Highly CO_2-soluble 5-Amido-8-hydroxyquinoline Chelating Agents for Extraction of Metals in Sc-CO_2

Fei Chang, Seohun Park, and Hakwon Kim*

*Department of Chemistry and Advanced Materials and Industrial Liaison Research Institute, College of Environment and Applied Chemistry, Kyung Hee University, Gyeonggi 446-701, Korea. *E-mail: hwkim@khu.ac.kr*

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Novel CO_2-soluble 8-hydroxyquinoline (8-HQ) chelating agents were synthesized and evaluated for solubility and metal ion extraction ability in supercritical CO_2 (Sc-CO_2). Among them, secondary amide-containing 8-HQ derivatives cannot be dispersed well into Sc-CO_2, but tertiary amide-containing derivatives can dissolve completely in Sc-CO_2 even at low CO_2 pressures, perhaps owing to the predominant intermolecular interaction between the chelating agent and the CO_2 molecule. Based on 8-HQ chelating agent solubility data, we investigated the extraction of metal ions (Co^{2+}, Cu^{2+}, Sr^{2+}, Cd^{2+}, and Zn^{2+}) using two highly CO_2-soluble 8-HQ derivatives (**4d**, **4e**) in Sc-CO_2. 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-CO_2 medium.

Key Words : CO_2-soluble chelating agent, Supercritical CO_2, Metal extraction, 8-Hydroxyquinoline derivatives, Synergistic effect

Introduction

From the viewpoint of “green process”, supercritical fluid extractions (SFE) have attracted much more attention[1] than conventional solvent extractions both academically and industrially, because of the ever-increasing regulations on the use of conventional solvents. Carbon dioxide (CO_2) is extensively used in SFE technology because of its non-toxicity, low cost, superior mass transfer properties, easy recyclability, and moderate critical constants (T_C = 31.1 ºC, P_C = 73.8 bar).[2] Extraction of organic compounds in Sc-CO_2 has already been confirmed to be successful in industry.[3] However, because of the low solubility of metal ions and conventional metal chelating agents, direct extraction of metals into Sc-CO_2 is still highly inefficient. If a suitable CO_2-soluble chelating agent is added and binds metal ions to form a CO_2-souble metal complex *in situ*, the resulting complex can be dissolved and hence easily extracted into Sc-CO_2 from sample matrices.[4,5] As a result, highly CO_2-soluble chelating agents are required for efficient metal extraction in Sc-CO_2.

Recently, in an attempt to find readily available and highly efficient chelating agents for removal of metals from matrices in Sc-CO_2, various compounds were tested, and some of these appeared to have potential for real application, such as dithiocarbamates,[6-8] β-diketones,[9,10] organophosphorous reagents,[5,11] macrocyclic compounds,[12,13] and fluorinated surfactants.[6-8,14] To choose appropriate chelating agents for use in Sc-CO_2, good CO_2-solubility and chemical stability are obviously required because low CO_2 solubility and chemical instability have been significant obstacles for the employment of chelating agents in Sc-CO_2.[2]

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.[15,16] Nevertheless, until now only a few studies have focused on metal extraction with 8-HQ or its derivatives in Sc-CO_2.[17-19] It was found that metal extraction with 8-HQ in pure Sc-CO_2 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 CO_2 in the presence of methanol.[18,19]

Recently, we have been involved in the development of *in situ*-chelation supercritical CO_2 extraction without co-solvent. Therefore, we have already designed and synthesized various highly CO_2-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.[20,21] We observed that all of these compounds were CO_2-soluble and therefore suitable for metal extraction investigations. In this paper, we describe the synthesis and evaluation of novel CO_2-soluble amide-group-containing 8-HQ chelating agents for the extraction of several metal ions (Co^{2+}, Cu^{2+}, Sr^{2+}, Cd^{2+}, and Zn^{2+}) into CO_2. In particular, the synergistic effect of diethyl amine (DEA) on enhancing the metal extraction efficiency of 8-HQ chelating agents in Sc-CO_2 is described.

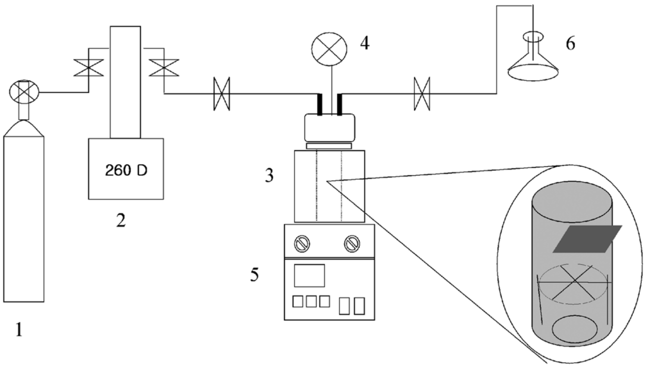
Apparatus and Materials

All manipulations involving air- or moisture-sensitive chemicals were carried out under nitrogen. Ethanol was treated with Mg/I_2 and refluxed for 6 h before use; methylene chloride (MC) was dried over anhydrous $MgSO_4$, and then distilled. 8-Hydroxy-5-nitroquinoline (96%), *tert*-

butyldimethylsilyl chloride (97%), hexanal (98%), pentadecafluorooctanoyl chloride (97%), heptafluorobutyryl chloride (98%), octanoyl chloride (99%), heptadecafluorooctanesulfonic acid tetraethylammoium salt (perfluorooctanesulfonic acid tetraethylammonium salt, PFOSANEt$_4$) (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 ^{1}H-NMR and 75 MHz for ^{13}C-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, CO_2 was pressed into the cell by a syringe pump (260D, ISCO, USA) from a liquid CO_2 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 (PFOSANEt$_4$), 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 HNO_3 (1 M aq.). Extraction recovery was determined by calculating the difference in concentration of metal ions in the specimen before and after extraction.



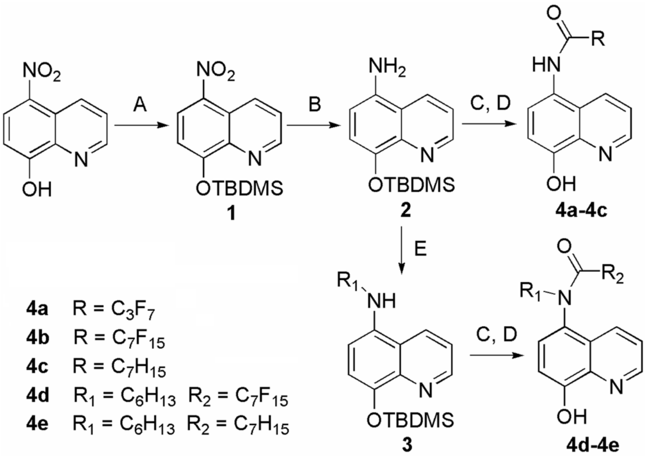
1. CO_2 tank 2. Syringe pump 3. Extraction cell 4. Pressure gauge 5. Thermal control heating system 6. Collecting vial

Figure 1. Schematic diagram of the Sc-CO_2 metal extraction set-up.

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

8-*tert*-Butyldimethylsilyloxy-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 Na_2SO_4 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). ^{1}H-NMR (CDCl$_3$, 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). ^{13}C-NMR (CDCl$_3$, 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*-Butyldimethylsilyloxyquinolin-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*-butyldimethylsilyloxy-5-nitroquinoline **1** (1 g, 3.38 mmol) in methanol (15 mL) at rt. The mixture was then allowed to stir for 1 h in the presence of hydrogen gas (1 atm), followed by filtration through celite



Scheme 1. Synthesis of new 8-hydroxyquinoline derivatives. A. TBDMSCl, imidazole, CH_2Cl_2; B. Pd/C, H_2, MeOH, THF; C. acyl chloride, TEA, CH_2Cl_2; D. TBAF, Acetic acid; E. hexanal, $NaB(CN)H_3$, THF.

and evaporation to an oily residue. Further purification by flash column chromatography (ethyl acetate:hexane = 1:8) offered a pure yellow solid. Yield: 70%. R_f = 0.18 (ethyl acetate:hexane = 1:4). UV (MC): λ_{max} (logε): 226 (4.19), 244 (4.28), and 529 (3.37) nm. ^{1}H-NMR ($CDCl_3$, 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 (dd, *J* = 4.3, 8.3 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), and 8.64 (d, *J* = 4.0 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 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 **2** (0.2 g, 0.73 mmol) was dissolved in MC (20 mL) and cooled to 0 ºC. Triethyl amine (0.3 mL, 2.19 mmol) was added dropwise, and the mixture was stirred for 30 min at rt. Heptafluorobutyryl chloride (0.15 mL, 0.88 mmol) was then added dropwise. 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 tetrabutylammonium 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. ^{1}H-NMR ($CDCl_3$+DMSO, 300 MHz): δ 7.15 (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* = 3.3 Hz, 1H), and 11.05 (br s, 1H). ^{13}C-NMR ($CDCl_3$+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. ^{1}H-NMR ($CDCl_3$+DMSO, 300 MHz): δ 7.16 (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). ^{13}C-NMR ($CDCl_3$+DMSO, 75 MHz): δ 108.56, 119.35, 120.23, 123.14, 124.19, 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. ^{1}H-NMR ($CDCl_3$+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). ^{13}C-NMR ($CDCl_3$+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, 3269, and 3317 cm^{-1}.

***N*-Hexyl-*N*-(8-hydroxyquinolin-5-yl)pentadecafluoro-octanamide (4d):** A solution of 8-*tert*-butyldimethylsilyl-oxyquinolin-5-amine **2** (0.5 g, 1.82 mmol) and hexanal (0.27 mL, 2.19 mmol) in dry THF (30 mL) was refluxed for 10 h, followed by addition of sodium cyanoborohydride (0.35 g, 5.46 mmol) in portions. The mixture was stirred for 30 min at rt, diluted with ethyl ether (30 mL), and then washed with water (20 mL) and brine (20 mL). The crude secondary amine **3** was directly used in the next step without purification. Penta- decafluorooctanoyl chloride (0.22 mL, 0.88 mmol) was added dropwise to a mixture of **3** (0.264 g, 0.74 mmol) and triethyl amine (0.31 mL, 2.22 mmol) in dry THF (10 mL) at 0 ºC. The mixture was allowed to stir at rt for 1 h. After dilution with ethyl ether (30 mL), and washing with brine (20 mL) and water (20 mL), the organic layer was treated with acetic acid (0.16 mL, 2.7 mmol) and TBAF (5 mL, 5 mmol) in sequence. Evaporation and purification by flash column chromatography (EA:hexane = 1:4) resulted in a pure yellow liquid **4d**. Yield: 11%. R_f = 0.2 (EA:hexane = 1:4). UV (MC): λ_{max} (logε): 228 (4.47), 241 (4.52), and 496 (2.72) nm. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.76 (br s, 3H), 1.17 (br s, 6H), 1.49 (br s, 1H), 1.59 (br s, 1H), 3.06-3.15 (m, 1H), 4.14-4.24 (m, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.47-7.51 (m, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), and 8.79 (d, *J* = 2.7 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 32.80, 52.21, 53.21, 108.66, 108.70, 122.88, 125.53, 125.55, 125.57, 125.59, 128.20, 128.22, 130.97, 138.26, 148.36, and 150.01. IR (KBr): 1142, 1211, 1240, 1484, 1698, 2580, 2919 cm^{-1}. MS (m/z): 243 (M-397), 186 (M-454), 159 (M-481), 130 (M-510), 85 (M-555), and 43 (M-597).

***N*-Hexyl-*N*-(8-hydroxyquinolin-5-yl)octanamide (4e):** Compound **4e** was synthesized by using the same procedure for **4d** and was obtained as a yellow liquid. Yield: 60%. R_f = 0.2 (EA:hexane = 1:4). UV (MC): λ_{max} (logε): 228 (4.47), 242 (4.45), and 486 (2.67) nm. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.72-0.84 (m, 6H), 1.20 (br s, 14H), 1.40-1.47 (m, 4H), 1.67-1.82 (m, 1H), 1.87-1.95 (m, 1H), 3.15-3.24 (m, 1H), 4.06-4.15 (m, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.41-7.50 (m, 1H), 8.06 (d, *J* = 7.3 Hz, 1H), and 8.81 (d, *J* = 2.9 Hz, 1H). IR (KBr): 1269, 1475, 1640, 2580, 2929, and 2958 cm^{-1}. MS (m/z): 243 (M-127), 186

Table 1. Solubility of 8-hydroxyquinoline derivatives in Sc-CO_2 at 40 ºC

	Concen. (mM)	Pressure (bar)	Concen. (mM)	Pressure (bar)
4a	3.6	160.0	1.4	141.8
	1.9	142.1	1.1	121.8
4b	1.1	280.7		
4c	trace	up to 300		
4d	67.6	113.8	47.8	109.9
	60.8	111.9	43.0	108.9
	53.9	112.7		
4e	9.8	128.5	6.6	113.9
	8.7	123.7	5.9	111
	7.4	117.8		

(M-184), 159 (M-211), 130 (M-240), 85 (M-285), and 43 (M-327).

Results and Discussion

Phase Behavior. The solubilities of all newly prepared 8-HQ derivatives in Sc-CO_2 were 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-CO_2 at 40 ºC, even at pressures up to 300 bar. Similarly, **4b** was not highly soluble in CO_2 (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.[14] However, compound **4a**, containing a shorter fluorinated alkyl chain than **4b**, could be dispersed at a comparably low CO_2 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[20] results from two main forces, self-interaction between chelating agents (solute-solute), and specific intermolecular interaction between the chelating agent (solute) and the CO_2 molecule (solvent).[22] Strong self-interaction of solute molecules would decrease their solubility in CO_2, but strong specific intermolecular solute-solvent (CO_2) interaction would enhance the CO_2-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 CO_2-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 CO_2 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-CO_2 was performed. To enhance extraction efficiency, PFOSANEt_4 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 PFOSANEt_4 dissociates to give a CO_2-philic perfluorosulfonic acid anion,[23] $[PFOSA]^-$. This resulting $[PFOSA]^-$ subsequently undergoes exchange with the anion (NO_3^-) of the metal complex in the aqueous phase. Consequently, the *in situ* substitution of the CO_2-phobic anion $[NO_3]^-$ to the CO_2-philic anion $[PFOSA]^-$ may enhance the affinity of the metal complex for CO_2 making the metal complex more CO_2-soluble and extractable in Sc-CO_2. Among the newly synthesized 8-HQ derivatives, compound **4d** was chosen for the specific metal removal test with and without PFOSANEt_4, because it showed superior CO_2-solubility. The extraction efficiency of **4d** alone is 12.9% and 31.5% for Co(II) and Cu(II), respectively. We observed that when PFOSANEt_4 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, PFOSANEt_4 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[24-27] have explored the synergistic effects of such agents on metal extraction in Sc-CO_2, such as the mixture of tributylphosphine (TBP) and 2-thenoyltrifluoroacetone (TTA) for lanthanide ions and uranyl ions,[24,25] and tri-*n*-octylphosphine oxide (TOPO) and bis(2-ethylhexyl)hydrogen phosphate (HDEPH) for uranyl ions.[26] We have investigated the synergistic effect of Cyanex-272 and sodium diethyldithiocarbamate (NaDDC) for metal extraction into Sc-CO_2.[27] 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-CO_2, would convert Cyanex-272 to a corresponding deprotonated form that could coordinate more strongly with metal ions, and thus enhance metal transportation for extraction.[27]

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 CO_2 medium cannot occur without additives because the pH of the aqueous CO_2 medium is around 2.9 due to the formation and dissociation of carbonic acid under Sc-CO_2 conditions.[28] 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

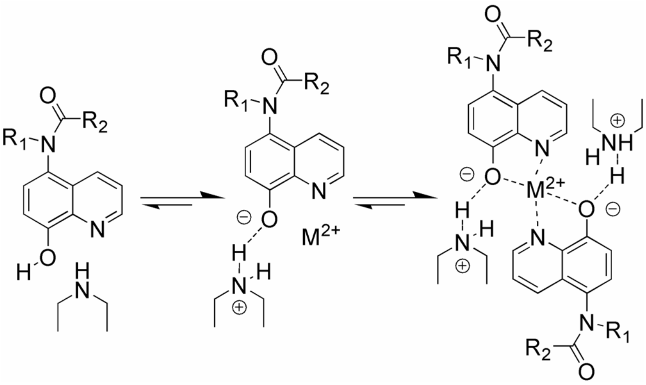


Figure 2. Proposed mechanism for a synergistic effect of DEA with the 8-HQ chelating agent in Sc-CO_2.

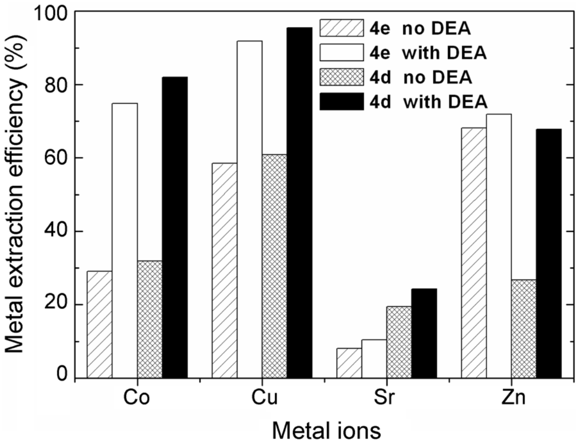


Figure 3. Percent extraction of metal ions using 8-HQ chelating agents (**4d**, **4e**) with/without DEA in Sc-CO_2. (mole ratio: ligand/co-ligand/M^+ = 150:150:1; DEA, 16 μL; CO_2 pressure, 200 bar; temperature, 40 ºC; reaction time, 1 h).

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 CO_2 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 CO_2-soluble 8-hydroxyquinoline (8-HQ) chelating agents were synthesized and tested for solubility and metal ion extraction ability in supercritical CO_2 (Sc-CO_2). Secondary amide-containing 8-HQ derivatives could not disperse well into Sc-CO_2, but tertiary amide-containing 8-HQ derivatives were soluble in CO_2 at low pressure, possibly due to the relatively strong intermolecular interaction between the chelating agent and the CO_2 molecule. Extraction of metal ions (Co^{2+}, Cu^{2+}, Sr^{2+}, Cd^{2+}, and Zn^{2+}) in Sc-CO_2 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-CO_2 would make the 8-HQ compound a stronger ligand. To further understand the mechanism of the synergistic effect of DEA on Sc-CO_2 metal extraction, we will conduct further research using other chelating agents and organic bases.

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