which was consistent with the slope method.

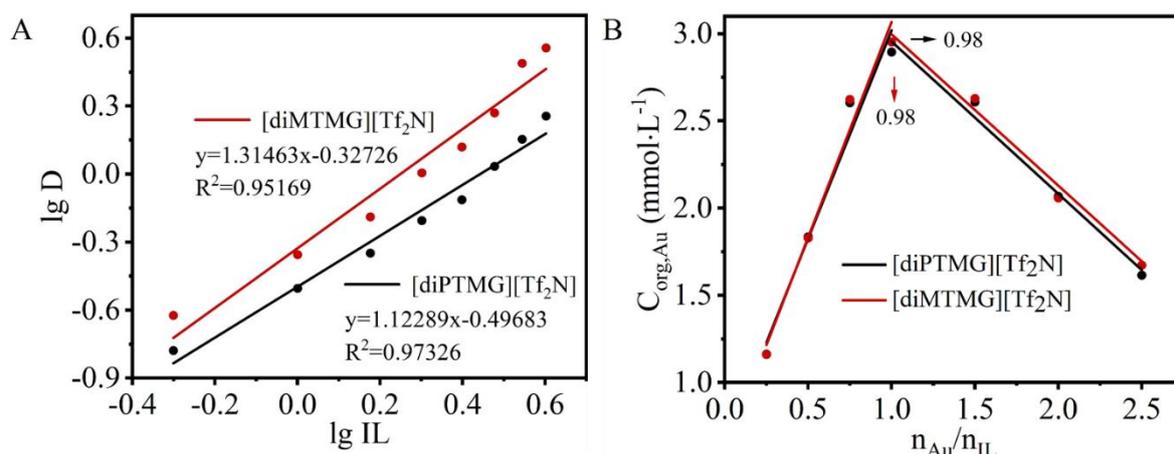


FIGURE 6 (A) Effect of IL concentration on extraction of Au(III). ($C_{\text{Au(III)}}=5\text{mmol/L}$, $C_{\text{IL}}=0.5\text{-}4\text{mmol/L}$, $t=2\text{h}$, $A/O=1$, $T=298\text{K}$, 250rpm). (B) Job's method for Au(III)-two ILs system ($C_{\text{Au(III)}}=1.2\text{-}4.3\text{mmol/L}$, $C_{\text{IL}}=1.7\text{-}4.8\text{mmol/L}$, $t=2\text{h}$, $A/O=1$, $T=298\text{K}$).

Subsequently, the morphology of gold before and after extraction was analyzed by UV-vis spectroscopy. As shown in Figure 7A, before extraction, AuCl_4^- exhibit two maximum absorption peaks at 226.5 and 314.5nm, respectively, and [diMTMG][Tf₂N] has a maximum absorption peak of 239.5nm. The extract [diMTMG][Tf₂N]-Au show two maximum absorption peaks at 243.5 and 324nm after extraction, respectively. The same phenomenon was observed for [diPTMG][Tf₂N]. The peak shift before and after extraction may be due to electrostatic interactions between cations of guanidinium ILs and AuCl_4^- , as well as solvent changes. Hence, the results indicated that the morphology of AuCl_4^- remained unchanged before and after extraction.

In order to further investigate the extraction mechanism, we also analyzed the ILs and the extracted species using ^{13}C NMR. As display in Figure 7B, compared to the pure ILs before extraction, the signal peak of the extracted species at 120ppm vanish, while the other peaks remain basically unchanged. It was worth noting that the 120ppm peak belongs to the $-\text{CF}_3$ of NTf_2^- . This suggests that the NTf_2^- anions of the ILs are transferred to the aqueous phase during extraction.

The results from slope method, Job's method, UV-vis, and ^{13}C NMR indicate that the extraction of Au (III) by the two guanidinium ILs follow the process of anion exchange. Then, the extraction equation can be obtained as follows:

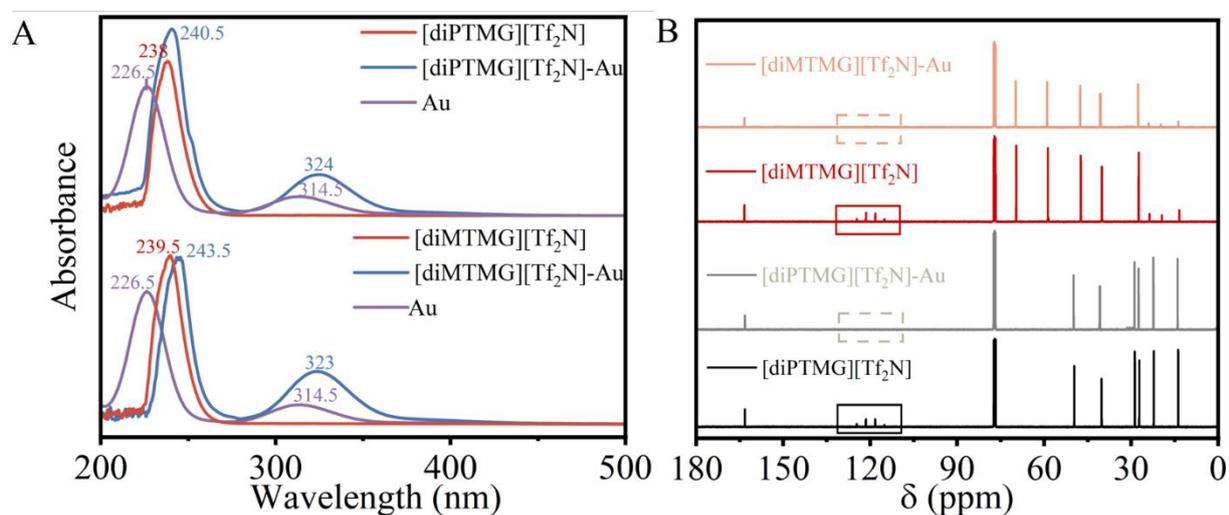
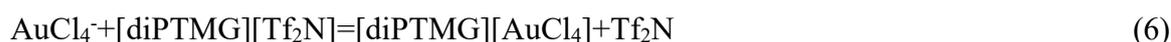


FIGURE 7 (A) UV-vis spectroscopy of Au(III), the two ILs, and extracted species. (B) ^{13}C NMR of the two ILs and extracted species.

3.6 Thermodynamic and kinetic Studies

To examine the impact of temperature on the extraction of Au(III), the temperature range from 278 to 318K was maintained. The resulting extraction rate (E%) and distribution ratio (D)

were recorded at various temperatures. As depicted in Figure 8A, increasing the temperature has an inhibitory effect on the extraction of Au(III), suggesting that the two guanidinium ILs are suitable for extraction at low or normal temperature.

The following formula can be used to calculate equilibrium constants K_1 and K_2 , standard Gibbs free energy (ΔG^θ), standard enthalpy change (ΔH^θ), and standard entropy change (ΔS^θ) at different temperatures.

$$K_1 = \frac{\{[\text{diPTMG}][\text{AuCl}_4^-]\} \cdot [\text{Tf}_2\text{N}]}{[\text{diPTMG}][\text{Tf}_2\text{N}] \cdot [\text{AuCl}_4^-]} \quad (8)$$

$$K_2 = \frac{\{[\text{diPTMG}][\text{AuCl}_4^-]\} \cdot [\text{Tf}_2\text{N}]}{[\text{diPTMG}][\text{Tf}_2\text{N}] \cdot [\text{AuCl}_4^-]} \quad (9)$$

$$\lg K_{1,2} = \lg D + \lg[\text{Tf}_2\text{N}^-] - \lg\{[\text{diPTMG}][\text{Tf}_2\text{N}] \text{ or } [\text{diMTMG}][\text{Tf}_2\text{N}]\} \quad (10)$$

$$\lg K_{1,2} = \frac{\Delta H^\theta}{-2.303RT} + C \quad (11)$$

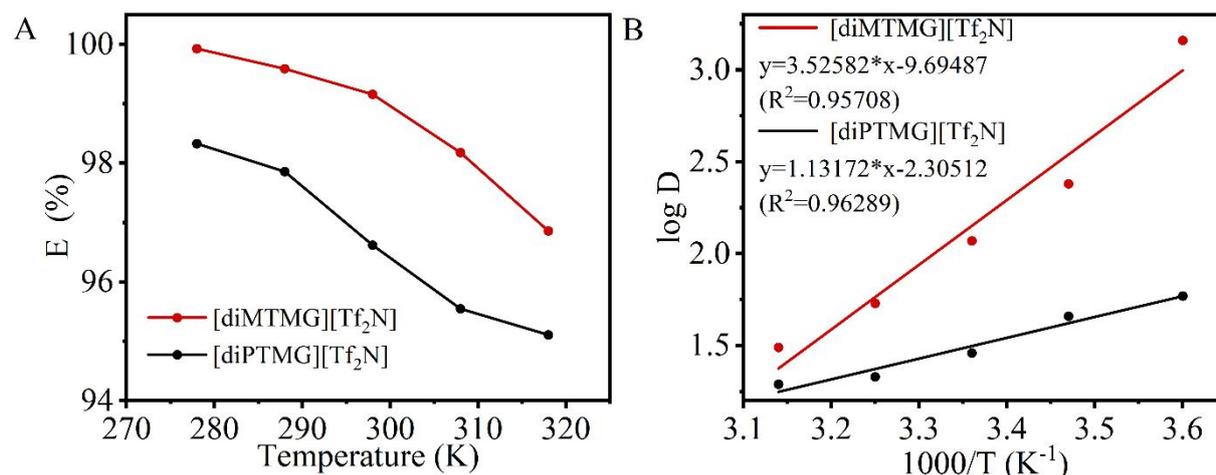
$$\Delta G^\theta = -2.303RT \lg K_{1,2} \quad (12)$$

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta \quad (13)$$

Figure 8B displays the fitting diagram for $\log D$ and $1000/T$. The slope of the diagram indicates that the ΔH^θ for extraction of Au(III) by $[\text{diPTMG}][\text{Tf}_2\text{N}]$ and $[\text{diMTMG}][\text{Tf}_2\text{N}]$ are -67.509 and -21.669 kJ/mol, respectively. These results indicate that the extraction processes of Au(III) by two guanidine ILs are exothermic.

Table 1 presents the equilibrium constants and thermodynamic parameters of Au(III) extraction by the two guanidinium ILs at varying temperatures. The negative values of ΔG^θ and ΔH^θ indicate that the extraction process is spontaneous and exothermic. More importantly, the absolute value of ΔG^θ decreases with increasing temperature, indicating that increasing temperature leads to a decrease in the spontaneous degree of the extraction process, which is

consistent with the situation described in Figure 8A. The negative ΔS^θ indicate that the extraction processes tend to produce highly ordered extract. Table 1 demonstrates that [diMTMG][Tf₂N] exhibits higher absolute values of ΔG^θ and ΔH^θ than [diPTMG][Tf₂N], indicating that the reaction of [diMTMG][Tf₂N] with Au (III) is easier.



FIGUER 8 (A) Effect of temperature on the extraction of Au(III) with the two guanidinium ILs. (B) Plot of ln K vs 1000/T. ($C_{Au(III)}=1\text{mmol/L}$, $C_{IL}=5\text{mmol/L}$, $t=2\text{h}$, $A/O=1$).

TABLE 1 Equilibrium constants and thermodynamic parameters of Au(III) extraction by the two guanidinium ILs at different temperatures

	T(K)	$K_{1,2}$	$\Delta G^\theta(\text{kJ/mol})$	$T\Delta S^\theta(\text{kJ/mol})$	$\Delta H(\text{kJ/mol})$
[diMTMG] [Tf ₂ N]	278	215.062	-12.416	-55.093	
	288	53.254	-9.520	-57.989	
	298	26.373	-8.109	-59.400	-67.509
	308	12.144	-6.395	-61.114	
	318	6.914	-5.113	-62.396	
[diPTMG] [Tf ₂ N]	278	15.520	-6.339	-15.330	
	288	11.852	-5.921	-15.748	
	298	7.239	-4.905	-16.764	-21.669
	308	5.374	-4.307	-17.362	
	318	4.803	-4.150	-17.519	

Equilibration time is also a key factor, which determines the extraction efficiency and is even more important in real industrial production. Kinetic experiments on Au(III) extraction by the two guanidinium ILs were conducted at 5mmol/L and 1mmol/L of ILs, respectively.

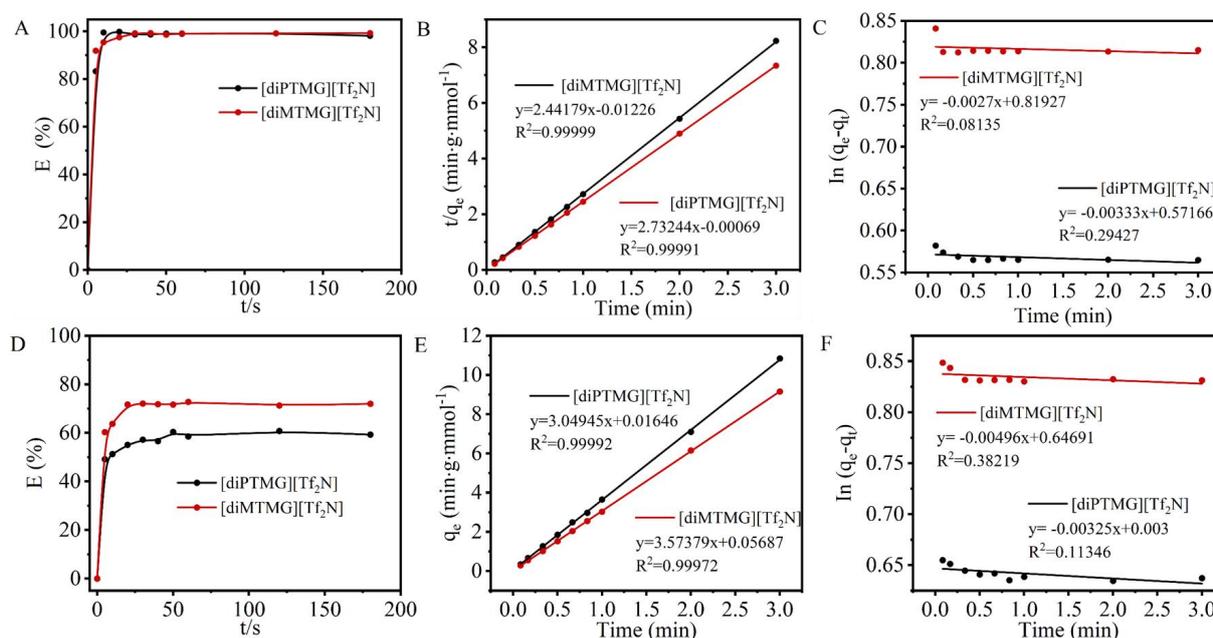
Figure 9A,D demonstrate that the extraction by the two guanidinium ILs achieve equilibrium within 30s at the tested concentrations of ILs. The extraction processes were examined using both first-order kinetic model (Equation 14) and pseudo-second-order kinetic model (Equation 15).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (14)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (15)$$

where q_e and q_t represent equilibrium time and extraction capacity at different times, respectively; k_1 and k_2 represent the constants of the pseudo-first-order equation and pseudo-second-order equation, respectively.

The fittings of experimental data show that the extraction reactions are more consistent with the quasi-second-order kinetic model at 5mmol/L and 1mmol/L of ILs. The quasi-second-order kinetic model can be explained by the "surface reaction" model. The reaction on the surface of IL droplets is the slowest in the whole extraction process and is the speed control step during the whole extraction process.



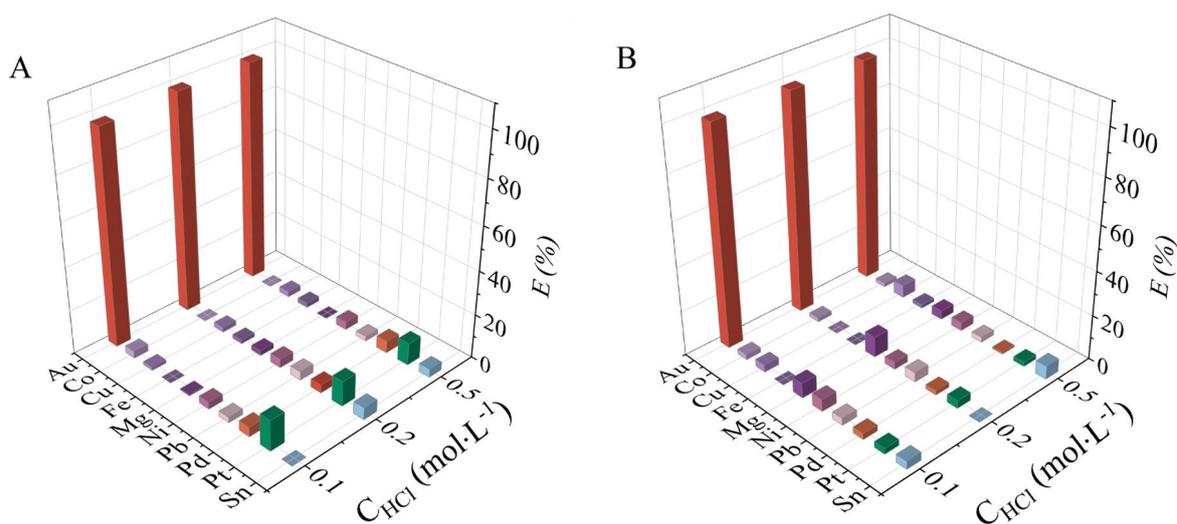
FIGUER 9 (A) Effect of time on extraction of Au(III). (B) quasi-second-order kinetic model for Au(III) on the two guanidinium ILs. (C) quasi-frist-order kinetic model for Au(III) on the two guanidinium ILs. ($C_{\text{Au(III)}}=1\text{mmol/L}$, $C_{\text{IL}}=5\text{mmol/L}$, $A/O=1$, $T=298\text{K}$). (D) Effect of time on extraction of Au(III). (E) quasi-second-order kinetic model for Au(III) on the two guanidinium ILs. (F) quasi-frist-order kinetic model for Au(III) on the two guanidinium ILs. ($C_{\text{Au(III)}}=1\text{mmol/L}$, $C_{\text{IL}}=1\text{mmol/L}$, $A/O=1$, $T=298\text{K}$).

3.7 Investigation of selectivity

Study on the selectivity of extraction of Au(III) from polymetal solutions is practically significant due to the coexistence of Au(III) with various metals in practice. The extraction selectivities of [diMTMG][Tf₂N] and [diPTMG][Tf₂N] were investigated in three different hydrochloric acid solutions containing precious metals (AuCl_4^- , PdCl_4^{2-} , PtCl_6^{2-}) and base metals (Mg^{2+} , Ni^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Pb^{2+}) with initial concentrations of 1mmol/L.

As shown in Figure 10, the extraction efficiencies of [diMTMG][Tf₂N] and [diPTMG][Tf₂N] for Au(III) were 100.0% and 97.4%, respectively, while the extraction efficiencies of other base metals were lower than 9.3% and 5.5%, respectively. It is worth noting that when the concentration of hydrochloric acid is 0.1mol/L, the extraction rate of Pt (IV) by [diPTMG][Tf₂N] reaches 14.0%. By comparing the structure of the two ILs and the selectivities of Au(III) in simulated polymetallic solutions, it is found that the introduction of O functional atoms can reduce the extraction of platinum. The excellent selectivities of [diMTMG][Tf₂N] and [diPTMG][Tf₂N] to Au (III) can be explained from the following four aspects: (1) According to the principle of "like attracts like" in soft and hard acid-base theory, precious metals belong to soft acids and have strong ability to form chlorine complexes, and

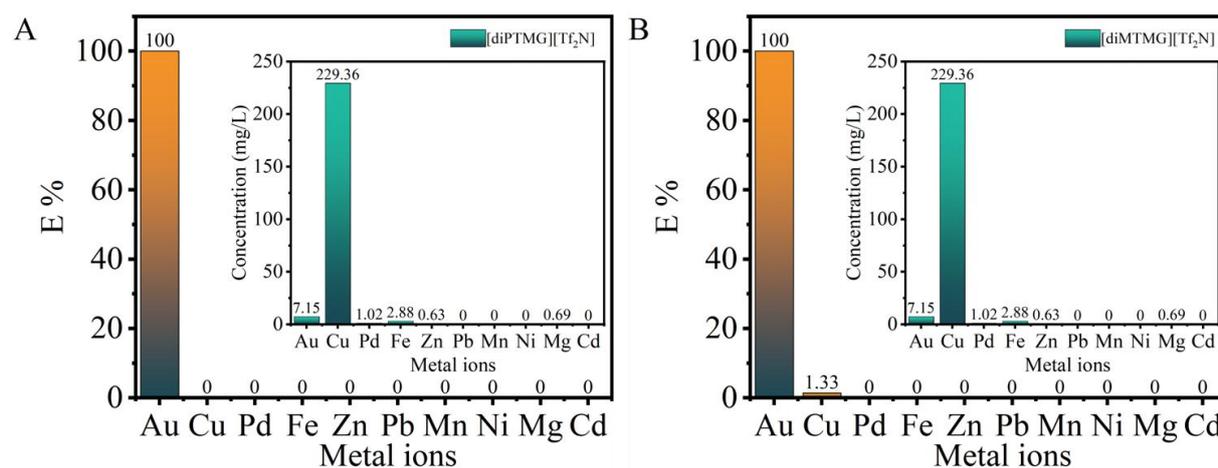
the extraction order of precious metals chlorine complexes is $\text{AuCl}_4^- > \text{PdCl}_4^{2-} > \text{PtCl}_6^{2-}$. $[\text{diMTMG}][\text{Tf}_2\text{N}]$ is an oxygen-containing extractant, belonging to soft base. Therefore, $[\text{diMTMG}][\text{Tf}_2\text{N}]$ is more inclined to exchange ions with Au (III), and has a weak ability to exchange ions with platinum. (2) PdCl_4^{2-} and PtCl_6^{2-} have more charge, while AuCl_4^- has less charge. In other words, the work of ion exchange with PdCl_4^{2-} and PtCl_6^{2-} by ILs is twice that with AuCl_4^- . This means that the ion exchange kinetics of ILs with AuCl_4^- is faster than those of other highly charged chloride complexes. (3) In general, planar tetragonal complexes are easier to extract than octahedral complexes. AuCl_4^- and PdCl_4^{2-} are planar complexes, with which ILs cations easily form ion pairs. The PtCl_6^{2-} complex is a regular octahedral configuration, and the cations of IL are difficult to access for ion exchange. (4) Base metal cations have strong electrostatic repulsion with $[\text{diMTMG}]^+$ and $[\text{diPTMG}]^+$, while AuCl_4^- and the two ILs cations have strong electrostatic attraction. In summary, $[\text{diMTMG}][\text{Tf}_2\text{N}]$ and $[\text{diPTMG}][\text{Tf}_2\text{N}]$ have excellent extraction selectivities for Au(III).



FIGUER 10 (A) Selectivity of $[\text{diPTMG}][\text{Tf}_2\text{N}]$ for noble and base metal ions. (B) Selectivity of $[\text{diMTMG}][\text{Tf}_2\text{N}]$ for noble and base metal ions. ($C_{\text{IL}}=5\text{mmol/L}$, $C_{\text{Au, Mg, Ni, Co, Cu, Fe, Pt, Pd, Pb}}=1\text{mmol/L}$, $C_{\text{HCl}}=0.1\text{mol/L}$, $t=2\text{h}$, $T=298\text{K}$)

3.8 Practical application of gold recovery from e-waste.

In order to verify the practicability of the extractants, the two guanidinium ILs were applied to extract Au(III) from abandoned e-waste. Aqua regia was used to leach e-waste. The obtained leachate was filtered and then diluted 10 times for extraction experiments. By elemental analysis, the leachate contained 229.36ppm of Cu(II), 7.15ppm of Au(III), 2.88ppm of Fe(III), 1.02ppm of Pd(II), 0.69 ppm Mg(II) and 0.63 ppm of Zn(II). As shown in Figure 11, even under the condition of high concentration of copper ions, the extraction rate of Au(III) of the two ILs can reach 100%, and there is almost no extraction of other ions. It is again proved that [diMTMG][Tf₂N] and [diPTMG][Tf₂N] have good selectivities for Au(III).



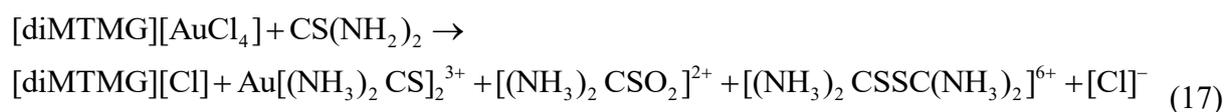
FIGUER 11 Initial concentrations of Cu, Fe, Pd, Mg, Zn, and Au and extraction efficiency of [diPTMG][Tf₂N] (A) and [diMTMG][Tf₂N] (B) toward e-waste leachate. ($C_{IL}=5\text{mmol/L}$, $C_{Cu}=229.36\text{ ppm}$, $C_{Au}=7.15\text{ ppm}$, $C_{Fe}=2.88\text{ ppm}$, $C_{Pd}=1.02\text{ ppm}$, $C_{Mg}=0.69\text{ ppm}$, $C_{Zn}=0.63\text{ ppm}$).

3.9 Stripping and reusability.

The reusability of IL determines the practical benefits it can bring in practical applications. To test the reusabilities of the two ILs, a series of extraction-stripping experiments were

performed. Stripping agents that can form stable complexes with gold are used, including HCl, HNO₃, NH₄Cl, NH₄OH, Na₂SO₃, NaOH, H₂O and CS(NH₂)₂. Table 2 shows the efficiencies of stripping gold from the ILs loaded with Au(III) by different stripping agents. When NaOH was used for stripping agent, the S% for [diMTMG][Tf₂N] and [diPTMG][Tf₂N] were 100.0% and 85.9%, respectively. However, in the strong alkaline environment of NaOH, gold will exist in the form of Au(OH)₄⁻, and it is difficult to carry out the next cycle. When CS(NH₂)₂ was used as the stripping agent, the S% of the two ILs reached 100.0% and 95.5%, respectively. CS(NH₂)₂, as a reducing agent and complexing agent, will first peel AuCl₄⁻ from [diMTMG][AuCl₄⁻]/[diPTMG][AuCl₄⁻], then reduce Au (III) to Au(I). Finally, CS(NH₂)₂ is complexed with Au (I) to form a highly charged water-soluble complex.³³

During extraction process, it is noteworthy that [Tf₂N]⁻ of IL is transferred to the aqueous phase by anion exchange. Two new ILs of [diMTMG][Cl]/[diPTMG][Cl] were formed when CS(NH₂)₂ was used to strip the extract phases containing [diMTMG][AuCl₄] and [diPTMG][AuCl₄], respectively.



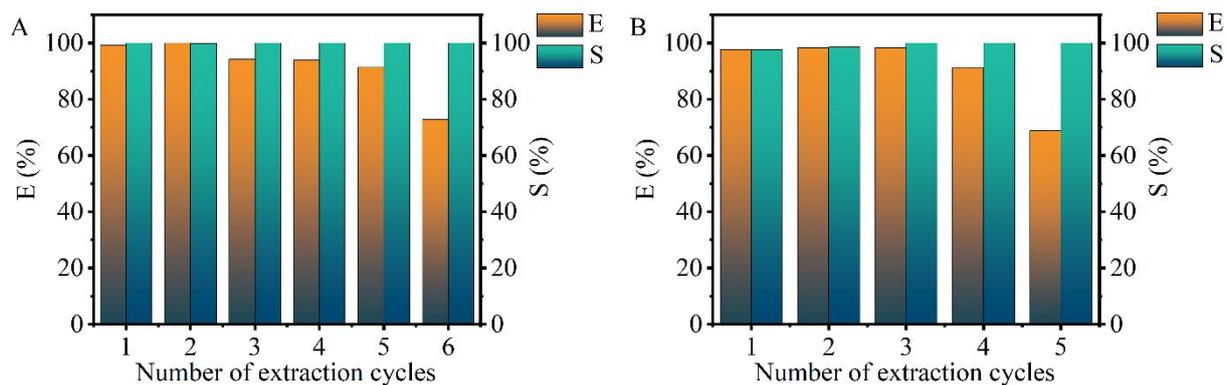
In subsequent reusability experiments, [diMTMG][Tf₂N] and [diPTMG][Tf₂N] can be regenerated by mixing with the raffinate containing [Tf₂N]⁻ anion and the stripping raffinate containing [diMTMG][Cl]/[diPTMG][Cl]. The regenerated ILs were washed three times with deionized water. As shown in Figure 12A, the extraction rate of Au(III) by [diPTMG][Tf₂N] slowly decreases from 99.2% to 72.8% after 6 cycles of

experiments, indicating that [diPTMG][Tf₂N] has good reusable performance. [diMTMG][Tf₂N] has a hydrophilic ether group, which significantly reduces the viscosity of [diMTMG][Tf₂N] while slightly increases their solubility in water. Therefore, [diMTMG][Tf₂N] has a certain loss during the cycle, and after 5 cycles of experiments, the extraction rate is reduced from 97.8% to 68.8%. The schematic illustration of the cycle process for the two ILs towards Au(III) as shown in figure 13.

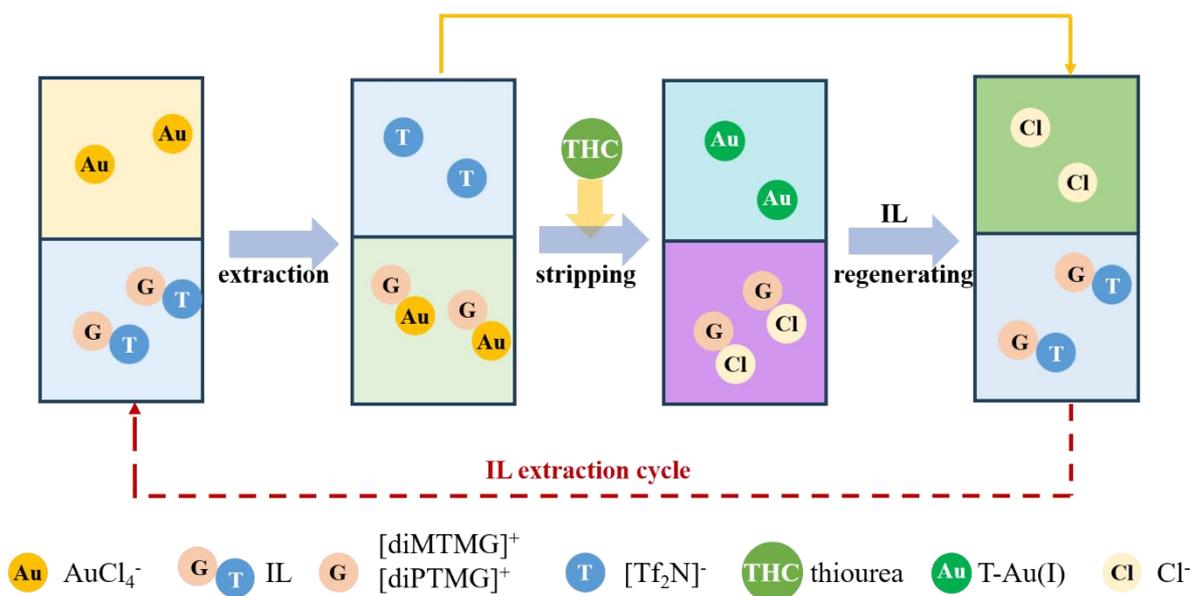
The guanidinium ILs are highly modifiable in structure, and they are usually modified by introducing functional atoms on the N substituent group to improve the extraction ability. Here, the Au(III) extraction properties of [diMTMG][Tf₂N] and [diPTMG][Tf₂N] were compared with those of other ILs. As shown in Table 3, few ILs are used to recover precious metals from actual e-waste, and most of them have slow kinetics. In contrast, [diMTMG][Tf₂N] and [diPTMG][Tf₂N] have the advantages of extremely fast kinetics, high extraction capacities, good selectivities and recycling, and can also efficiently and selectively extract Au(III) from the actual e-waste acid leaching solution.

TABLE 2 Stripping behavior of Au(III) from loaded ILs using different stripping agent

	[diPTMG][Tf ₂ N] (S%)	[diMTMG][Tf ₂ N] (S%)
HCl	0.0	2.0
HNO ₃	0.0	2.2
NH ₄ Cl	24.9	1.1
NH ₄ OH	0.0	2.2
Na ₂ SO ₃	87.2	81.1
H ₂ O	0.0	0.4
NaOH	100.0	85.9
CS(NH ₂) ₂	100.0	95.5



FIGUER 12 (A) Reusability of extracting Au(III) with [diPTMG][Tf₂N] (B) Reusability of extracting Au(III) with [diMTMG][Tf₂N] ($C_{Au(III)}=1\text{mmol/L}$, $C_{IL}=5\text{mmol/L}$, $C_{thiourea}=1\text{mol/L}$, $A/O=1$, $T=298\text{K}$, $t=2\text{h}$)



FIGUER 13 Schematic illustration of the cycle process for [diPTMG][Tf₂N] and [diMTMG][Tf₂N] towards Au(III)

TABLE 3 Comparison of [diMTMG][Tf₂N] and [diPTMG][Tf₂N] with other ILs for recovering Au.

material	maximum capacity (mg/g)	equilibrium time (min)	extraction rate (%)	maximum number of cycles	practical application	Ref.
[diMTMG][Tf ₂ N]	519.4	0.17	99.5	4	E-waste	This work
[diPTMG][Tf ₂ N]	427.9	0.5	99.6	5	E-waste	This work
[Pyr-EA][Tf ₂ N]	524.6	10	99.4	5	CPU	28
[Pyr-Bu][Tf ₂ N]	457.3	10	NA	NA	NA	28
[Pyr-C ₂ OC ₂][Tf ₂ N]	403.5	10	NA	NA	NA	28
[C6-Et-TMEDA-PIP][Tf ₂ N]	390.1	20	98.5	5	NA	34
[EtbetmMor][Tf ₂ N]	447.19	40	98.4	4	NA	24
[Suc][Tf ₂ N] ₂	423.55	2	99.0	5	NA	25
CyIL101	63.45	10	99.0	NA	NA	26
CyIL102	44.79	10	95.0	NA	NA	26

4 CONCLUSIONS

In summary, two guanidinium ILs were successfully prepared and applied to selectively extract Au(III) from hydrochloric acid solutions. The maximum extraction capacities of [diMTMG][Tf₂N] and [diPTMG][Tf₂N] were 519.4mg/g and 427.9mg/g, respectively. The anion exchange mechanism was determined by slope method, Job's method, UV-vis, and ¹³CNMR. Under the optimal conditions, both of [diMTMG][Tf₂N] and [diPTMG][Tf₂N] showed excellent selectivities and extraction capacities for Au(III), and can extract 100% Au(III) from the actual e-waste leach solution. The introduction of O functional atoms can increase the positive charge of the ionic liquid cations, thus enhancing the electrostatic

attraction between AuCl_4^- and $[\text{diMTMG}][\text{Tf}_2\text{N}]$. Therefore, the addition of O atom enhanced the ability of IL to extract Au(III). However, the introduction of O atoms increased the aqueous solubility of $[\text{diMTMG}][\text{Tf}_2\text{N}]$, resulting in a slight decrease in its recycling effect. The two ILs showed excellent kinetic properties for gold extraction, and the extraction equilibrium time was less than 30s. $[\text{diMTMG}][\text{Tf}_2\text{N}]$ and $[\text{diPTMG}][\text{Tf}_2\text{N}]$ have great potential to recover Au(III) from actual e-waste.

AUTHOR CONTRIBUTIONS

Qing Liu: Data curation (equal); formal analysis (equal); investigation (equal); writing—original draft (equal). **Wanru Wang:** Formal analysis (equal); methodology (equal); project administration (equal); writing—review and editing (equal). **Kewen Tang:** Funding acquisition (equal); project administration (equal); writing—review and editing (equal).

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DATA AVAILABILITY STATEMENT

The numerical data from Figures 2-12 are tabulated in Supporting Materials.

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