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MODIFIER EFFECT ON EXTRACTION OF MERCURY WITH SODIUM DIETHYLDITHIOCARBAMATE IN SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

The modifier effect on the extraction of mercury ion with sodium diethyldithiocarbamate dissolved in supercritical carbon dioxide was investigated. The extraction of the mercury ion spiked on filter paper was experimentally studied in a supercritical carbon dioxide extraction experimental installation. Several organic solvents were used as co-solvents to modify supercritical carbon dioxide. Water and HNO_3 aqueous solutions were used to modify the solid matrix to be extracted. The enhancement of the exaction efficiency of the mercury ion depends on the polarity and amount of co-solvent. The extraction efficiency was also enhanced by modifying the solid matrix with water or HNO_3 aqueous solution, and we found that the extraction depended on the concentration of HNO_3 in the modifier for the solid.

Key Words: Mercury; Extraction; Supercritical; Carbon dioxide; Modifier; Sodium diethyldithiocarbamate

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INTRODUCTION

Supercritical carbon dioxide ($scCO_2$) extraction is a well-proven technology for many separation purposes. The extraction of metal ions through the use of supercritical carbon dioxide with coordinating ligands was recently explored (1). The use of supercritical carbon dioxide instead of organic solvents for the extraction of metals from liquid or solid matrices has several potential advantages. The residual contamination of the matrices by the organic solvent may be eliminated by substitution with $scCO_2$. Because of relative low viscosity and high solute diffusivity of $scCO_2$, the mass transfer characteristics of it are excellent compared to those of organic solvents, and the replacement of organic solvent by $scCO_2$ may enhance the rates of extraction and stripping. The selective extraction schemes and easy separation of the solute from the solvent may also be realized with the manipulation of the solvency characteristics of scCO2 with small changes in temperature and pressure. CO_2 is cheap, nontoxic, and environmental benign. As a result of these favorable properties, the use of $scCO_2$ as a solvent for extraction of metals is gaining more interest among those in research and development (2–4).

The nonpolar nature of $scCO_2$ means that ligands and metal complexes have limited solubility in it. The addition of modifiers into $scCO_2$ can affect the solubility and enhance the extraction efficiency of it. Methanol has already been used to modify $scCO_2$ for the extraction of heavy metal ions by Wai and co-workers (5–7). We modified $scCO_2$ with several organic solvents. The effects of different modifiers on the extraction of mercury from solid samples with sodium diethyldithiocarbamate (NaDDC) in $scCO_2$ were investigated. The roles of water and HNO_3 aqueous solution in modifying the solid matrix to be extracted were also explored.

EXPERIMENTAL

Materials

NaDDC, $Hg(NO_3)_2$, nitric acid, dithizone, chloroform, methanol, toluene, dichloromethane, hexane, and acetic acid are all A.R. grade. They were all purchased from Beijing Chemicals Co (Beijing, China) and used without further purification. The filter paper (quantitative analysis grade with 0.1-μm diameter pores) was obtained from Hangzhou Fuyang Special Paper Co (Hangzhou, China), and used as received. CO_2 of 99.9% (wt) purity was supplied by Beijing Analytical Instrument Co (Beijing, China). MOS grade water was obtained from the Institute of Microelectronic Technology in Tsinghua University (Beijing, China).

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Preparation of Solid Samples

Solid samples were prepared by spiking a 5-g filter paper with 5-mL Hg $(NO_3)_2$ aqueous solution. The filter was subsequently dried in air at 40°C for 10 hours.

Analysis of Mercury Ion

The Hg^{2+} content in the solid samples before and after the extraction were determined by the following method: The Hg^{2+} in the solid sample was transferred into the nitrate acid solution by boiling the solution with the sample, then it was extracted with dithizone dissolved in chloroform, and the concentration of the formed orange Hg-dithizone complex in chloroform was analyzed by a spectrophotometric method at 490 nm (7,8). The detection limit of this analysis method is 5×10^{-6} g Hg^{2+}/g dry solid. Because the Hg^{2+} concentration in this work ranged from 10^{-4} g Hg^{2+}/ g dry solid to 10^{-2} g Hg^{2+}/g dry solid, the analysis is suitable for this work and can be realized with relatively simple and cheap instruments.

Extraction with NaDDC in $scCO_2$

All the extraction experiments were performed with the supercritical carbon dioxide extraction apparatus schematically shown in Fig. 1. Carbon dioxide from the CO_2 cylinder (no. 1) was compressed to high pressure by compressor (no. 2) and adjusted to the extraction pressure by the pressure regulator (no. 3). The high pressure CO_2 was heated to the extraction temperature by the preheater (no. 4). The solid samples, which were treated by adding a water or HNO_3 aqueous solution into it for the solid modification experiments, were put in the upper part of the 50-mL extractor (no. 8). For each experiment, a 5-g solid sample with a known initial Hg^{2+} concentration was extracted. NaDDC was in the lower part of the extractor for all experiments. The amount of NaDDC was always 500% the level of stoichiometric excess. The sample and the ligand were separated with inert quartz wool. The spare space in the extractor was also filled with quartz wool. The liquid modifier for CO_2 was put into the liquid extractor (no. 7) and dissolved by supercritical carbon dioxide. The metal ions on the spiked solid samples were extracted by supercritical carbon dioxide and in the process dissolved the NaDDC and modifiers. The formed metal complexes were precipitated in a 50-mL separator (no. 10) under reduced pressure. The flow rate of CO_2 was controlled by a valve located between the extractor and the separator, and was measured by a gas meter. After the dynamic extraction, the CO_2 supply was cut off and the pressure

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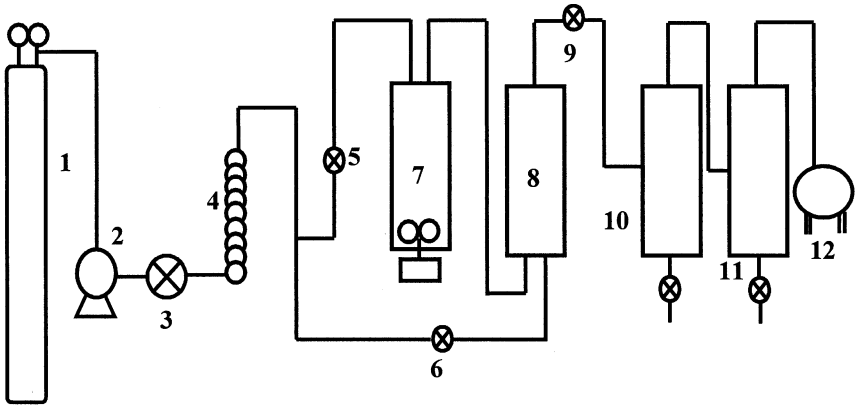

Figure 1. The schematic of supercritical carbon dioxide extraction apparatus. (1) carbon dioxide gas cylinder, (2) compressor, (3) pressure regulator, (4) preheater, (5) switch valve, (6) switch valve, (7) liquid extractor, (8) solid extractor, (9) reduction valve, (10) primary separator, (11) secondary separator, and (12) wet gas flow gauge.

of the extraction system was lowered to ambient pressure. The extracted solid sample was taken out of the extractor and analyzed to determine the residual concentration of Hg^{2+}.

The extraction efficiency was calculated as

$$E = 1 - C_e/C_0 \quad (1)$$

where, E is the extraction efficiency; C_0 is the initial concentration of Hg^{2+} in a solid; and C_e is the concentration of Hg^{2+} in the solid after the extraction.

RESULTS AND DISCUSSION

Using the experimental setup and procedure described, we determined that the extraction efficiency of Hg was 85.09% at 45°C, 20 MPa, a CO_2 flow rate of 50 Nl/min, an extraction time of 80 minutes, and an initial Hg^{2+} concentration of 3.5815×10^{-3} g/g. The amount of the solid sample was 5 g, and the amount of NaDDC was 500% excess and included 120 mL of the modifier methanol. Although the details of our experimental setup, the extraction procedure, and conditions are different than those of Wai et al. (7), the results are the same. In the work by Wai et al. (7), 87% of Hg^{2+} was recovered from 300-mg filter paper spiked by 50 mg NaDDC in methanol-modified $scCO_2$ (5 μg) with

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Table 1. Some Properties of Organic Modifiers

Modifier	Dipole Moment	Acidic/Basic/Neutral
Methanol	2.9	neutral (p*K*a = 16)
Dichloromethane	1.6	neutral
Toluene	0.4	neutral
Hexane	0.0	neutral
Acetic acid	1.7	acidic (p*K*a = 4.8)

a 15-minute static extraction followed by a 15-minute dynamic extraction at 60°C and 200 atm.

Effects of Modifiers Dissolved in $scCO_2$

Methanol, dichloromethane, hexane, toluene, and acetic acid were used as modifiers for CO_2. Select properties of the modifiers are listed in Table 1.

The effects of the different modifiers dissolved in supercritical carbon dioxide on the extraction of mercury ion were experimentally compared. Table 2 shows the results of the extraction of solid samples under the same initial concentration of Hg^{2+}, 3.0607×10^{-3} g Hg/g dry solid; the same amount of NaDDC, 500% excess; the same amount of the solid sample, 5 g; and the same amount of the modifier, 150 mL, at the operation conditions, 20 MPa, 45°C, and 46.0 NL/min CO_2 flow rate.

According to Table 1, the modifiers are in the order: hexane < toluene < dichloromethane < acetic acid < methanol, as their dipole moments increase. Table 1 shows that methanol has lower acidity than does acetic acid.

Table 2. Effect of Different Modifiers on Extraction Efficiency

Modifier	Extraction Time (min)	Extraction Efficiency (%)
acetic acid	84	88.98
methanol	85	79.53
dichloromethane	86	77.95
toluene	87	66.93
hexane	90	62.20
None	90	62.35

$P = 20$ MPa; $T = 45$°C; $F = 46$ NL/min; $C_0 = 3.0607 \times 10^{-3}$ g/g; 150 mL modifier; 5.0 g solid sample; NaDDC = 500% excess.

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As shown in Table 2, the enhancement of the extraction efficiency with the modifiers is in the order hexane < toluene < dichloromethane < methanol < acetic acid. The modifier effect is heavily dependent on the polarity of the modifier. The polar modifiers, methanol, acetic acid, and dichloromethane, can obviously improve the extraction of Hg^{2+} with NaDDC in supercritical carbon dioxide. The enhancement of the extraction efficiency increases as the polarity of the modifier increases. The nonpolar modifier hexane had no effect on the extraction. Acetic acid was the best modifier for extraction because the acidic environment helps to free Hg from the solid matrix.

The amount of the modifier dissolved in supercritical carbon dioxide also affects the extraction of Hg^{2+}. Figure 2 shows the extraction efficiency of Hg^{2+} at 45°C, 20 MPa, CO_2 flow rate of 50 Nl/min, extraction time of 80 minutes, initial Hg^{2+} concentration of 3.5815×10^{-3} g/g, a 5-g solid sample, a 500% excess amount of NaDDC, and different amounts of methanol. The extraction efficiency increases as the amount of methanol is increased.

Effect of the Modifier Added into the Solid Matrix

For modifying the solid matrix, water and HNO_3 aqueous solutions were added into the dry solid samples to be extracted. The effect of the amount of wa-

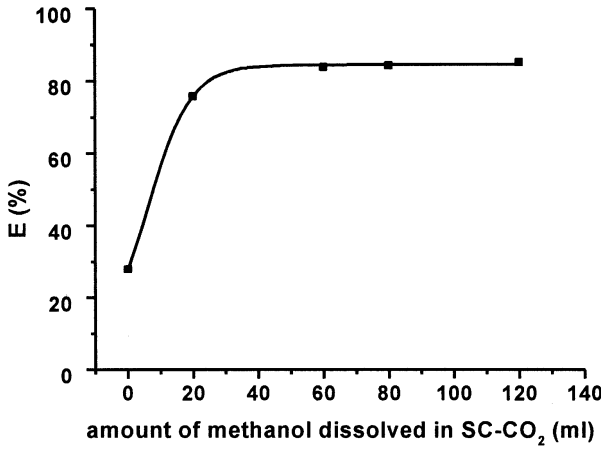

Figure 2. Effect of the amounts of methanol on the extraction efficiency of Hg^{2+} (T = 45°C; P = 20 MPa; F = 50 Nl/min; t = 80 minutes; $C_0 = 3.5815 \times 10^{-3}$ g/g; 5 g solid sample; NaDDC = 500% excess).

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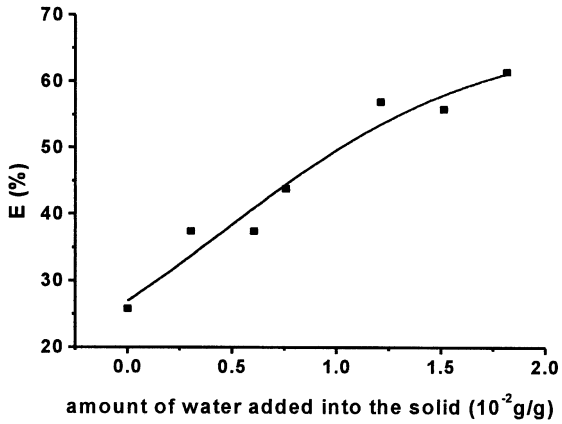

Figure 3. The effect of the amount of water added into the solid sample on the extraction of Hg^{2+} ($T = 40°C$; $P = 17$ MPa; $F = 28.0$ Nl/min; $t = 100$ minutes; $C_0 = 5.190 \times 10^{-3}$ g/g; 5 g solid sample; NaDDC = 500% excess).

ter added into the solid sample on the extraction of Hg^{2+} is shown in Fig. 3. The extraction of Hg^{2+} increases as the amount of water added increases. The presence of water makes the solid matrix swell, and then supercritical carbon dioxide in which the NaDDC is dissolved can more easily reach the interior of the solid matrix. Therefore, adding water into the solid facilitates the chelation of Hg^{2+} with DDC and the transport of the formed complex $Hg(DDC)_2$ from the solid into the fluid phase. Water may also block the active sites of the solid matrix and thus reduce the resorption of Hg^{2+} onto the active site of the solid or substitute Hg^{2+} on the coordinate sites of the solid matrix. Because of the presence of water, the acidic environment is generated when CO_2 is passed over the solid matrix. This increased acidity leads to the formation of carbonic acid and a pH of 3 during the extraction process. Hg in the solid matrix becomes free relatively easily in the resulting acidic environment. This ease of dissociation also facilitates the extraction.

The effect of the concentration of HNO_3 solution added into the solid matrix was studied. The results are listed in Table 3. The extraction efficiency of Hg^{2+} from the solid sample with NaDDC dissolved in $scCO_2$ became higher as increased amounts of concentrated HNO_3 solution added to the matrix. These results indicate that the acidic environment in the solid matrix is favorable to free the Hg from any acetate groups that may be bound to it on the cellulose acetate surface. They also show that the acidic environment helps the formation of the complex $Hg(DDC)_2$ and thus facilitates the extraction of Hg^{2+} from the solid matrix into the supercritical carbon dioxide phase.

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Table 3. The Effect of the Concentration of HNO_3 Solution Added into the Solid on the Extraction

Concentration of Solution Added into the Solid (mol/L HNO_3)	Extraction Efficiency (%)
0	35.01
0.001	39.39
0.01	42.67
0.1	45.46
1	53.17
5	53.83

$P = 20$ MPa; $T = 45$°C; $F = 46$ NL/min; $C_0 = 3.0607 \times 10^{-3}$g/g; 150 mL modifier; 5.0 g solid sample; NaDDC = 500% excess

CONCLUSIONS

The modifiers dissolved into supercritical carbon dioxide and the modifiers added into the solid matrix to be extracted play important roles for the extraction of mercury ion by supercritical carbon dioxide in which sodium diethyldithiocarbamate is dissolved. The polar modifiers dissolved in $scCO_2$ can improve the extraction of Hg^{2+}. The enhancement of the extraction efficiency depends on the polarity and acidity of the modifier dissolved into $scCO_2$. Adding modifiers, water and HNO_3 solutions, into the solid matrix to be extracted can improve the extraction of Hg^{2+} for this system. The enhancement of the extraction efficiency is dependent on the concentration of HNO_3 solution and the amount of the modifier added.

NOMENCLATURE

C_0	initial concentration of Hg^{2+} in the solid sample to be extracted (g Hg^{2+}/g dry solid)
C_e	concentration of Hg^{2+} in the solid sample after extraction (g Hg^{2+}/g dry solid)
C_m	concentration of the modifier added into the solid sample to be extracted (g /g dry solid)
E	extraction efficiency defined as Eq. (1) (%)
F	flow rate of carbon dioxide (Nl/min)
P	pressure (MPa)
T	temperature (°C)
t	extraction time (minutes)

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