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A 1-dodecanethiol-based phase transfer protocol for the highly efficient extraction of noble metal ions from aqueous phase

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ABSTRACT

A 1-dodecanethiol-based phase-transfer protocol is developed for the extraction of noble metal ions from aqueous solution to a hydrocarbon phase, which calls for first mixing the aqueous metal ion solution with an ethanolic solution of 1-dodecanethiol, and then extracting the coordination compounds formed between noble metal ions and 1-dodecanethiol into a non-polar organic solvent. A number of characterization techniques, including inductively coupled plasma atomic emission spectroscopy, Fourier transform infrared spectroscopy, and thermogravimetric analysis demonstrate that this protocol could be applied to extract a wide variety of noble metal ions from water to dichloromethane with an efficiency of >96%, and has high selectivity for the separation of the noble metal ions from other transition metals. It is therefore an attractive alternative for the extraction of noble metals from water, soil, or waste printed circuit boards.

Introduction

Noble metals, *e.g.*, gold, silver, rhodium and palladium, have been extensively used in many applications such as catalysis, electronics, optical, anti-corrosion materials and jewelry (Duan and Wang, 2013; Kowlgi et al., 2011; Lam et al., 2008; Roduner, 2006; Fontàs et al., 2002; Fricker, 1996), because of their unique chemical and physical properties (Swain et al., 2010). These applications have increased the demand for noble metals, whereas the natural resources are scarce (Swain et al., 2010; Lam et al., 2008; Begerow et al., 1997). Therefore, it is necessary to develop various methods for recycling and separation of noble metals from diverse secondary resources (Ahamed et al., 2013; Cieszynska and Wiśniewski, 2012). Solvent extraction (also called liquid–liquid extraction) is considered to be one of the most effective techniques for recycling of noble metal ions from their metal aqueous solutions (Cieszynska and Wiśniewski, 2010; Regel-Rosocka et al., 2007). Indeed, liquid–liquid extraction for noble metal ions has been known and used for many years. The examples include electrostatic interaction based extraction of gold(III) ions from an aqueous solution to a hydrocarbon phase (toluene) by means of a chemical agent, such as tetraoctylammonium bromide (Brust et al., 1994, 1995), Cyanex 301 based extraction of Ag(I) ions from aqueous HNO_3 solution to hexane (Shi et al., 2005, 2006), ionic liquid-based extraction of noble metal ions (Ag(I), Pd(II), and Au(III)) from their aqueous solutions (Lee, 2012), selective extraction of Pd(II) from hydrochloric acid solutions to toluene with phosphonium extractants (Cieszynska and Wiśniewski, 2011), and separation and recovery of gold(III) from base metal ions using melamine–formaldehyde–thiourea chelating resin (Aydin et al., 2008). However, these methods usually make use of complex ligands to facilitate the metal ion extraction, and have only been applied to specific systems. Therefore, a universal and facile approach to extract ions for a sufficiently wide spectrum of noble metals is still lacking and poses significant challenges.

In the present work, we demonstrate a general phase transfer protocol, which is based on 1-dodecanethiol (DDT), for the highly

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efficient extraction of noble metal ions from aqueous phase to a non-polar organic medium. This protocol involves mixing the aqueous solution of noble metal ions with an ethanolic solution of DDT, and extracting the coordinating compounds formed between metal ions and DDT into dichloromethane. A number of characterization techniques, including inductively coupled plasma atomic emission spectroscopy (ICP-AES), Fourier transform infrared spectroscopy (FT-IR), and thermogravimetric analysis (TGA) were used to characterize the coordinating compounds formed between noble metal ions and DDT, and to address the following critical issues: (1) the transfer efficiency of noble metal ions; (2) the transfer mechanism of this DDT-based protocol; and (3) the selectivity of this phase transfer protocol for the extraction of noble metal ions.

1. Experimental section

1.1. Chemicals

Silver nitrate ($AgNO_3$, ACS reagent, ≥99.0%), gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, ACS reagent, ≥49.0% Au basis), ruthenium(III) chloride trihydrate ($RuCl_3 \cdot 3H_2O$, technical grade), rhodium(III) chloride ($RhCl_3$, 98%), sodium tetrachloropalladate(II) (Na_2PdCl_4, 98%), iron(III) chloride ($FeCl_3$, 97%), zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, ≥99.0%), and osmium(III) chloride ($OsCl_3$, 99.9% trace metals basis) were purchased from Sigma-Aldrich (St. Louis, USA). DDT (98.0%) was from J&K Chemical (Bei Jing, China). Ethanol (>99.7%) and dichloromethane (>99.5%) were purchased from Beijing Chemical Works (Bei Jing, China). Deionized water was distilled by a Milli-Q Ultrapure-water purification system. All glassware and Teflon-coated magnetic stirring bars were cleaned with aqua regia, followed by copious rinsing with deionized water before drying in an oven.

1.2. Phase transfer of noble metal ions from aqueous phase to dichloromethane

In a typical experiment, 50 mL of 1 mmol/L aqueous metal salt solution of Ag(I), Au(III), Os(III), Rh(III), Pd(II), or Ru (III) was mixed with 50 mL of ethanol containing 1 mL of DDT. After 5 min of vigorous stirring, 50 mL of dichloromethane was added and stirring was continued for 10 min. Phase transfer of metal ions from water to dichloromethane would then occur quickly and completely, as evident by the complete color bleaching of the aqueous phase. Assuming complete transfer of the metal ions from water, the metal ion concentration in dichloromethane would be 1 mmol/L. The metal ions in dichloromethane were separated from the aqueous phase, and collected for further characterization. The aqueous phase remaining was analyzed by ICP-AES to determine the transfer efficiency of the different kinds of noble metal ions.

1.3. Characterization

Concentrations of the initial and final metal ions in aqueous phases were analyzed with ICP-AES (Optima 5300DV, Perkin Elmer, Waltham, Massachusetts, USA) to determine the transfer efficiency of noble metal ions from aqueous phase to dichloromethane. The interaction between DDT and noble metal ions was confirmed by FT-IR spectra recorded on a Alpha-T spectrometer (Bruker, Ettlingen, Germany) using a KBr pellet technique. TGA was carried out on a SAT449F3 Jupiter instrument (Netzsch, Sleb, Germany) from room temperature to 1073 K at a heating rate of 5 K/min under N_2 atmosphere with a flow rate of 20 mL/min. The sample (4 mg) was heated in a standard platinum sample pan.

2. Results and discussion

2.1. Extraction of noble metal ions by phase transfer

The phase transfer of noble metal ions has not only been widely used as an important step for the synthesis of metal nanomaterials (Yang et al., 2011), but is also of great interest for applications in environmental remediation, such as the extraction of heavy metals from water and soil (Roundhill, 2001). If an aqueous solution of noble metal salt was directly contacted with dichloromethane containing DDT, the noble metal ions would not be transferred to the dichloromethane phase. Prolonged agitation only resulted in a turbid mixture, but no ion transfer took place after the mixture was settled down into two immiscible layers in a separating funnel. As the interaction between metal ions and DDT could only occur at the interface between water and dichloromethane, the failure to transfer the metal ions might be the result of poor contact between the two phases because of their lack of mutual solubility. However, the transfer of noble metal ions could take place using ethanol as an intermediate solvent, based on the fact that water and ethanol are completely miscible and maximum contact between the noble metal ions and DDT would be ensured. The phase transfer photographs of Ag(I), Pd(II), Ru(III), Rh(III), and Au(III) noble metal ions are exhibited in Fig. 1, which display the complete bleaching of the upper aqueous phase (the density of dichloromethane is greater than water), implying the successful transfer of these noble metal ions from the aqueous phase to dichloromethane.

The transfer efficiency (TE) and the distribution ratio (DR) in two phases after transfer could be calculated using the following equations:

$$\mathrm{TE} = \left([M^{n+}]_i - [M^{n+}]_f\right) \Big/ [M^{n+}]_i \times 100\% \tag{1}$$

$$\mathrm{DR} = \mathrm{TE}/(100 - \mathrm{TE}) \tag{2}$$

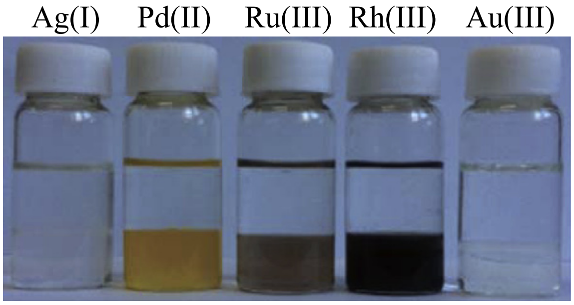

Fig. 1 – Photographs showing the successful transfer of Ag(I), Pd(II), Ru(III), Rh(III) and Au(III) metal ions from the aqueous phase to dichloromethane.