

# Extraction of arsenic-containing anions by supercritical CO<sub>2</sub> with ion-pairing

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## Abstract

The extraction of arsenic-containing anions from solid matrices by supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>) extraction coupled with ion-pairing was investigated. Tetra-butylammonium bromide (Bu<sub>4</sub>NBr), tetra-hexylammonium bromide (Hex<sub>4</sub>NBr), tetra-octylammonium bromide (Oct<sub>4</sub>NBr), dodecyltrimethylammonium bromide (Dod(Me)<sub>3</sub>NBr), myristyltrimethylammonium bromide (Myr(Me)<sub>3</sub>NBr) and hexadecyltrimethylammonium bromide (Hex(Me)<sub>3</sub>NBr) were used as the ion-pairing reagents. A model of the extraction of the arsenic-containing anions by supercritical CO<sub>2</sub> extraction with pre-ion-pairing was proposed, and verified with experimental results. The extraction efficiency depends on two parameters, which are the theoretical extraction efficiency ( $E_{\max}$ ) and the rate constant ( $k$ ). The effects of the molecular structure and size of the ion-pair reagent on  $E_{\max}$  and  $k$  were discussed. The process parameter effects on the extraction efficiency, including the temperature, pressure, the mole flow rate of CO<sub>2</sub>, the mole ratio of alcohol to CO<sub>2</sub> and the dosage of the ion-pair reagent were investigated using Bu<sub>4</sub>NBr and Myr(Me)<sub>3</sub>NBr as the ion-pairing reagents.

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**Keywords:** Arsenic; Anion; Extraction; Supercritical carbon dioxide; Ion-pairing

## 1. Introduction

Supercritical carbon dioxide (sc-CO<sub>2</sub>) has been receiving increasing attentions for many applications due to its unique properties such as liquid-like density and solvent power, gas-like transport properties, sensitivity of the properties with temperature and pressure, and its benignity to environment. However, the non-polarity of CO<sub>2</sub> limits its solvent power for strong polar solutes and then its applications. For ionic solutes without the specific modifications, the supercritical CO<sub>2</sub> is a poor solvent even with polar organics as the co-solvents. In recent years, the solubilization of ionic solutes in supercritical CO<sub>2</sub> for various applications has become an active topic. For metal cations, chelating using coordinating ligands dissolved in supercritical carbon dioxide has been developed, and applied for the extraction of metal cations by supercritical CO<sub>2</sub> from various matrixes [1–6]. However, it is necessary to transform the ionic solute to be the form which

allows it to be coordinated with the ligand for forming the supercritical carbon dioxide soluble chelate [7].

Another method for solubilizing ionic solutes in supercritical CO<sub>2</sub> is to associate the solute with a counter ion to form an ion-pair, which is hydrophobic enough to dissolve in supercritical CO<sub>2</sub>. This hydrophobic ion-pairing method has many potential applications. It has been used for analysis of ionic analytes using supercritical fluid chromatography [8–11], and also used to solubilize hydrophilic chemically sensitive materials in supercritical CO<sub>2</sub> for applications to chemical optical sensors [12]. Supercritical CO<sub>2</sub> extraction with ion pairing can be applied to preparation of samples for analysis of ionic solutes [13–16]. In a previous work [17], we primarily explored a new process for the removal of arsenic-containing anions such as arsenite and arsenate by supercritical CO<sub>2</sub> extraction with ion-pairing, in which the arsenic-containing anions were associated with tetra-butylammonium cation to form the hydrophobic ion-pairs, and effectively extracted into supercritical CO<sub>2</sub>. So far, there is no available information about modeling and kinetics of the extraction of ionic solutes by ion-pairing/supercritical CO<sub>2</sub>. In this work, a model of the

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## Nomenclature

### Notation

$a$	specific area of the sample (m <sup>2</sup> /g)
$C^s$	concentration of As in solid sample (mol/g)
$C^f$	concentration of As in supercritical CO <sub>2</sub> (mol/mol CO <sub>2</sub> )
$E$	extraction efficiency
$F$	mole flow rate of CO <sub>2</sub> (mol/min)
$f$	specific mole flow rate of CO <sub>2</sub> (mol/(min g))
$K$	stability constant of the ion-pair
$K_e$	equilibrium constant of the ion-pair between supercritical fluid and solid sample
$k$	extraction rate constant (min <sup>-1</sup> )
$k_f$	mass transfer coefficient (mol/(min m <sup>2</sup> ))
$M$	molecular weight (g/mol)
$m$	mass of the solid sample (g)
$P$	extraction pressure (MPa)
$t$	extraction time (min)
$T$	extraction temperature (°C)
$X$	dosage of the ion-pairing reagent (mol/mol)
$Y$	mole ratio of ethanol to CO <sub>2</sub> (mol/mol)

### Subscripts

0	before extraction
I	ion-pair
*	in equilibrium

extraction of the arsenic-containing anions by supercritical CO<sub>2</sub> with ion-pairing was established, and verified by experiments with six tetra-butylammonium bromides as the ion-pairing agents. The evaluation of the ion-pairing reagents and process parameter effects on the extraction efficiency were also investigated.

## 2. Experimental

### 2.1. Materials

Tetra-butylammonium bromide (Bu<sub>4</sub>NBr) (99.5 wt%, Beijing Chemicals Co.), tetra-hexammonium bromide (Hex<sub>4</sub>NBr) (99%, ACROS), tetra-octylammonium bromide (Oct<sub>4</sub>NBr) (99%, Aldrich), dodecyltrimethylammonium bromide (Dod(Me)<sub>3</sub>NBr) (99%, Aldrich), myristyltrimethylammonium bromide (Myr(Me)<sub>3</sub>NBr) (99%, ACROS), hexadecyltrimethylammonium bromide (Hex(Me)<sub>3</sub>NBr) (99%, ACROS) and ethanol (99.7 wt%, Beijing Chemicals Co.) were used as received. Standard As solution (GSB G 62027–90, 1000 μg As/ml, As<sub>2</sub>O<sub>3</sub> dissolved in 5 wt% H<sub>2</sub>SO<sub>4</sub> solution) was obtained from National Steel Material Testing Center of China (Beijing, China). CO<sub>2</sub> (99.9%) was supplied by Beijing Analytical Apparatus

Co. (Beijing, China) and purified with an activated carbon column (1 m in length and 2 cm i.d.). The filter paper (quantitative analysis grade with 0.1 μm diameter pores) was obtained from Fuyang Special Paper Co. (Hangzhou, China), and used without any further treatment.

### 2.2. Analysis

The arsenic contents were determined by atomic fluorescence spectrophotometry after the digestion of solid samples before and after the extraction. The analytical method was the same as that described in another paper [7].

### 2.3. Experimental set-up and procedure

#### 2.3.1. Sample preparation

The solid sample was prepared by spiking the filter paper with the arsenic solution. A 100 μg As/ml aqueous solution was made by diluting 25 ml standard arsenic solution with water to 250 ml, and adjusting its pH to 7 by dropping 2 M NaOH aqueous solution. The filter paper was immersed in the solution for 2 h, and then dried in air at 40 °C for 4 h.

#### 2.3.2. Ion-pairing

The desired amount of the ion-pairing reagent was dissolved in 15 ml ethanol to form the reagent solution. The pH of this solution was also adjusted using NaOH aqueous solution. The solid sample was mixed with the reagent solution for 2 h to transform the anions to be ion-pairs, and then dried at 40 °C in air for 4 h to evaporate ethanol. After that, the samples were extracted by supercritical CO<sub>2</sub> with ethanol as the modifier.

The dosage of the ion-pairing reagent was expressed as  $X$  (mol/mol):

$$X = \frac{M_{A^+}}{M_{As}} \quad (1)$$

where  $M_{A^+}$  is the moles of the ion-pairing reagent and  $M_{As}$  is the moles of arsenic atoms in the sample.

#### 2.3.3. Supercritical CO<sub>2</sub> extraction

The apparatus for supercritical CO<sub>2</sub> extraction was schematically shown in Fig. 1. A sample of 5 g after ion-pairing was loaded in a sample holder (20 ml), and placed into the extractor (30 mm i.d. × 150 mm in length). The liquefied CO<sub>2</sub> was charged and pressurized using a high-pressure metering pump (2J-X 5/45, Zhijiang Instruments, Hangzhou, China). A back pressure regulator (BY50, Yixin Co., Beijing, China) was used to control the outlet pressure of the CO<sub>2</sub> pump. The flow rate of CO<sub>2</sub> was controlled by the metering pump with an accuracy of ±0.1 NL/min, and measured by a gas flow meter. High pressure CO<sub>2</sub> was heated to the desired temperature. Ethanol as the co-solvent was delivered by a syringe pump (LB-10C, Xingda Company, Beijing, China), and mixed with supercritical CO<sub>2</sub> in the mixing column (30 mm i.d. × 150 mm in length). The extraction pressure

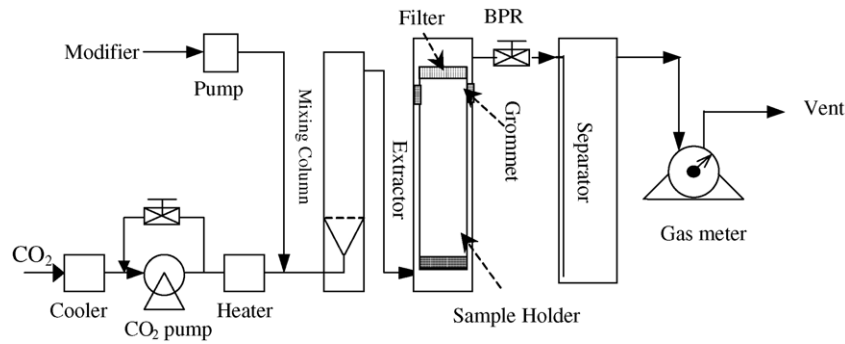


Fig. 1. Schematic diagram of supercritical CO<sub>2</sub> extraction system.

was controlled by using another back-pressure regulator (BPR) (BY45, Yixin Co., Beijing, China) with an accuracy of  $\pm 0.1$  MPa. The extraction temperature was measured with thermocouples and controlled with an accuracy of  $\pm 0.2$  °C by flowing the heating water through the jackets. Every experiment was repeated more than three times. The average extraction efficiency was reported with the standard deviation less than 2.5%.

The content of ethanol in sc-CO<sub>2</sub> was denoted by the mole ratio of ethanol to CO<sub>2</sub> as following:

$$Y = \frac{L}{F} (\text{mol/mol}) \quad (2)$$

where  $L$  is the mole rate of ethanol (mol/min);  $F$  is the mole rate of CO<sub>2</sub> (mol/min).

The extraction efficiency was defined as:

$$E = \frac{C_0^s - C^s}{C_0^s} \quad (3)$$

where  $E$  is the extraction efficiency;  $C_0^s$  is the initial content of arsenic in the sample (mol/g); and  $C^s$  is the residual content of arsenic in the sample (mol/g).

### 3. Model

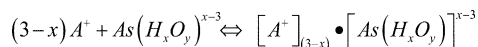
#### 3.1. Ion-pairing equilibrium

The ion-pairing reagent, tetra-alkylammonium bromide, disassociated to be tetra-alkylammonium cation and bromide anion in the solution according to Scheme 1.

The arsenic-containing anions associate with tetra-alkylammonium cations to form ion-pairs in the solid sample according to Scheme 2. Where  $A^+$  is tetra-alkylammonium



Scheme 1.



Scheme 2.

cation;  $As(H_xO_y)^{x-3}$  is arsenic-containing anion;  $y$  is 3 and 4, respectively for As(III) and As(V); depending on the pH,  $x$  might be 0, 1 or 2;  $[A^+]_{(3-x)}[As(H_xO_y)]^{x-3}$  is the ion-pair and denoted as I, which is extractable using supercritical CO<sub>2</sub>.

The total content of arsenic in the sample was:

$$C^s = C_{As(H_xO_y)^{x-3}}^s + C_I^s \quad (4)$$

where  $C_I^s$  is the content of the formed ion-pair; and  $C_{As(H_xO_y)^{x-3}}^s$  is the content of the arsenic-containing anion.

Because the arsenic-containing anions were not extractable by supercritical CO<sub>2</sub>, so the content of arsenic-containing anions in the sample is constant during the extraction, that is,

$$C_{As(H_xO_y)^{x-3}}^s = C_{As(H_xO_y)^{x-3},0}^s \quad (5)$$

The total content of arsenic in the sample during the extraction is:

$$C^s = C_{As(H_xO_y)^{x-3},0}^s + C_I^s \quad (6)$$

With infinite extraction time, the ion-pair should be completely extracted by supercritical CO<sub>2</sub>, and the total content of arsenic in the sample became:

$$C_\infty^s = C_{As(H_xO_y)^{x-3},0}^s \quad (7)$$

The content of the ion-pair in the sample can be expressed as:

$$C_I^s = C^s - C_\infty^s \quad (8)$$

The ion-pairing reaction in the solid sample could be reasonably considered to be in equilibrium due to the enough long time for ion-pairing treatment. The equilibrium constant of the ion-pairing reaction be expressed as:

$$K = \frac{C_{I,0}^s}{(C_{A,0}^s)^{3-x} C_\infty^s} \quad (9)$$

where  $C_{A,0}^s$  is the content of the ion-pairing reagent in the sample before extraction.

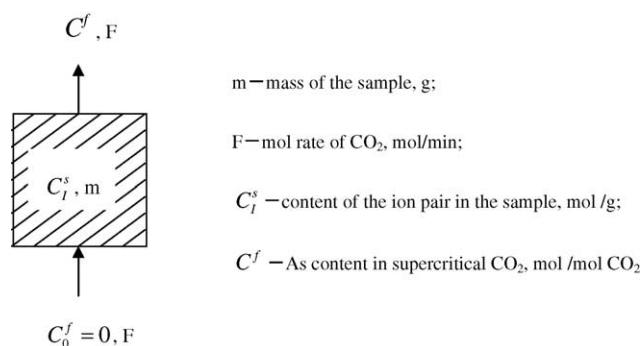


Fig. 2. Modeling for supercritical CO<sub>2</sub> extraction of the ion-pairs.

The total content of the ion-pairs before extraction was:

$$C_{1,0}^s = C_0^s - C_\infty^s \quad (10)$$

And, then:

$$K = \frac{C_0^s - C_\infty^s}{(C_{A,0}^s)^{3-x} C_\infty^s} \quad (11)$$

### 3.2. Supercritical CO<sub>2</sub> extraction of the ion-pairs

Considering a low height of the sample packed in the sample holder, the following assumptions were made for modeling the dynamic extraction of the formed ion-pairs (Fig. 2):

1. The arsenic species are uniformly distributed in the solid sample.
2. The flow of supercritical CO<sub>2</sub> phase is a well-mixed flow.

The mass balance for the time period  $t \rightarrow t + dt$  is:

$$-d(mC_1^s) = FC^f dt \quad (12)$$

$$FC^f dt = mak_f(C_*^f - C^f) dt \quad (13)$$

where  $a$  is the specific area of the sample (m<sup>2</sup>/g);  $k_f$  is the mass transfer coefficient in sc-CO<sub>2</sub> phase (mol/(m<sup>2</sup> min));  $C^f$  is the As content in sc-CO<sub>2</sub> phase (mol/mol CO<sub>2</sub>);  $C_*^f$  is the As content in sc-CO<sub>2</sub> phase equilibrated with the solid sample (mol/mol CO<sub>2</sub>).

For this system, the equilibrium relation was considered to be linear, and

$$C_*^f = K_e C_1^s \quad (14)$$

where  $K_e$  is the equilibrium constant of the ion-pair between the sc-CO<sub>2</sub> phase and the solid sample.

From Eqs. (12)–(14) and  $f = F/m$ , which was defined as the specific flow rate of CO<sub>2</sub> (mol/(min g)),

$$-\frac{dC_1^s}{dt} = \frac{fak_f}{f + ak_f} K_e C_1^s \quad (15)$$

Define

$$\frac{1}{k} = \frac{1}{K_e} \left( \frac{1}{ak_f} + \frac{1}{f} \right) \quad (16)$$

Eq. (15) became as:

$$-\frac{dC_1^s}{dt} = kC_1^s \quad (17)$$

where  $k$  is the extraction rate constant (min<sup>-1</sup>).

With Eq. (8),

$$-\frac{d(C^s - C_\infty^s)}{dt} = k(C^s - C_\infty^s) \quad (18)$$

Then,

$$C^s - C_\infty^s = (C_0^s - C_\infty^s)e^{-kt} \quad (19)$$

So, the extraction efficiency defined as Eq. (3) is:

$$E = \frac{C_0^s - C_\infty^s}{C_0^s} (1 - e^{-kt}) \quad (20)$$

Defining  $E_{\max} = C_0^s - C_\infty^s / C_0^s$ , which is the theoretical extraction efficiency, the extraction efficiency can be expressed as:

$$E = E_{\max}(1 - e^{-kt}) \quad (21)$$

From Eq. (11),  $E_{\max}$  could be written as:

$$\frac{1}{E_{\max}} = 1 + \frac{1}{K(C_{A,0}^s)^{3-x}} \quad (22)$$

As shown in Eq. (21), the extraction efficiency  $E$  depends positively on the theoretical extraction efficiency  $E_{\max}$ , the extraction rate constant  $k$  and the extraction time  $t$ . The extraction rate constant  $k$  is the function of the equilibrium constant  $K_e$ , the specific flow rate of CO<sub>2</sub>  $f$  and the mass transfer coefficient  $k_f$ . The extraction rate constant  $k$  depends on the extraction temperature and pressure, CO<sub>2</sub> flow rate, ethanol concentration in CO<sub>2</sub> and the dissolution power of sc-CO<sub>2</sub> for the ion-pair. The theoretical extraction efficiency  $E_{\max}$  is related with the stability constant of the ion-pair, and depends on the chemical structures of the anion and the ion-pairing conditions.

## 4. Results and discussion

### 4.1. Model validation and ion-pairing reagents evaluation

Eq. (21) was well validated by the experimental data of the extraction efficiency at different extraction time for the six tetra-alkylammonium bromides as the ion-pairing agents. The theoretical extraction efficiency  $E_{\max}$  and the extraction rate constant  $k$  were found by fitting experimental data with Eq. (21). In the experiment, 0.5 g of sample, which was treated using the ion-pairing reagent solution (pH 7) with the dosage ( $X$ ) of 140 mol/mol for ion-pairing and had the As content before extraction ( $C_0^s$ )  $8.8 \times 10^{-6}$  mol/g, was extracted using ethanol modified sc-CO<sub>2</sub> ( $Y=0.04$ ) at 20 MPa

Table 1  
The parameters found by fitting experimental extraction efficiency with Eq. (21)

Ion-pairing reagent	$E_{\max}$	$k$ (min <sup>-1</sup> )	$r$	AARD%	MARD%
Dod(Me) <sub>3</sub> NBr	0.4460 ± 0.0120	0.0162 ± 0.0013	0.998	1.26	2.22
Myr(Me) <sub>3</sub> NBr	0.4448 ± 0.0129	0.0167 ± 0.0099	0.998	1.27	2.82
Hex(Me) <sub>3</sub> NBr	0.4327 ± 0.0229	0.0169 ± 0.0027	0.995	2.59	4.89
Bu <sub>4</sub> NBr	0.3627 ± 0.0037	0.0102 ± 0.0003	0.999	0.38	0.69
Hex <sub>4</sub> NBr	0.3169 ± 0.0121	0.0139 ± 0.0014	0.998	1.58	2.69
Oct <sub>4</sub> NBr	0.2605 ± 0.0099	0.0145 ± 0.0015	0.998	1.63	2.80

Here,  $r$  is the correlation coefficient of the regression; AARD is the average absolute relative deviation in predicting the reported values of the extraction efficiency; MARD is the maximal absolute relative deviation in predicting the reported values of the extraction efficiency.  $X$ : 140 mol/mol; pH of ion-pairing reagent solution: 7;  $C_0^S$ :  $8.8 \times 10^{-6}$  mol/g;  $T$ : 40 °C;  $P$ : 20 MPa;  $f$ : 0.332 mol/(mol g);  $Y$ : 0.04.

and 40 °C with 0.332 mol/(min g) of CO<sub>2</sub> flow rate. The tetra-alkylammoniums containing three methyl groups and a long  $n$ -alkyl (type I), and the tetra-alkylammonium with four short  $n$ -alkyl groups (type II) were used as the ion-pairing reagents.

As listed in Table 1, the correlation coefficient  $r$  was greater than 0.995. The average absolute relative deviation (AARD) of the extraction efficiency was less than 2.59% with the maximal absolute relative deviation (MARD) less than 4.89%. The results indicated that the model proposed could describe the sc-CO<sub>2</sub> extraction of arsenic-containing anions with ion-pairing with the satisfactory accuracy.

With same dosage of the ion-pairing reagent and pH of the reagent solution,  $E_{\max}$  was only dependent on the stability constant of the ion-pairing reaction  $K$ , and increased as  $K$  increasing. The  $E_{\max}$  could characterize the ability of the ion-pairing reagent to form the ion-pair with the As containing anion. With the certain extraction condition, the extraction rate constant  $k$  positively depends only on the dissolution power of sc-CO<sub>2</sub> for the ion-pair. As shown in Table 1,  $E_{\max}$  and  $k$  were significantly affected by the chemical structure and molecular size of the ion-pairing reagent. Using type I tetra-alkylammoniums,  $E_{\max}$  and  $k$  are larger than ones in the case of using type II tetra-alkylammoniums.  $E_{\max}$  was decreased as increasing the length of the  $n$ -alkyl contained in the tetra-alkylammonium. These results disclosed that the ability of the tetra-alkylammonium to associate with arsenic anions to form ion-pairs was negatively dependent on its molecular size. For both two kinds of tetra-alkylammonium,  $k$  increased as the length of the  $n$ -alkyl. In order to obtain high extraction efficiency, it is necessary to maximize  $E_{\max}$  and  $k$  by selecting the ion-pairing reagent with suitable molecular structure and size, and optimizing the conditions of the ion-pairing reaction and sc-CO<sub>2</sub> extraction. As the  $E_{\max}$  and  $k$  values with 95% confidence intervals shown in Table 1, the tetra-alkylammoniums containing three methyl groups and a long  $n$ -alkyl are obviously more effective than the tetra-alkylammonium containing four short  $n$ -alkyl groups.

#### 4.2. Process parameter effects on the extraction efficiency

The extraction of the arsenic-containing anion was strongly affected by the conditions of ion-pairing reaction

and sc-CO<sub>2</sub> extraction. The effects of the process parameters, including the dosage and pH of the ion-pairing reagent solution, extraction time, pressure, temperature, specific CO<sub>2</sub> mole flow rate and ethanol content in CO<sub>2</sub>, on the extraction efficiency were investigated using Myr(Me)<sub>3</sub>NBr and Bu<sub>4</sub>NBr as the ion-pairing reagents.

##### 4.2.1. Extraction time

The dependence of the extraction efficiency on the extraction time is governed by Eq. (21), which was validated with the experiments using the six ion-pairing reagents. As Eq. (21) disclosed, the extraction efficiency increases exponentially as increasing the extraction time. Fig. 3 shows the effect of extraction time on the extraction efficiency with Myr(Me)<sub>3</sub>NBr as the ion-pairing reagent under following conditions: a 0.5 g of sample with initial As content  $C_0^S$ :  $8.8 \times 10^{-6}$  mol/g treated by using the ion-pairing reagent solution (pH 7) with the dosage ( $X$ ) of 140 mol/mol for ion-pairing, and extracted using ethanol modified sc-CO<sub>2</sub> ( $Y = 0.04$ ) under 20 MPa and 40 °C with 0.332 mol/(min g) of CO<sub>2</sub>. As shown in Fig. 3, the extraction efficiency was close to the theoretical extraction efficiency  $E_{\max}$  with enough long extraction time.

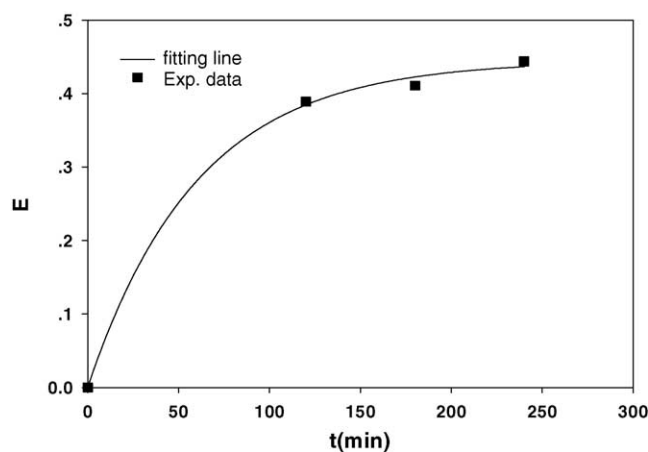


Fig. 3. Extraction efficiency vs. extraction time using Myr(Me)<sub>3</sub>NBr as the ion-pairing reagent.  $X$ : 140 mol/mol; pH 7;  $C_0^S$ :  $8.8 \times 10^{-6}$  mol/g;  $T$ : 40 °C;  $P$ : 20 MPa;  $f$ : 0.332 mol/(mol g);  $Y$ : 0.04.



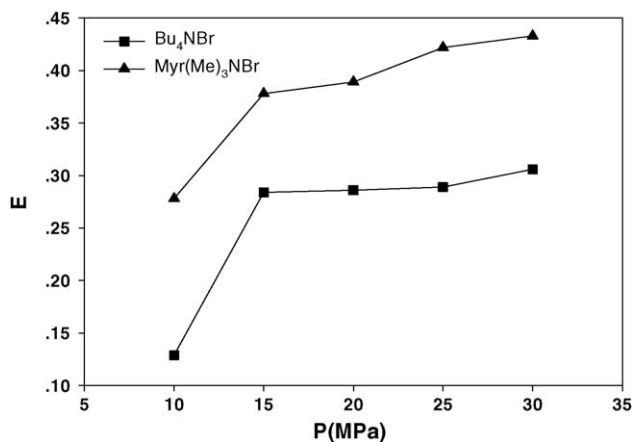


Fig. 4. Pressure effect on extraction efficiency.  $X$ : 140 mol/mol; pH 9;  $C_0^s$ :  $9.5 \times 10^{-6}$  mol/g;  $T$ : 40 °C;  $f$ : 0.332 mol/(mol g);  $Y$ : 0.04;  $t$ : 120 min.

#### 4.2.2. Pressure

Pressure is an important factor for the sc-CO<sub>2</sub> extraction of the arsenic-containing-anion which was ion-paired with the tetra-alkylammonium cation. The density and polarity of sc-CO<sub>2</sub> increase with pressure increase. The dissolution power of sc-CO<sub>2</sub> for the ion-pair was enhanced as elevating the extraction pressure. The equilibrium constant of the ion-pair between the solid sample and sc-CO<sub>2</sub>,  $K_e$ , could be increased using higher pressure. As disclosed by Eq. (16), the extraction rate constant  $k$  should increase as pressure increased, and then the extraction efficiency increases. The experimental extraction efficiencies at different pressures were plotted in Fig. 4 for the extractions of the samples, which were treated by the ethanol solutions (pH 9) of Bu<sub>4</sub>NBr or Myr(Me)<sub>3</sub>NBr with the dosage of 140 mol/mol, by using 0.332 mol/(min g) of ethanol modified sc-CO<sub>2</sub> ( $Y=0.04$ ) at 40 °C for 120 min. As shown in Fig. 4, the extraction efficiency was enlarged as the pressure elevated. Compared with the value at 10 MPa, the extraction efficiency was significantly enhanced at 15 MPa. At the pressures above 15 MPa, the extraction efficiency was increased slowly as pressure increased. The experimental results were qualitatively consistent with the argument using the model proposed.

#### 4.2.3. Temperature

Another factor, which significantly affects the extraction efficiency, is the extraction temperature. The dependence of the extraction efficiency on the temperature was experimentally determined, and shown in Fig. 5. The extraction efficiency could be enhanced by increasing the extraction temperature both for the cases using Bu<sub>4</sub>NBr and Myr(Me)<sub>3</sub>NBr as the ion-pairing reagents. The temperature dependence of the extraction efficiency could be reasonably explained by consideration of two aspects. One reason is that elevating temperature can facilitate the mass transfer from the solid sample to the supercritical fluid, that is,  $k_f$  is enlarged at higher temperature. As verified by many experimental and theoretical works, the solubility of solid

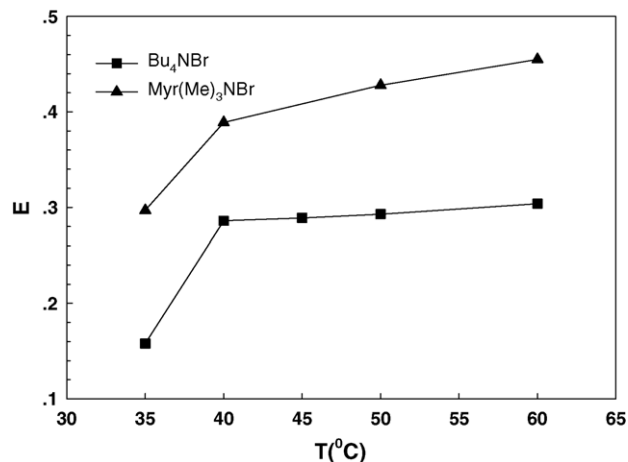


Fig. 5. Temperature effect on extraction efficiency.  $X$ : 140 mol/mol; pH 9;  $C_0^s$ :  $9.5 \times 10^{-6}$  mol/g;  $P$ : 20 MPa;  $f$ : 0.332 mol/(mol g);  $Y$ : 0.04;  $t$ : 120 min.

solutes in supercritical fluids will be enhanced by elevating temperature when the pressure is above a specific value [18]. So, another possible reason is that the dissolution power of sc-CO<sub>2</sub> for the ion-pair, and then  $K_e$  will be enhanced by raising temperature at the experimental pressure (20 MPa). As indicated by Eq. (16) and (21), the increments of both  $k_f$  and  $K_e$  could make the extraction rate constant  $k$  be enlarged, and then the extraction efficiency be enhanced.

#### 4.2.4. Specific flow rate of CO<sub>2</sub>

In the dynamic extraction mode, the specific flow rate of CO<sub>2</sub> is also an important factor, which affects considerably the extraction efficiency. As described by Eq. (16), the extraction rate constant  $k$  would be enhanced by increasing the CO<sub>2</sub> specific flow rate  $f$ . On the other hand, the mass transfer constant  $k_f$  depends positively on the specific flow rate of CO<sub>2</sub>. As a result, increasing the specific flow rate of CO<sub>2</sub> could enhance the extraction efficiency. However, the influence of the specific flow rate of CO<sub>2</sub> on the mass transfer  $k_f$  becomes very slight when the value of  $f$  is above a specific value. In such case,  $f \gg ak_f$  and  $k \cong K_e ak_f$  from Eq. (16), that is,  $k$  is independent on  $f$ , and the extraction efficiency  $E$  becomes also independent on the specific flow rate of CO<sub>2</sub>. The experimental results thus confirm the model proposed. Fig. 6 show the extraction efficiencies with different specific flow rate of CO<sub>2</sub>, which were experimentally determined by using the ethanol solutions (pH 9) of Bu<sub>4</sub>NBr or Myr(Me)<sub>3</sub>NBr with a dosage of 140 mol/mol for the ion-pairing, and using ethanol modified sc-CO<sub>2</sub> ( $Y=0.04$ ) for the extraction at 20 MPa and 40 °C for 120 min.

#### 4.2.5. The mole ratio of ethanol to CO<sub>2</sub>

The modifier, ethanol, affects the extraction in two aspects. Firstly, ethanol is a solvating agent for the ion-pair. In our case, the ion-pair was formed with the small arsenic-containing anion and the tetra-alkylammonium cation that is large and lipophilic. According to the solvation theory proposed by Higuchi [19], the external surface of the ion-pair

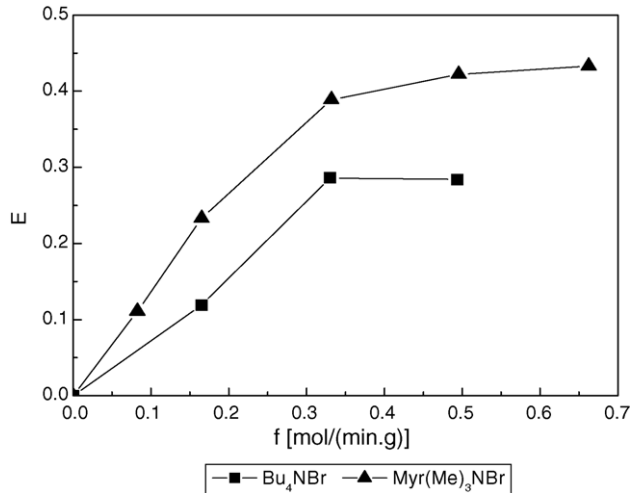


Fig. 6. Dependence of extraction efficiency on specific CO<sub>2</sub> flow rate.  $X$ : 140 mol/mol; pH 9;  $C_0^s$ :  $9.5 \times 10^{-6}$  mol/g;  $T$ : 40 °C;  $P$ : 20 MPa;  $Y$ : 0.04;  $t$ : 120 min.

would be expected to carry a relatively negative charge per unit area. Such ion-pairs may be effectively solvated by the molecules with acidic protons such as alcohols. Since the bonded solvating molecules of ethanol would have their polar end buried adjacent to the anion, the appearance presented to the surrounding solvent by the solvated ion-pair would be that of a relatively non-polar aggregate, and favorable to be dissolved in sc-CO<sub>2</sub>. On the other hand, the modification of sc-CO<sub>2</sub> with ethanol would improve its solvent power for dissolving the ion-pair. As to results of these two effects, the equilibrium constant of the ion-pair between the supercritical fluid and the solid sample  $K_e$ , and then the extraction rate constant  $k$ , would be enhanced in the presence of ethanol in the system. According to the above argument, increasing the mole ratio of ethanol to CO<sub>2</sub> would increase the extraction efficiency. This was validated by the experiments using the ethanol solutions (pH 9) of Bu<sub>4</sub>NBr with the dosage of 140 mol/mol for the ion-pairing, and 0.332 mol/(min g) of sc-CO<sub>2</sub> for the extraction at 20 MPa and 40 °C for 120 min (as shown in Fig. 7).

#### 4.2.6. The dosage of the ion-pairing reagent

According to Scheme 1, the content of the ion-pairing reagent in the sample before extraction,  $C_{A,0}^s$  would increase with the increased dosage of the ion-pairing reagent. As Eq. (22) indicated, increasing  $C_{A,0}^s$  would enhance  $E_{\max}$  and then increase the extraction efficiency  $E$  when the pH of the solution of the ion-pairing reagent is fixed. However, with excess dosage of the ion-pairing reagent, the adsorption of tetraalkylammonium cation on the solid sample would be saturated although the concentration of the tetra-alkylammonium cation in the solution of the ion-pairing reagent increased. In such a case,  $C_{A,0}^s$  would approach a certain value and lead to a constant  $E_{\max}$ . It could be predicted that  $E$  would be a constant when the dosage of the ion-pairing reagent was beyond a specific value. The experimental results shown

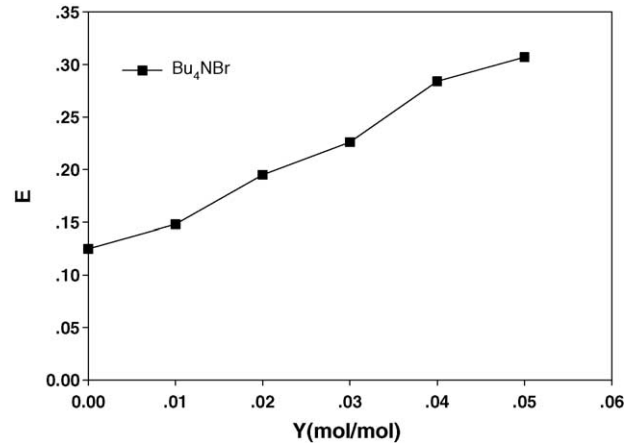


Fig. 7. Dependence of extraction efficiency on mole ratio of ethanol to CO<sub>2</sub>.  $X$ : 140 mol/mol; pH 9;  $C_0^s$ :  $9.5 \times 10^{-6}$  mol/g;  $T$ : 40 °C;  $P$ : 20 MPa;  $f$ : 0.332 mol/(mol g);  $t$ : 120 min.

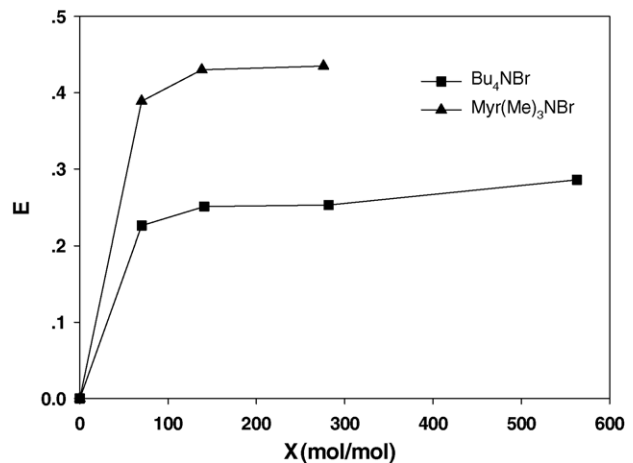


Fig. 8. The dependence of extraction efficiency on dosage of the ion-pairing reagent.  $C_0^s$ :  $9.5 \times 10^{-6}$  mol/g; pH 9;  $T$ : 40 °C;  $P$ : 20 MPa;  $f$ : 0.332 mol/(mol g);  $Y$ : 0.02;  $t$ : 120 min.

in Fig. 8 bears above argument. Using Bu<sub>4</sub>NBr as the ion-pairing reagent, the extraction efficiency was enhanced by increasing the dosage of Bu<sub>4</sub>NBr when  $X$  was less than 141 mol/mol, and almost not changed with the dosage of Bu<sub>4</sub>NBr above 141 mol/mol. With Myr(Me)<sub>3</sub>NBr, the extraction efficiency approached the constant value when  $X$  was larger than 138 mol/mol.

#### 4.2.7. pH of the solution of the ion-pairing reagent

During the ion-pairing process, pH of the ion-pairing reagent solution influences the speciation of arsenic-containing ions in the solid sample. The values of  $x$  and  $y$  in Scheme 2 and the stability constant  $K$  of the ion-pair would be different with different pH of the ion-pairing reagent solution, that would lead to different  $E_{\max}$  as Eq. (11) indicated. On the other hand, the equilibrium constant  $K_e$  of the ion-pair consisting of the arsenic-containing anion in the different chemical form and tetra-alkylammonium cation would be different, that would make the extraction rate constant  $k$  be

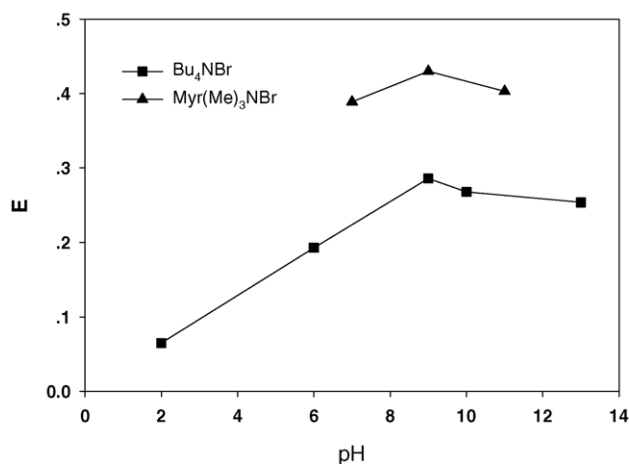


Fig. 9. The dependence of extraction efficiency on pH of the ion-pairing reagent solution.  $X$ : 140 mol/mol;  $C_0^s$ :  $9.5 \times 10^{-6}$  mol/g;  $T$ : 40 °C;  $P$ : 20 MPa;  $f$ : 0.332 mol/(mol g);  $Y$ : 0.02;  $t$ : 120 min.

different. Due to these two reasons, changing pH of the solution of the ion-pairing reagent would change the extraction efficiency.

Fig. 9 shows the dependence of the extraction efficiency on pH of the ion-pairing reagent Bu<sub>4</sub>NBr or Myr(Me)<sub>3</sub>NBr solution, which was experimentally determined under the conditions with the dosage of 140 mol/mol for the ion-pairing and the extraction using 0.332 mol/(min g) of sc-CO<sub>2</sub> modified with ethanol at 40 °C and 20 MPa for 120 min. Using Bu<sub>4</sub>NBr as the ion-pairing reagent, the extraction efficiency was quite low when the pH of the ion-pairing reagent solution was 2. As shown in Fig. 9, the extraction efficiency was obviously enlarged as the pH increasing, and approached the maximal value at 9 of pH. The extraction efficiency decreased tardily as the pH increasing when the pH was larger than 9. The same dependence of extraction efficiency on pH of the ion-pairing reagent solution was observed for the case using Myr(Me)<sub>3</sub>NBr as the ion-pairing reagent.

## 5. Conclusion

Supercritical CO<sub>2</sub> extraction of arsenic-containing anions ion-paired with tetra-alkylammonium cations can be described by the model proposed in this paper. As the equation  $E = E_{\max}(1 - e^{-kt})$  indicated, the extraction efficiency  $E$  depends positively on the theoretical extraction efficiency  $E_{\max}$ , the extraction rate constant  $k$  and the extraction time  $t$ . The theoretical extraction efficiency  $E_{\max}$  is the function of the stability constant of the ion-pair  $K$ , and dependent on the chemical structures of the ion-pairing reagent and the condition for ion-pairing. The extraction rate constant  $k$  is the function of the phase equilibrium constant  $K_e$ , the specific flow rate of CO<sub>2</sub>  $f$  and the mass transfer coefficient  $k_f$ , and dependent on the extraction temperature and pressure, CO<sub>2</sub> flow rate, ethanol content in CO<sub>2</sub> and also the chemical structures of the ion-pairing reagent.

The theoretical extraction efficiency  $E_{\max}$  and the extraction rate constant  $k$  are strongly dependent on the chemical structure and molecular size of the ion-pairing reagent. Using the tetra-alkylammoniums containing three methyl and a long  $n$ -alkyl,  $E_{\max}$  and  $k$  are larger than the values in the case of the tetra-alkylammonium containing four short  $n$ -alkyl groups. For both two kinds of tetra-alkylammonium cation, increasing the length of the  $n$ -alkyl group leads to  $E_{\max}$  decreased and  $k$  increased. The tetra-alkylammoniums containing three methyl groups and a long  $n$ -alkyl are more effective than the tetra-alkylammonium containing four same short  $n$ -alkyl groups.

The process parameters, extraction time, pressure, temperature, the specific mole flow rate of CO<sub>2</sub>, the mole ratio of ethanol to CO<sub>2</sub>, the dosage of the ion-pairing reagent and the pH of the ion-pairing reagent solution affect the extraction efficiency. The process parameter effects on the extraction efficiency experimentally determined coincide with the analysis using the model proposed.

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