Highly CO₂-soluble 5-Amido-8-hydroxyquinoline Chelating Agents for Extraction of Metals in Sc-CO₂

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Novel CO₂-soluble 8-hydroxyquinoline (8-HQ) chelating agents were synthesized and evaluated for solubility and metal ion extraction ability in supercritical CO₂ (Sc-CO₂). Among them, secondary amide-containing 8-HQ derivatives cannot be dispersed well into Sc-CO₂, but tertiary amide-containing derivatives can dissolve completely in Sc-CO₂ even at low CO₂ pressures, perhaps owing to the predominant intermolecular interaction between the chelating agent and the CO₂ molecule. Based on 8-HQ chelating agent solubility data, we investigated the extraction of metal ions (Co²⁺, Cu²⁺, Sr²⁺, Cd²⁺, and Zn²⁺) using two highly CO₂-soluble 8-HQ derivatives (4d, 4e) in Sc-CO₂. The extraction efficiency of tertiary amide-containing 8-HQ ligands, both fluorinated and non-fluorinated forms, was dramatically increased in the presence of diethyl amine (organic base). We suggest that diethyl amine could play an important synergistic role in the stronger metal binding ability of 8-HQ through an in situ deprotonation reaction in Sc-CO₂ medium.

Key Words: CO₂-soluble chelating agent, Supercritical CO₂, Metal extraction, 8-Hydroxyquinoline derivatives, Synergistic effect

Introduction

From the viewpoint of “green process”, supercritical fluid extractions (SFE) have attracted much more attention than conventional solvent extractions both academically and industrially, because of the ever-increasing regulations on the use of conventional solvents. Carbon dioxide (CO₂) is extensively used in SFE technology because of its non-toxicity, low cost, superior mass transfer properties, easy recyclability, and moderate critical constants (Tc = 31.1 °C, Pc = 73.8 bar). Extraction of organic compounds in Sc-CO₂ has already been confirmed to be successful in industry. However, because of the low solubility of metal ions and conventional metal chelating agents, direct extraction of metals into Sc-CO₂ is still highly inefficient. If a suitable CO₂-soluble chelating agent is added and binds metal ions to form a CO₂-soluble metal complex in situ, the resulting complex can be dissolved and hence easily extracted into Sc-CO₂ from sample matrices. As a result, highly CO₂-soluble chelating agents are required for efficient metal extraction in Sc-CO₂.

Recently, in an attempt to find readily available and highly efficient chelating agents for removal of metals from matrices in Sc-CO₂, various compounds were tested, and some of these appeared to have potential for real application, such as dithiocarbamates, β-diketones, organophosphorous reagents, macrocyclic compounds, and fluorinated surfactants. To choose appropriate chelating agents for use in Sc-CO₂, good CO₂-solubility and chemical stability are obviously required because low CO₂ solubility and chemical instability have been significant obstacles for the employment of chelating agents in Sc-CO₂. Of the previously-known metal chelating agents, 8-hydroxyquinoline (8-HQ) is interesting as it can produce stable metal complexes with various metal ions in organic solvents. Nevertheless, until now only a few studies have focused on metal extraction with 8-HQ or its derivatives in Sc-CO₂. It was found that metal extraction with 8-HQ in pure Sc-CO₂ could not provide satisfactory results (< 50% yield by analysis). However, good metal extraction efficiency with methanol as a co-solvent has been achieved, which could be explained by the enhanced polarity and dispersing property of CO₂ in the presence of methanol.

Recently, we have been involved in the development of in situ-chelation supercritical CO₂ extraction without co-solvent. Therefore, we have already designed and synthesized various highly CO₂-soluble chelating agents, which are amide-group-containing pyridine derivatives containing fluorinated or non-fluorinated alkyl chains on the amide group in the 4-position of the pyridine ring. We observed that all of these compounds were CO₂-soluble and therefore suitable for metal extraction investigations. In this paper, we describe the synthesis and evaluation of novel CO₂-soluble amide-group-containing 8-HQ chelating agents for the extraction of several metal ions (Co²⁺, Cu²⁺, Sr²⁺, Cd²⁺, and Zn²⁺) into CO₂. In particular, the synergistic effect of diethyl amine (DEA) on enhancing the metal extraction efficiency of 8-HQ chelating agents in Sc-CO₂ is described.

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. 8-Hydroxy-5-nitroquinoline (96%), tert-
butyldimethylsilyl chloride (97%), hexanal (98%), pentadecafluorooctanoyl chloride (97%), heptafluorobutryl chloride (98%), octanoyl chloride (99%), heptadecafluorooctanesulfonic acid tetraethylammonium salt (perfluorooctanesulfonic acid tetraethylammonium salt, PFOSANEt4) (98%), tetrabutylammonium fluoride (1.0 M in THF), sodium cyanoborohydride (95%), triethylamine (99.5%), and diethylamine (99.5%) were purchased from Aldrich Chemicals. Five percent (5%) Pd/C and imidazole (99%) were purchased from Fluka Corp. All other reagents and solvents were readily obtained from commercial sources, and used as received without further purification unless stated otherwise. UV spectra were recorded on a MultiSpec-1501 spectrometer. NMR experiments were performed with a JEOL AL-300 (300 MHz for 1H-NMR and 75 MHz for 13C-NMR) spectrometer, and chemical shifts were recorded with respect to TMS as an internal reference. FT-IR experiments were conducted on a JASCO FT/IR-430 spectrometer. Metal analyses were carried out with an inductively coupled plasma spectrometer (Direct Reading Echelle ICP). GC/Mass spectra were obtained from a HP 6890 plus GC/HP 5973 MSD.

Apparatus for Solubility Testing and Metal Extraction. The apparatus for solubility testing and metal extraction have been described in our former work.20,21 A brief introduction is given here. A compound was charged in a variable-volume view cell equipped with two sapphire windows (V_{min} = 10 mL, V_{max} = 20 mL, 0.2 mL/rotation; Hanwoul Eng., Korea) by a micropipette, and the cell was sealed tightly. After heating to the desired temperature, CO2 was pressed into the cell 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, the pressure was decreased slowly 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 × 1 cm), loaded with an aqueous solution of metal ions, which was subsequently dried. A reference solution (1000 ppm) for atomic absorption spectroscopy was used to prepare the metal solution, and the loading amount was 10 μL. Additional water (10 μL) was added to the specimen before each experiment. Extractants, including ligand and co-ligand (PFOSANEt4), were added to the high-pressure stainless cell (10 mL, Hanwoul Eng., Korea) along with the filter paper specimen and 10 μL water (shown in Fig. 1). After completion of extraction, ICP analysis was performed after an acid digestion of the extraction with HNO3 (1 M aq.). Extraction recovery was determined by calculating the difference in concentration of metal ions in the specimen before and after extraction.

Synthesis of 8-HQ Derivatives. The general procedure for the synthesis of 8-HQ derivatives is described in Scheme 1.

8-tert-Butyldimethylsiloxy-5-nitroquinoline (1): Ten mL of dry methylene chloride (MC) containing tert-butyldimethylsilyl chloride (0.87 g, 5.79 mmol) was added to a solution of 8-hydroxy-5-nitroquinoline (1 g, 5.26 mmol) and imidazole (0.38 g, 5.52 mmol). The mixture was stirred for 10 h at room temperature (rt). The solution was then diluted with diethyl ether (50 mL) and washed with 1 M HCl (5 mL), brine (10 mL), and water (10 mL). The organic phase was dried over anhydrous Na2SO4 and evaporated. The resulting residue was purified by recrystallization (methanol: MC = 1:40) to provide a green crystalline solid. Yield: 90%, R_{f} = 0.72 (ethyl acetate:hexane = 1:4). 1H-NMR (CDCl3, 300 MHz): δ 0.0 (br s, 6H), 0.74 (br s, 9H), 6.84 (d, J = 8.6 Hz, 1H), 7.31 (dd, J = 4.2, 8.9 Hz, 1H), 8.15 (d, J = 8.8 Hz, 1H), 8.61 (t, J = 2.0 Hz, 1H), and 8.88 (dd, J = 1.3, 8.8 Hz, 1H). 13C-NMR (CDCl3, 75 MHz): δ −3.61, 18.95, 25.75, 115.38, 123.33, 124.28, 127.73, 132.42, 137.62, 140.70, 148.70, and 159.65.

8-tert-Butyldimethylsiloxyquinolin-5-amine (2): To a suspension of 5% Pd/C catalyst (0.2 g, 2.8 mol% Pd) in THF (15 mL) was added 8-tert-butyldimethylsiloxy-5-nitroquinoline 1 (1 g, 3.38 mmol) in methanol (15 mL) at rt. The mixture was then stirred for 1 h in the presence of hydrogen gas (1 atm), followed by filtration through celite.
and evaporation to an oily residue. Further purification by flash column chromatography (ethyl acetate:hexane = 1:8) offered a pure white solid. Yield: 70%. Rf = 0.18 (ethyl acetate:hexane = 1:4). UV (MC): λ_max (logε): 226 (4.19), 244 (4.28), and 529 (3.37) nm. 1H-NMR (CDCl₃, 300 MHz): δ 0.00 (br s, 6H), 0.84 (br s, 9H), 3.63 (br s, 2H), 6.50 (d, J = 8.1 Hz, 1H), 6.79 (d, J = 8.1 Hz, 1H), 7.12 (d, J = 4.3, 8.3 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H), and 8.64 (d, J = 4.0 Hz, 1H). 13C-NMR (CDCl₃, 75 MHz): δ -4.16, 18.75, 27.75, 110.73, 118.02, 119.27, 120.15, 129.55, 135.51, 142.29, 145.68, and 148.52.

2,2,3,3,4,4,4-Heptafluoro-N-(8-hydroxyquinolin-5-yl)octanamide (4a): 8-tert-Butyldimethylsilyloxyquinolin-5-amine (0.2 g, 0.73 mmol) was dissolved in MC (20 mL) and cooled to 0°C. Triethyl amine (0.3 mL, 2.19 mmol) was added dropwise, and the mixture was stirred for 30 min at rt. Then, the mixture was stirred for 1 h at rt, and then diluted with 30 mL of ethyl acetate (EA), washed with brine (20 mL), and water (20 mL). The resulting organic layer was treated with acetic acid (0.16 mL, 2.7 mmol) and tetrabutyrammonium fluoride (TBAF, 5 mL, 5 mmol) in sequence. After evaporation, the residue was purified by recrystallization (EA:MC = 1:20) to obtain a pure white solid, 4a. Yield: 12%. UV (MC): λ_max (logε): 227 (4.59) and 243 (4.73) nm. 1H-NMR (CDCl₃+DMSO, 300 MHz): δ 17.5 (d, J = 8.1 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.53 (dd, J = 4.0, 8.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.87 (d, J = 3.5 Hz, 1H), and 11.05 (br s, 1H). 13C-NMR (CDCl₃+DMSO, 75 MHz): δ 108.89, 120.24, 120.96, 123.80, 124.87, 130.56, 137.44, 147.31, 151.73, and 156.42. IR (KBr): 1690, 1741, 3039, and 3266 cm⁻¹.

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-N-(8-hydroxyquinolin-5-yl)octanamide (4b): Compound 4b was obtained as a pure white solid by using the same synthetic procedure for 4a. Yield: 41%. UV (MC): λ_max (logε): 229 (4.71) and 239 (4.68) nm. 1H-NMR (CDCl₃+DMSO, 300 MHz): δ 17.6 (d, J = 8.2 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 4.2, 8.6 Hz, 1H), 7.69 (br s, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.88 (d, J = 4.0 Hz, 1H), and 11.03 (br s, 1H). 13C-NMR (CDCl₃+DMSO, 75 MHz): δ 108.56, 119.35, 120.23, 123.14, 129.19, 129.65, 136.18, 138.87, 146.63, and 151.44. IR (KBr): 1525, 1560, 1642, 1697, 2936, 3286, and 3348 cm⁻¹.

N-(8-Hydroxyquinolin-5-yl)octanamide (4c): Compound 4c was prepared using the same procedure for 4a and was obtained as a pure white solid with a yield of 30%. UV (MC): λ_max (logε): 226 (4.40), 246 (4.61), and 325 (3.67) nm. 1H-NMR (CDCl₃+DMSO, 300 MHz): δ 0.70 (br s, 3H), 1.12 (br s, 8H), 1.53 (br s, 2H), 2.25 (br s, 2H), 6.87 (d, J = 7.9 Hz, 1H), 7.25 (d, J = 8.2 Hz, 1H), 8.09 (d, J = 7.9 Hz, 1H), 8.64 (br s, 1H), and 9.42 (br s, 1H). 13C-NMR (CDCl₃+DMSO, 75 MHz): δ 12.68, 21.04, 24.39, 27.50, 27.76, 30.16, 34.91, 95.42, 108.58, 119.86, 122.95, 123.16, 123.31, 130.85, 137.02, 146.46, and 149.68. IR (KBr): 1584, 1653, 2919, 3296, and 3317 cm⁻¹.

N-Hexyl-N-(8-hydroxyquinolin-5-yl)pentadecafluoro-

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Table 1. Solubility of 8-hydroxyquinolin derivatives in Sc-CO₂ at 40 °C
A derivative, did not dissolve in Sc-CO2 at 40 ºC, even at relatively weak self-interaction and strong intermolecular interaction, because it showed superior CO2-solubility. The extraction efficiency of this compound was measured, and the results are summarized in Table 1. As expected, solubility generally increased with pressure in all cases. Compound 4c, a non-fluorinated secondary amide 8-HQ derivative, did not dissolve in Sc-CO2 at 40 ºC, even at pressures up to 300 bar. Similarly, 4b was not highly soluble in CO2 (1.1 mM at 280.7 bar). A slightly higher solubility of 4b compared to 4c under the same condition could be explained by the presence of fluorinated alkyl chains in 4b, which is consistent with Beckman's observation. However, compound 4a, containing a shorter fluorinated alkyl chain than 4b, could be dispersed at a comparably low CO2 pressure (1.1 mM at 121.8 bar). Interestingly, a fluorinated tertiary amide-containing 8-HQ derivative (4d) created a single phase with a surprisingly low pressure compared to other 8-HQ derivatives in this study. In previous work, we have described that the solubility difference between secondary and tertiary amide analogs results from two main forces, self-interaction between chelating agents (solute-solute), and specific intermolecular interaction between the chelating agent (solute) and the CO2 molecule (solvent). Strong self-interaction of solute molecules would decrease their solubility in CO2, but strong specific intermolecular solute-solvent (CO2) interaction would enhance the CO2-solubility of the solute. Therefore, relatively strong self-interaction together with weak intermolecular interaction with the secondary amide, due to hydrogen bonding between amides, results in poor CO2-solubility. On the contrary, relatively weak self-interaction and strong intermolecular interaction with the tertiary amide, due to the absence of hydrogen bonding, greatly enhances miscibility in the CO2 phase.

Metal Extraction. Since dynamic extraction of metal ions did not obviously improve extraction compared to static methods under identical conditions, static metal extraction with 8-HQ chelating agents in Sc-CO2 was performed. To enhance extraction efficiency, PFOSANEt4 was chosen as a co-ligand to extract Cu(II), Co(II), Zn(II), Sr(II), and Cd(II) ions from the filter paper matrix. It is well known that PFOSANEt4 dissociates to give a CO2-philic perfluorosulfonic acid anion, [PFOSA]−. This resulting [PFOSA]− subsequently undergoes exchange with the anion (NO3−) of the metal complex in the aqueous phase. Consequently, the in situ substitution of the CO2-phobic anion [NO3−]− with the CO2-philic anion [PFOSA]− may enhance the affinity of the metal complex for CO2, making the metal complex more CO2-soluble and extractable in Sc-CO2. Among the newly synthesized 8-HQ derivatives, compound 4d was chosen for the specific metal removal test with and without PFOSANEt4, because it showed superior CO2-solubility. The extraction efficiency of 4d alone is 12.9% and 31.5% for Co(II) and Cu(II), respectively. We observed that when PFOSANEt4 was introduced into the system as a co-ligand, the metal removal efficiency increased (Co: 31.8%; Cu: 60.8%), as expected. Based upon this observation, PFOSANEt4 was utilized for subsequent extraction experiments.

To enhance metal extraction efficiency, we also investigated the synergistic effect of 8-HQ chelating agents on metal extraction. It has already been suggested that mixed chelating agents and other chemicals could interact with each other, thus achieving more powerful extraction ability than independent chelating agents. Previous studies have explored the synergistic effects of such agents on metal extraction in Sc-CO2, such as the mixture of tributylphosphate (TBP) and 2-thenoyltrifluoroacetone (TTA) for lanthanide ions and uranyl ions, and tri-n-octylphosphine oxide (TOPO) and bis(2-ethylhexyl)hydrogen phosphate (HDEPH) for uranyl ions. We have investigated the synergistic effect of Cyanex-272 and sodium diethylthiocarbamate (NaDDC) for metal extraction into Sc-CO2. To explain the observed synergistic effect of NaDDC, we proposed that diethylamine (DEA), the in situ-formed product formed by the dissociation of NaDDC in Sc-CO2, could convert Cyanex-272 to a corresponding deprotonated form that could coordinate more strongly with metal ions, and thus enhance metal transportation for extraction.

It is well known that 8-HQ becomes a stronger ligand after deprotonation of the hydroxyl group due to greater bonding with metal ions. However, deprotonation of 8-HQ in CO2 medium cannot occur without additives because the pH of the aqueous CO2 medium is around 2.9 due to the formation and dissociation of carbonic acid under Sc-CO2 conditions. Based on our previous work, we found that DEA was a suitable base for this purpose. We surmised that DEA could attack the hydroxyl group of the 8-HQ molecule causing deprotonation, and that the resulting oxygen anion would be ionized more easily than the hydroxyl group (Fig. 2). The oxygen anion thus might more readily coordinate with metal ions, and subsequently produce a much more stable complex, which could be easily removed from the matrix. The resulting DEA-enhanced interaction of 8-HQ with metal ions would be expected to improve metal extraction efficiency. To confirm our proposal, we carried out extraction of Cu(II), Co(II), Zn(II), Sr(II), and Cd(II) ions with and without DEA, respectively. We observed that when DEA was introduced into the system as a co-ligand, the metal removal efficiency increased (Co: 31.8%; Cu: 60.8%), as expected. Based upon this observation, DEA was utilized for subsequent extraction experiments.
metal ions with and without DEA under fixed condition. Two 8-HQ derivatives were selected as test candidates, namely 4d and 4e. From the data summarized in Figure 3, we draw two main conclusions. First, the metal recovery efficiency obtained with DEA is much higher than that without DEA, especially for Cu(II) and Co(II)), regardless of whether 4d or 4e is used as a chelating agent. For example, metal extraction using 4d with DEA showed near perfect efficiencies (Cu: 95.5%; Co: 82.0%), but extraction without DEA showed only moderate efficiencies (Cu: 60.8%; Co: 31.8%). Second, as expected when using DEA as a base additive, the fluorinated agent 4d showed a somewhat higher affinity for metals than the non-fluorinated agent 4e under identical conditions. This result may be because of the higher solubility of 4d, which could further contribute to enhanced metal binding and consequently allow easier transportation of metal chelates to the CO2 phase. Interestingly, we found our synthesized 5-amido-8-hydroxyquinoline chelating agents showed much more affinity to Cu than to other tested metal ions, especially Sr. This result supports potential possibility to extract Cu ion selectively from mixture of other metal ions. To understand this selectivity fully, further studies should be done.

Conclusion

New CO2-soluble 8-hydroxyquinoline (8-HQ) chelating agents were synthesized and tested for solubility and metal ion extraction ability in supercritical CO2 (Sc-CO2). Secondary amide-containing 8-HQ derivatives could not disperse well into Sc-CO2, but tertiary amide-containing 8-HQ derivatives were soluble in CO2 at low pressure, possibly due to the relatively strong intermolecular interaction between the chelating agent and the CO2 molecule. Extraction of metal ions (Co2+, Cu2+, Sr2+, Cd2+, and Zn2+) in Sc-CO2 using 8-HQ chelating agents only did not provide satisfactory results. However, when DEA was added, high extraction efficiency was observed with and without fluorinated or non-fluorinated chelating agents. We propose that this finding can be explained by the synergistic effect of DEA in the 8-HQ system. Deprotonation of a 8-hydroxy group in the 8-HQ compound by DEA in Sc-CO2 would make the 8-HQ compound a stronger ligand. To further understand the mechanism of the synergistic effect of DEA on Sc-CO2 metal extraction, we will conduct further research using other chelating agents and organic bases.

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References