

A new room temperature ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate as a solvent for extraction and preconcentration of mercury with determination by cold vapor atomic absorption spectrometry

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Abstract

A new room temperature ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate abbreviated as [C₄tmsim][PF₆] was synthesized and developed as a novel medium for liquid/liquid extraction of inorganic mercury in this work. Under optimal condition, *o*-carboxyphenyldiazoamino-*p*-azobenzene abbreviated as CDAA reacted with inorganic mercury to form a neutral Hg–CDAA complex, the complex was rapidly extracted into ionic liquid phase. After back-extracting into aqueous phase with sulfide sodium solution, the mercury concentration was detected by cold vapor atomic absorption spectrometry. The extraction and back-extraction efficiencies were 99.9 and 100.1% for 5.0 μg L⁻¹ standard mercury in 1000 mL of water solution, respectively. The detection limit, calculated using three times the standard error of estimate of the calibration graph, is 0.01 ng of mercury per milliliter water sample. The proposed method has been used to the determination of trace inorganic mercury in natural water with satisfactory results. Moreover, Zeta potential and surface tension of [C₄tmsim][PF₆] solution were measured and applied to explain the extraction mechanism of [C₄tmsim][PF₆] system.

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1. Introduction

Mercury is a global pollutant and is identified as a highly toxic element because of its accumulative and persistent character in the environment and living organisms. Therefore, routine monitor and control of mercury is becoming increasingly important, especially in water system. In literatures, many modern technologies such as atomic absorption/emission spectrometry [1,2], inductively coupled plasma mass spectrometry [3,4], atomic fluorescence spectrometry [5] and voltammetric determination [6] have been reported to the determination of trace mercury, but these methods are difficult to directly apply to the determination of trace mercury in natural water due to their limited sensitiv-

ity. Recent years, professor Wang and Hansen developed many sample separation and preconcentration procedures based on the solvent extraction. The solvent extraction can effectively decrease the detection limit and eliminate matrix interference, these coupling above methods have been applied to determination of ultra-trace level heavy metals [7–9]. However, the use of classical extraction method requires large amounts of high purity solvents for the extraction, this may also result environmental and safety problems due to volatilization of the solvents

Room temperature ionic liquid has aroused increasing interest for their promising role as alternative medium in synthesis [10], separation [11,12] and electrochemistry [13] as a result of their unique chemical and physical properties [14]. As ionic liquids have no detectable vapor pressure and are relatively thermal stable, hence many environmental and safety problems associated with organic solvents are avoided. Recently, the applications of ionic liquid in analytical chemistry have also

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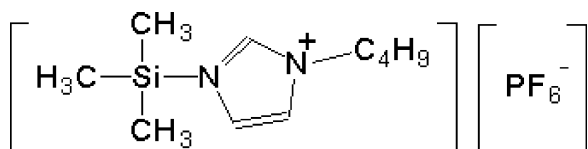


Fig. 1. The molecule structure of [C₄tmsim][PF₆].

started to receive attention [15–19], in which a typical room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate abbreviated as [C₄mim][PF₆] was often studied as extraction medium [20]. Because the volume of the sample is usually smaller than 5 mL in the most of previous works, the enrichment effect usually was not very ideal. In this study, we attempt to use [C₄mim][PF₆] as solvent for the extraction of inorganic mercury in a relatively large water sample (1000 mL of water). It was found that the extraction efficiency of the inorganic mercury is very low due to its relatively high water solubility when the volume of [C₄mim][PF₆] was smaller than 25 mL. In order to resolve the problem, a new room temperature ionic liquid, 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate abbreviated as [C₄tmsim][PF₆], was designed and synthesized in the laboratory (shown in Fig. 1). Experiment indicated that [C₄tmsim][PF₆] has much lower water solubility (0.5 g L⁻¹) than [C₄mim][PF₆] (18 g L⁻¹), but also can extract the mercury complex more effectively. So, [C₄tmsim][PF₆] can be used as an excellent solvent for liquid/liquid extraction of trace mercury in a relatively large volume samples.

o-Carboxyphenyl diazoamino *p*-azobenzene abbreviated as CDAA is a sensitive and selective chromogenic reagent for spectrophotometric determination of mercury [21]. Unlike dithizone, CDAA reacts with inorganic mercury to form a stable complex, which do not react with organic mercury in the same conditions, the reaction condition is simple and easy to control. Therefore in this work CDAA was employed as chelator to form a neutral mercury complex to evaluate the [C₄tmsim][PF₆] extraction system. After the preconcentration, cold vapor atomic absorption spectrometry was used to as a detection method for the determination of trace mercury in natural water. Proposed method offers the advantages of rapidity, simplicity and high sensitivity without the need for potentially toxic organic solvent.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade and ultra pure water (18.2 MΩ cm) was used throughout the experiment. A stock solution of 1.0 mg mL⁻¹ mercury(II) was prepared by dissolving appropriate amounts of analytical reagent grade Hg(NO₃)₂ in 2% nitric acid solution. Working solutions were prepared immediately before use. All glassware used was soaked with 10% nitric acid for 1 day and rinsed with ultra pure water before use. The chelating agent, CDAA was purchased from Shanghai Zhongke Chemical Limit Company (Shanghai, China). A 1.0 × 10⁻³ mol L⁻¹ CDAA solution was prepared by dissolving appropriate amounts of CDAA in 95% ethanol. 1-

Trimethylsilylimidazole was provided by Linhai Kaile Chemical Company (Linhai city, China), and other all reagents employed were purchased from Shanghai Chemical Company (Shanghai, China).

2.2. Apparatus

The mercury measurements were performed with a Perkin-Elmer 2380 atomic absorption spectrometer, equipped with a deuterium background corrector, a hollow cathode mercury lamp, a PE3030 mercury vapor generator with MHS-20 hydride atomizer. A UV-240 spectrophotometer (Shimadzu, Tokyo) was used for recording the UV spectra. A DRX-500 nuclear magnetic resonance (NMR) spectrometer was used for ¹H NMR and ¹³C NMR analyses (Bruker, Russ, Germany).

2.3. Preparation of ionic liquid

Transfer equal amounts (0.5 mol) of 1-bromobutane and 1-trimethylsilylimidazole (distilled freshly) to 500 mL round bottom flask which is fitted with reflux condenser and nitrogen protecting facilities. Add 50 mL of toluene to the flask as solvent. After the mixture was stirred at 70 °C for 18 h, a transparent viscous product, 1-butyl-3-trimethylsilylimidazolium bromide was formed. The liquid was cooled and transferred to a 2000 mL beaker. And then 500 mL of potassium hexafluorophosphate (0.5 mol) was added to the well stirred mixture. After the addition of the reagent, the mixture was continuously stirred for 4 h. And then the water phase was discarded and the formed ionic liquid [C₄tmsim][PF₆] was washed with water until bromide ion was wiped off completely using a silver nitrate test. The collected ionic liquid was heated to 110 °C under vacuum to remove water, the solvent and unreacted reagents, total yield was about 80%. The NMR data of the product were listed in the following: ¹H NMR (500 MHz, CD₃OCD₃), 0.454 (s, 9H), 0.886 (t, 3H), 1.316 (m, 2H), 1.862 (m, 2H), 4.24 (m, 2H), 7.495 (d, 1H), 7.661 (d, 1H), 8.64 (d, 1H); ¹³C NMR (500 MHz, CD₃OCD₃), 136.74, 123.78, 122.93, 50.72, 32.96, 20.46, 14.14, 14.11.

2.4. Measurement extraction efficiencies of the complex and CDAA

A 1000 mL of the synthesized water sample containing 5 μg of standard mercury and 1.0 × 10⁻⁶ mol L⁻¹ CDAA was used to investigate extraction efficiencies of the complex. After addition of 5 mL [C₄tmsim][PF₆] to above solution, the biphasic system was shaken to ensure it was fully mixed. Wait until the phase separation complete, the upper aqueous phase was taken out and the concentration of mercury that was left in the aqueous phase was measured by cold vapor atomic absorption spectrometry. The extraction efficiencies of the complex abbreviated as *E_c* were calculated by *E_c* (%) = (C₀ - C₁)/C₀ × 100, where C₀ and C₁ are the concentration of mercury in aqueous phase before and after extraction, respectively. The extraction efficiency of CDAA was determined using a similar preparation procedure, but without the addition of standard mercury. Absorption spectrum of the aqueous phase was measured on the spectrophotometer against

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