

Novel CO₂-soluble pyridine derivatives and the extraction of heavy metals into Sc-CO₂

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Abstract

New CO₂-soluble, 4-aminopyridine derivatives (**3a–f**) for use as chelating agents were designed and synthesized from the parent compound 4-aminopyridine (**1**) by simple chemical modifications and tested for solubility and metal ion extraction ability in supercritical CO₂ (Sc-CO₂). All of the newly prepared derivatives showed much higher solubility in Sc-CO₂ than the corresponding 4-aminopyridine parent compound, and good or moderate extraction efficiencies for several metal ions (Cu²⁺, Co²⁺, Zn²⁺, and Sr²⁺) in 50–90% yield under different conditions, such as temperature, ligand:co-ligand ratio, extraction time, and CO₂ pressure. Interestingly, it was observed that *N*-(4-pyridyl)pentadecafluorooctanamide (**3f**) with the ‘CO₂-philic’ fluoroalkyl moiety had the lowest CO₂ solubility among the new amide-group-containing pyridine derivatives (**3a–f**), possibly owing to stronger self-interaction. The highest extraction efficiency, especially for copper ions (91%), was achieved with *N*-hexyl-*N*-(4-pyridyl)octanamide (**3e**) including a tertiary amide group with only nonfluorous alkyl chains. It is proposed that a tertiary amide group can be considered as a new ‘CO₂-philic’ moiety.

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1. Introduction

Supercritical fluids have become promising alternative solvents for separation and extraction processes in the last two decades because of strengthened environmental legislation that restricts the use of conventional solvents [1,2]. By far the most commonly used supercritical fluid is carbon dioxide (CO₂), because it is nontoxic, inexpensive, environmentally benign, readily available in relatively pure form, and has moderate critical constants ($T_C = 31.1\text{ }^\circ\text{C}$, $P_C = 73.8\text{ bar}$). Due to its superior mass transfer properties, easy recycling, and the lack of secondary waste formation during its use, supercritical carbon dioxide (Sc-CO₂) has been extensively studied as an extraction solvent for metals [3]. Though Sc-CO₂ has been applied successfully for the extraction of organic compounds in industry [4], direct extraction of metal ions using neat Sc-CO₂ was found to be inefficient, owing to the charge neutralization requirement and the weak solute–solvent interaction [3]. A solution

to this problem is to add a CO₂-soluble organic chelating agent; if chosen properly, this will produce a metal complex that can be extracted easily into Sc-CO₂ from sample matrices [5–8]. A great deal of organic chelating compounds have been investigated as metal ion extractants, for example, dithiocarbamates [7–9], β -diketones [6,10,11], organophosphorous reagents [2,12,13], macrocyclic compounds [14,15] and fluorinated surfactants [7–9,16]. Most of these compounds have been found to be satisfactory candidates for metal extraction in Sc-CO₂. Among them, organophosphorous reagents have attracted much interest from both the academic and industrial communities because of their commercial availability and their promising extraction performance in a variety of solid and liquid sample matrices. However, the design and synthesis of highly CO₂-soluble, often called as ‘CO₂-philic’, and selective chelating agents for highly efficient extraction of metals in Sc-CO₂ is still a great challenge.

High CO₂ solubility of the chelating agent plays an important role during the extraction or separation process because low CO₂ solubility is a significant obstacle for the employment of the chelating agent in this medium. According to references, the designed molecules containing ‘CO₂-philic’ moieties provide

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excellent solubility behavior. Several kinds of CO₂-soluble functional groups have been studied, such as fluoroalkyls [6,9,17], siloxanes [16], perfluorinated ethers and esters [18,19], normal carbonyls, and ethers [20,21]. Among these CO₂-soluble groups, the fluorinated compounds have drawn more attention than others. Generally, pyridine and its derivatives are used in the synthesis of functional compounds and are suitable ligands for the *d*-transition metal ions [22]. Extraction studies with these compounds related to Fe(II) [23], Ni(II) and Co(II) [24], and especially Cu(II) [25] are more prominent than one with other chelating agents.

We have designed and synthesized highly CO₂-soluble chelating agents for the development of the efficient supercritical CO₂ metal extraction by modifying conventional chelating agents with 'CO₂-philic' moieties, such as carbonyl, ether, fluoroalkyl, or amide groups. In this report, we describe the synthesis and evaluation of a series of amide-group-containing pyridine derivatives that contain fluorinated or nonfluorinated alkyl chains of amide group in the 4-position of pyridine. Comparison of tertiary amide group moiety with secondary amide group moiety of amide-group-containing pyridine derivatives for CO₂ solubility and the extraction of copper, cobalt, zinc and strontium with newly prepared pyridine derivatives into Sc-CO₂ are described.

2. Apparatus and materials

All manipulations involving air- or moisture-sensitive chemicals were carried out under nitrogen. Ethanol was treated with Mg/I₂ and refluxed for 6 h before use; methylene chloride (MC) was dried over anhydrous MgSO₄ and then distilled; acetone was dried with anhydrous CaSO₄ and then distilled. 4-Amino pyridine (98%), octanal (99%), hexanal (98%), butyraldehyde (99.5%), pentadecafluorooctanoyl chloride (97%), heptafluorobutyl chloride (98%), octanoyl chloride (99%), heptafluorooctanesulfonic acid tetraethylammonium salt (perfluorooctanesulfonic acid tetraethylammonium salt, PFOSANEt₄) (98%) and triethylamine (99.5%) were purchased from Aldrich Chemicals. Five percent Pd/C was purchased from Fluka Corp. All other reagents and solvents were obtained from commercial sources and used as received without further purification unless stated otherwise. NMR experiments were performed with a JEOL AL-300 (300 MHz for ¹H NMR and 75 MHz for ¹³C NMR) and JEOL ECX-400 (376 MHz for F NMR) spectrometer, and the chemical shifts were recorded with respect to TMS as an internal reference. FT-IR experiments were conducted on a JASCO FT/IR-430 spectrometer. Mass spectra were recorded with a JEOL JMS-AX-505WA apparatus, and metal analyses were carried out with an inductively coupled plasma spectrometer (Direct Reading Echelle ICP).

3. Apparatus for solubility test and metal extraction in Sc-CO₂

A variable-volume view cell with two sapphire windows ($V_{\min} = 10$ mL, $V_{\max} = 20$ mL, 0.2 mL/rotation; Hanwoul Eng., Korea) was used to continuously determine solubility points of

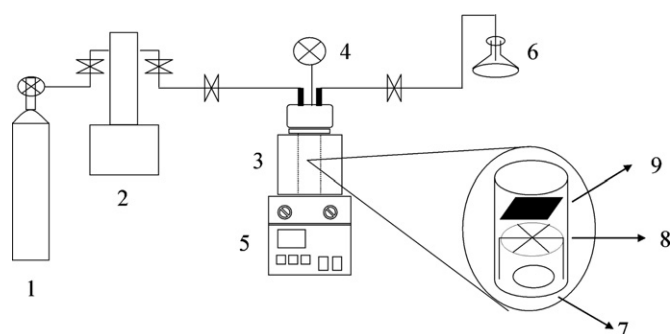


Fig. 1. Schematic diagram of experimental setup for metal extraction in supercritical CO₂. (1) CO₂ tank, (2) syringe pump, (3) extraction cell, (4) pressure gauge, (5) magnetic stirrer and heater, (6) collecting vial, (7) magnetic bar and chelating reagent, (8) wire netting and (9) filter paper.

each extractant in the high-pressure medium. A compound was placed into the cell using a micropipette or weighing paper, and the cell was sealed tightly. After heating to the desired temperature, CO₂ was introduced by a syringe pump (260D, ISCO, USA) from a liquid CO₂ cylinder (99.95% purity, Air Tech., Korea). When a single phase was observed at a fixed pressure, we slowly decreased the pressure until two phases appeared at a fixed temperature. The solubility point could be determined visually through sapphire windows placed on both sides.

The extraction specimen was a piece of filter paper (Whatman 2, 1 cm × 1 cm), loaded with an aqueous solution of metal ions (Cu²⁺, Co²⁺, Zn²⁺, and Sr²⁺) and then dried. A 1000 ppm reference solution for atomic absorption spectroscopy for each ion was used to prepare the metal solution, and there was 10 ng of each ion. Additional water (10 μL) was added to the specimen before each experiment.

Extractants (PFOSANEt₄ and pyridine-type chelating agent) were added to the high-pressure stainless cell (10 mL, Hanwoul Eng., Korea) along with the filter specimen and 10 μL water. The interior of the cell was separated into two parts by wire netting; the extractant and a magnetic stir bar were in the bottom, and the specimen was placed on the wire netting to avoid contacting with ligands and magnetic bar directly. Liquid CO₂ was then pressed into the cell by a syringe pump until an assigned pressure was obtained (Fig. 1). After the extraction period, ICP analysis was performed following an acid digestion with HNO₃ (1 M aq.). The extraction recovery was determined by calculating the difference in concentration of metal ions in the specimen before and after extraction.

4. Preparation of new pyridine derivatives

The general procedure for the synthesis of pyridine-type chelating ligands is as follows (Scheme 1). Preparation of 4-(*n*-octylamino)-pyridine (**2a**), 4-(*n*-hexylamino)-pyridine (**2b**) and 4-(*n*-butylamino)-pyridine (**2c**) was completed according to a procedure modified from the literature [26]. A typical procedure for the synthesis of 4-(*n*-alkylamino)-pyridine derivatives (**2a–c**) is as follows: to a high-pressure stainless cell were added 4-aminopyridine (1 mmol), the corresponding aldehyde (3 mmol),

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