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Extraction of palladium (II) by a silicone ionic liquid-based microemulsion system from chloride medium

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ABSTRACT

The silicone ionic liquid, 1-methyl-3-[tri-(trimethylsiloxy)]silylpropyl-imidazolium chloride ([Si_4mim]Cl), was first used for the construction of the W/O microemulsion system and the [Si_4mim]Cl/*n*-heptane/*n*-hexanol/NaCl microemulsion system was applied for palladium extraction for the first time. The stability of [Si_4mim]Cl/*n*-heptane/*n*-hexanol/NaCl microemulsion system was characterized by the Turbiscan Lab. For the Pd (II) extraction by the [Si_4mim]Cl/*n*-heptane/*n*-hexanol/NaCl microemulsion system, primary parameters (namely, the vibration time, the [Si_4mim]Cl concentration, the phase ratio and the additives) affecting the palladium extraction was investigated to optimize the process. Under the optimum conditions, the extraction percentage of Pd (II) is up to 98%. Afterwards, the ionic-exchange mechanism of Pd (II) extraction by the [Si_4mim]Cl/*n*-heptane/*n*-hexanol/NaCl microemulsion system was confirmed by the Job Method and analyzed by FT-IR spectra. The stripping of Pd (II) from the microemulsion phase was also studied using the NaCl solutions, indicating a high stripping efficiency. At last, the selectivity of the [Si_4mim]Cl/*n*-heptane/*n*-hexanol/NaCl microemulsion system to Pd (II) from other metals (Cu (II), Co (II), Ni (II), Fe (III), Al (III) Zn (II), Ce (III), Li (I), Mg (II) and Sn (IV)) was demonstrated to be quite high. The results of our work indicate that the [Si_4mim]Cl/*n*-heptane/*n*-hexanol/NaCl microemulsion system is a promising approach for Pd (II) extraction.

1. Introduction

Palladium occupies a relevant place and is widely used with progressively growing demands in jewelries, hydrogen storage [1–3], anti-cancer agent [4–6], catalysis [7–10] and sensors [3,11,12], etc. for its unique physical and chemical properties. However, the nature sources of palladium are very scarce, which implies the recovery and recycle of Pd (II) from the secondary resources become essential to fulfill the worldwide requirements of the critical metal. Currently, as one of vital separation technologies, solvent extraction still plays an important role [13–15] in the separation and purification of Pd (II), for its advantages of rapid kinetics effectiveness, high selectivity, easy recycling and recovery for many extraction processes. But it also has disadvantages of multi-stage cycles, solvent loss, high time consuming and formation of stable emulsions, etc. [16,17].

Microemulsion, formed by surfactant, oil phase and water phase (occasionally need a short-chain alcohol as co-surfactant), is a kind of thermodynamically stable, homogeneous and isotropic solution. Since Hoar and Schulman discovered and denominated microemulsion systems, the theories and applications of microemulsion have obtained substantial development making microemulsion an important and attractive branch of interfacial chemistry. In contrast with conventional solvent extraction systems, microemulsion extraction has several advantages, such as low viscosity, high efficiency, homogeneity, enhanced selectivity, ultralow interfacial tension, low cost and less time consumption, no need of processing at high temperature or pressure [18–20]. In the past decades, ionic liquid-based microemulsion has attracted much attention for combing the advantages of ionic liquids and microemulsion and expanding the potential application of ionic liquids [21]. Ionic liquids, totally consist of cations and anions, are a group of environment benign solvents which attracted much attention for their "green" property, such as non-flammability, no significant vapor pressure, high thermal stability, strong solubility and wide liquid temperature ranges [22–26].

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Among the applications, ionic liquid based-microemulsions have been widely researched as a novel approach for metal ion extractions. For instance, Nguyen et al. have used Cyphos IL 109 as surfactant to construct the microemulsion to extract gold (III) from acidic chloride media and found it efficient for gold (III) recovery [27]. Tong et al. have applied [C_{14}mim]Cl as the extractant and surfactant for gold (III) extraction from hydrochloride acid media and confirmed the anion-exchange mechanism [28]. Though ionic liquids have made great progress in separation, the high viscosity of ionic liquids limits their development. In 2005, Shirota and Castner discovered that the existence of silicon in the cation of ionic liquid could decrease the viscosity [29]. Besides, the introduction of silicon in the cation of the ionic liquids could enhance their hydrophobility and surface activity [30,31]. Up to now, silicone ionic liquids have received increased attention and the properties have been investigated [32–39]. However, the application of silicone ionic liquids has been rarely studied. For example, Li et al. have synthesized [C_4tmsim][PF_6] for mercury extraction and preconcentration and achieved satisfactory consequence [40]. Cheng et al. have first applied [Btmsim][PF_6] for the selective extraction of hemoglobin [41]. However, researches on Pd (II) extraction by ionic liquids with silicon in the cation have not been found in the literature. Also, Pd (II) extraction by microemulsion has not been reported so far.

In our work, the silicone ionic liquid, 1-methyl-3-[tri-(trimethyl siloxy)]silylpropyl-imidazolium chloride ([Si_4mim]Cl), was first applied for the construction of the W/O microemulsion, which was studied on palladium (II) extraction. The structure of [Si_4mim]Cl was shown in Fig. 1. In the extraction system, [Si_4mim]Cl bears the functions of a palladium (II) extractant as well as a surfactant. The influence of several parameters on the palladium (II) extraction was explored to optimize the extraction process. The mechanism of this process was primarily investigated by the Job Method and FT-IR spectra. Meanwhile, the stripping of palladium (II) from the Pd (II)-loaded microemulsion phase and the selectivity of the microemulsion system were also considered.

2. Experiments

2.1. Reagents

γ-Chloropropyltri(trimethylsiloxy)silanewas purchased from Shandong Qiquan Silicon Co., Ltd. 1-Methylimidazole was obtained from Aladdin Chemical Reagent Co., Ltd. Chlorotrimethylsilane, isopropanol and diethyl ether were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. Diethyl ether was distilled from sodium-benzophenone before use. *n*-Heptane and *n*-hexanol were procured from Damao Chemical Reagent Tianjin Corp. (Tianjin, China). The feed solutions were prepared by dissolving metal chlorides in hydrochloric acid solutions: $PdCl_2$, Guangfu Institute of Fine Chemical (Tianjin, China); $CuCl_2{\cdot}2H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, $AlCl_3{\cdot}6H_2O$ and $SnCl_4{\cdot}5H_2O$, Kermel Chemical Reagent Tianjin Co., Ltd. (Tianjin, China). Distilled water was used to prepare the aqueous solutions in all experiments. Distilled water was used to prepare the aqueous solutions in all experiments. All the other chemicals were of analytical or reagent grade and used without further purification.

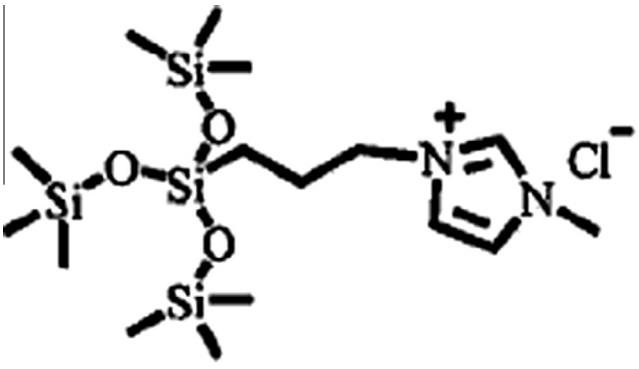

Fig. 1. The structure of [Si_4mim]Cl.

2.2. Methods

2.2.1. Synthesis of [Si_4mim]Cl

The silicone ionic liquid, [Si_4mim]Cl ($C_{16}H_{39}ClN_2O_3Si_4$), was synthesized similarly to the literature [42]. Certain amount of γ-Chloropropyltri(trimethylsiloxy)silane was added to 1-methylimidazole in isopropanol at N_2 atmosphere in a round flask. Afterward, the solution was heated to 95 °C and stirred for 3 days. The solvent was removed by distilling in vacuum. The crude product was dissolved with dry diethyl ether and placed in the refrigerator for 10 h and then the liquid was decanted carefully. Recrystallization was repeated three times. The pure [Si_4mim]Cl was dried at 313 K for more than 3 days in vacuo. The [Si_4mim]Cl was characterized by ^{1}H NMR (Fig. 2) and FT-IR (Fig. 8). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.04–0.11 (m, 27H), 0.41–0.47(m, 2H), 1.84–1.95 (m, 2H), 4.14 (d, 3H), 4.25–4.30 (m, 2H) 7.24 (d, 1H), 7.53 (d, 1H), 10.04 (s, 1H); IR (KBr, cm^{-1}): 3144, 3075, 2958, 2900, 1569, 1254, 1056, 843, 757.

2.2.2. Preparation and stability evaluation of the microemulsion

A certain amount of [Si_4mim]Cl was added into the mixture of *n*-heptane and *n*-hexanol where the volume ratio of *n*-hexanol in the mixtures was 30%. After ultrasonicated to dissolve all the ionic liquid, the mixed organic phase was gradually diluted by NaCl solution until the aqueous phase arose, and then equilibrated for 8 h. Afterward, the microemulsion phase and the NaCl solution were separated and the transparent organic phase was the [Si_4mim]Cl/*n*-heptane/*n*-hexanol/NaCl microemulsion. The microemulsion was centrifugated for 5 min, and no phase separation phenomena were observed, which was used to preliminarily estimate the formation of microemulsion. The stability of the microemulsion was evaluated using a Turbiscan Lab (Formulation, France). The microemulsion was sampled immediately after preparation and the sample was scanned by a light beam emitted in near infrared (880 nm) wavelength. Two synchronous optical sensors received respectively light transmitted through the sample and light backscattered by the sample. The sample in the cell was scanned every 2 min for 2 h at 30 °C. The transmission (T) and the backscattering (BS) in unit time were taken as a measure of the stability of the microemulsions.

2.2.3. Extraction of metal ions

For the metal extractions, certain volumes of the [Si_4mim]Cl/*n*-heptane/*n*-hexanol/NaCl microemulsion and the aqueous solution containing Pd (II) or mixed metal ions (Cu (II), Co (II), Ni (II), Fe (III), Al (III) Zn (II), Ce (III), Li (I), Mg (II) and Sn (IV)) were added to a glass tube and then equilibrated mechanically in an orbital shaker for 10 min. Afterward, the microemulsion phase and the aqueous phase were separated quickly by centrifuge at 2000 rpm for 2 min. The separated microemulsion phase and aqueous phase were both clear and transparent. Before and after Pd (II) extraction, the Pd (II) concentration in the aqueous phase was determined by an atomic absorption spectrophotometer (3150, Precision & Scientific Instrument Shanghai Co., Ltd., Shanghai, China). Other metal ion (Cu (II), Co (II), Ni (II), Fe (III), Al (III) Zn (II), Ce (III), Li (I), Mg (II) and Sn (IV)) concentrations in solutions were determined by an inductively coupled plasma atomic emission spectrometer (IRIS Intrepid II XSP, Thermo Electron Corp., Boston, MA, USA). Then the