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A Comparative Study of Extraction of Selenium(IV) Using Various Organic Solvents in Hydrochloric Acid Media

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To date, suitable organic solvents for the extraction of tetravalent selenium (Se(IV)) in highly concentrated hydrochloric acid have not been clarified systematically. In this study, the extraction of Se(IV) using various organic solvents was compared. Se(IV) was extracted from 8.0 mol/dm^3 hydrochloric acid using various ketones. Se(IV) extraction using ethers was lower, while that using hydrocarbons was negligible. The correlation between the extraction and log*P* value of solvents was small, however, the extraction using a hydrophobic dicyclohexyl ketone was lower. The extractability of Se(IV) by most solvents can be classified with the Hansen solubility parameters of the solvents. However, Se(IV) extracted by 2-nonanone was not stripped by contact with fresh aqueous solutions containing HCl, HNO_3, NaOH, or EDTA.

1. Introduction

Selenium is an essential nutrient for humans and animals, but intake of elevated concentrations can result in toxic effects [1]. In industry, selenium is an important element to prepare semiconductors due to its properties such as high photoconductivity and anisotropic thermal conductivity [2]. Copper indium gallium selenide (CIGS) based solar cells are powerful for solar power generation [3].

Tetravalent selenium Se(IV) is present as a tetrachlorocomplex ($SeCl_4$) in hydrochloric acid media and is extracted using ketones [4,5]. Extraction of Se(IV) using methyl isobutyl ketone (MIBK) in 8.5 N hydrochloric acid was reported in 1958 [6]. Extraction using methyl ethyl ketone was also studied [5]. Ethereal compounds such as dibutyl carbitol (DBC) and cyclopentyl methyl ether (CPME) also extract Se(IV) [7]. Therefore Se(IV) can be extracted using various oxygen-containing organic solvents. Recently, the authors have investigated extraction of Au(III), Ga(III), and As(III) using ethers and ketones in hydrochloric acid media [8-15]. Aromatic 1,2-diethers with two ether oxygens in the vicinity shows extractability for Au(III) [10]. Various aliphatic and aromatic ketones also extract Au(III) [11,12]. More polar solvents tend to be favorable as extracting solvents: ethers and ketones with shorter alkyl side chains exhibit higher extractability [10-13]. However, more polar solvents also have higher aqueous solubility, resulting in leakage into the aqueous phase in continuous extraction operations. Although such the extraction behavior may also be the similar to that of Se(IV), there have been few comparative studies on the extraction of Se(IV) using various organic solvents in the past.

In this study, extraction using various organic solvents such as DBC and 2-nonanone (2-NON) was compared to clarifiy the requirements for suitable solvents for the Se(IV) extraction (Figure 1). According to the precedents for the extraction of metal chlorides [13-15], the effect of the hydrophilic/hydrophobic balance and solubility parameters of the solvents on the extractability of Se(IV) was investigated. Stripping of Se(IV) extracted in typical solvents was also examined.

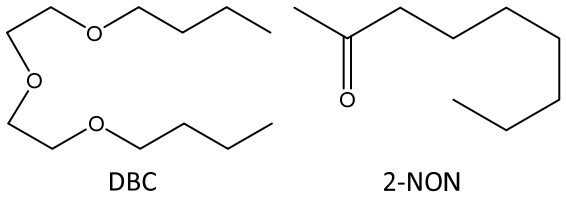

Figure 1. Structures of DBC and 2-NON.

2. Experimental

2.1 Reagents

Analytical grade sodium selenite(IV) (Wako Pure Chemical Ind. Ltd., Japan) was used to prepare test solutions. All the organic solvents used in the extraction tests are analytical grade and used without further purification. All other reagents were of analytical grade and were used as received.

2.2 Extraction of Se(IV) using various organic solvents in hydrochloric acid media

Extraction tests for Se(IV) were conducted by the batchwise method. An aqueous solution was prepared by dissolving Se(IV) to form 1.0×10^{-3} mol/dm^3 solutions in 3.0 – 8.0 mol/dm^3 hydrochloric acid. The aqueous solution (5.0 cm^3) was contacted using an organic solvent (1.0 cm^3) and the mixture (organic-to-aqueous phase ratio (O/A) = 0.2) was shaken at 30 °C for 1.0 h. After phase separation, the concentration of Se(IV) in the aqueous phase was measured using an atomic absorption photometer (AAS, AA-7000, Shimadzu, Japan) to determine the extraction percentage according to the following eq. (1):

$$\text{Extraction}\,[\%] = \frac{[\mathrm{M}]_{\mathrm{aq,init}} - [\mathrm{M}]_{\mathrm{aq,eq}}}{[\mathrm{M}]_{\mathrm{aq,init}}} \times 100 \qquad (1)$$

where $[\mathrm{M}]_{\mathrm{aq,init}}$ and $[\mathrm{M}]_{\mathrm{aq,eq}}$ represent the initial and equilibrium concentrations of Se(IV) in the aqueous phase, respectively.

The logarithm values of the partitioning coefficient between 1-octanol and water (log*P*) for various organic solvents were obtained using MarvinSketch 6.2.1 software (ChemAxon Ltd., Hungary) and the KLOP method [16], to estimate the hydrophilic/hydrophobic balance for the solvents. The relationship between Hansen solubility parameters (HSPs) of the extracting solvents and the extractability for Se(IV) was also studied [13-15]. The HSPs of the solvents were obtained using a special software HSPiP (Hansen Solubility Parameters in Practice) software ver.5 [17,18].

2.3 Stripping of Se(IV) from DBC and 2-NON

Forward extraction of Se(IV) (1.0×10^{-3} mol dm^{-3}) was performed by contacting an aqueous solution (30 cm^3) containing 8.0 mol dm^{-3} HCl and an organic solvent DBC or 2-NON (30 cm^3) (O/A = 1.0) for 1.0 h in a similar manner as described the section 2.2. After phase separation, the organic phase containing Se(IV) (5.0 cm^3) was contacted with a 5.0 cm^3 distilled water or fresh aqueous solution containing a different concentration of hydrochloric acid, nitric acid, sodium hydroxide, or EDTA disodium salt. Both phases were mixed and shaken at 30 ˚C for 24 h. The stripping solution was separated from the organic phase and the stripping percentage was calculated according to eq. (4):

$$\text{Stripping } [\%] = \frac{[\text{Se(IV)}]_{\text{aq,strip}}}{[\text{Se(IV)}]_{\text{org,init}}} \times 100 \quad (2)$$

where $[\text{Se(IV)}]_{\text{org,init}}$ and $[\text{Se(IV)}]_{\text{aq,strip}}$ are the Se(IV) concentrations in the organic phase before stripping and the aqueous phase after stripping, respectively.

3. Results and Discussion

3.1 Rate of Se(IV) extraction

The extraction rate of Se(IV) using DBC and 2-NON is shown in Figure 2. Extraction tests were performed with 8.0 M HCl for DBC and 6.0 M HCl for 2-NON to give moderate extraction percentages. Extraction of Se(IV) using 2-NON is rapid, which is similar to that of Ga(III) and As(III) from hydrochloric acid [14,15]. However, the extraction profile using DBC showed two stages: In the initial stage, the extraction increased rapidly within 1.0 h. After 15 h, the extraction further increased. The change of species of chloride complexes of Se(IV) may be the reason for the stepwise extraction. As metal extractions based on ion solvation are typically short processes, the extraction tests in the following sections were conducted for 1.0 h. Although the extraction may not be at equilibrium state, the extraction percentage should be an index value for the extractability using each solvent.

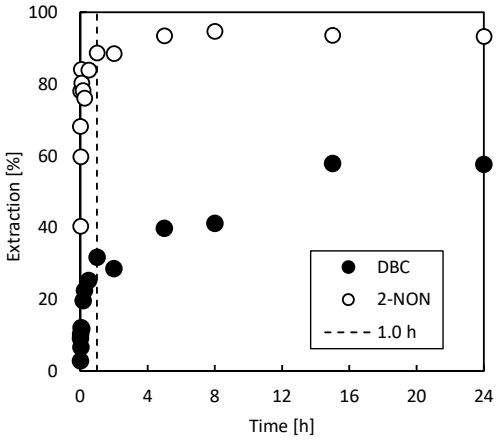

Figure 2. Rate of Se(IV) extraction using DBC (in 8.0 M HCl) and 2-NON (in 6.0 M HCl). $[\text{Se(IV)}] = 1.0 \times 10^{-3}$ mol/dm^3.

3.2 Dependence of the extractability on the HCl concentration

Figure 3 shows the extraction profiles of Se(IV) using various solvents as a function of HCl concentration. Alkanes did not extract Se(IV). The extraction using an aliphatic monoether dibutyl ether was also very low. DBC extracted Se(IV) only in 8 mol/dm^3 HCl. In contrast, monoketone compounds MIBK and 2-NON showed high extraction. MIBK with greater polarity showed higher extractability, and the order of the extractability (MIBK > 2-NON) is consistent with the extraction of Au(III), Ga(III), and As(III) [11-15]. 2-NON has a lower extractability but is preferred for industrial processes due to its low water solubility (0.5 g/dm^3) and higher flash point (76 °C) [11]. In the extraction of Au(III) and Ga(III), the extractabilities using DBC and 2-NON are comparable [11,15]. However, the extractability using ethereal compounds in Figure 3 is very low, which

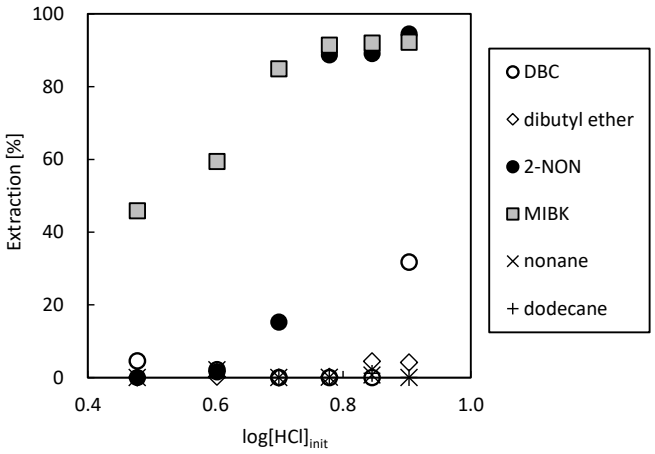

Figure 3. Extraction of Se(IV) using various organic solvents as a function of HCl concentration: O/A = 0.2, $[\text{Se(IV)}] = 1.0 \times 10^{-3}$ mol/dm^3.

is inconsistent with the results in a previous study [7]. The slow extraction using ethers as shown in Figure 2 might be the reason of the low extraction at 1.0 h.

3.3 Relationships between Se(IV) extractability and properties of solvents

In this study, extraction of Se(IV) using hydrocarbons, ethers, and ketones was compared because these solvents are chemically stable in hydrochloric acid media. Table 1 summarizes the values of log*P* and Hansen solubility parameters (HSPs) of organic solvents as well as extraction of Se(IV) in 8.0 mol/dm^3 HCl. All hydrocarbons hardly extract Se(IV). Among the 11 ketone solvents examined, most of the ones showed high extractabiilities. On the other hand, the extraction using ethers was in the range of 8.2 to 54.9%. In previous studies on Au(III) extraction using ketone solvents, the Au(III) extractability decreased as the decrease of the polarity of the solvents [12]. However, the relationship between Se(IV) extractability in 8.0 mol/dm^3 HCl and log*P* values of the solvents seems to be small (Figure 4). In case of the similar log*P* values of the solvents, the order of extractability was ketone > ether > hydrocarbon. Dicyclohexyl ketone, which has the highest log*P* in all ketones used, showed lower extraction. Therefore, less polar ketones may be unsuitable for the extraction.

In our recent study, Hansen solubility parameters were suggested to be useful for the prediction of the extractability of Au(III) [13], As [14], and Ga(III) [15]. Therefore, the relationship between HSPs and the extractability of Se(IV) was also investigated. Solvents were classified using an extraction of 50% as a threshold, and a Hansen solubility sphere was created so that solvents valid for the extraction were located inside. Additionally, the HSPs of the following 25 solvents with high aqueous solubility were added as invalid for the extraction to refine the Hansen sphere [13-15]; acetamide, acetic acid, acetone, acetylacetone, diethylene glycol, *N*,*N*-dimethyl acetamide, 1,4-dioxane, 1,3-dioxolane, glycerol, *N*-methyl-2-pyrrolidone, 1-propanol, propionamide, 2-propanol, propionic acid, propylene glycol, propylene glycol monoethyl ether, tetrahydrofuran, tripropylene glycol monomethyl ether, water, 1,1,3,3-tetramethoxypropane, *N*-methyl acetamide, *N*-methyl formamide, 3-methoxy butanol, isobutyric acid, and methoxy methanol.

Three-dimensional Hansen solubility parameter (HSP) diagrams of solvents based on the Se(IV) extractability are shown in Figure 5. In the resulting Hansen solubility sphere, all ketones were located inside the sphere, and all hydrocarbons and ethers were located outside the sphere, regardless the extractability. Of the 30 solvents in Table 1, 28 solvents (93.3%) are correctly classified based on the HSPs. An aliphatic ether methyl-*t*-butyl ether was classified as a valid solvent (Extraction=54.9%), however, the HSP was located outside the sphere (wrong out). The ether has a high aqueous solubility (51 g/dm^3) and is actually not suitable as an extracting solvent. In contrast, extraction using dicyclohexyl

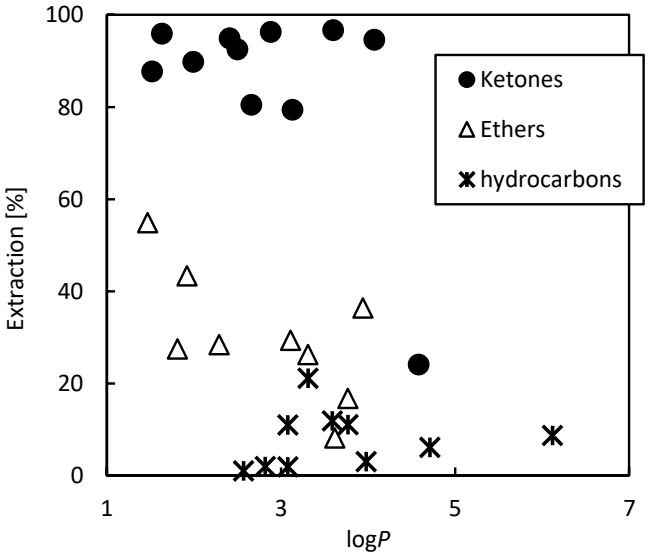

Figure 4. Relationship between the solvent log*P* and extraction of Se(IV) from 8.0 mol/dm^3 HCl: organic phase/aqueous phase (O/A) = 0.2.

Table 1. Values of log*P*, Hansen solubility parameters (HSPs) of organic solvents, and extraction of Se(IV) in 8.0 mol/dm^3 HCl: Shaded solvents showed the extraction at more than 50%.

Classification	Solvent	log*P*	δ_D	δ_P	δ_H	Extraction of Se(IV) [%]
ketone	methyl isobutyl ketone (MIBK)	1.52	15.3	6.1	4.1	87.8
ketone	2-heptanone	2.50	16.2	5.7	4.1	92.6
ketone	methyl isoamyl ketone	1.99	16	5.7	4.1	89.9
ketone	2-octanone	2.66	16.1	5.2	3.8	80.6
ketone	acetophenone	1.63	18.8	9.0	4.0	96.0
ketone	2-nonanone (2-NON)	3.13	16.1	5.1	3.5	79.4
ketone	propiophenone	2.41	18.2	6.3	4	95.0
ketone	2-decanone	3.60	16.1	4.4	3.1	96.7
ketone	butyrophenone	2.88	17.4	5.5	4.1	96.4
ketone	2-undecanone	4.07	16.2	4.2	3	94.7
ketone	dicyclohexyl ketone	4.58	17.4	3.8	2.9	24.2
ether	methyl-*t*-butyl ether	1.47	14.8	4.3	5.0	54.9
ether	cyclopentyl methyl ether (CPME)	1.81	16.7	4.3	4.3	27.5
ether	anisole	1.92	17.8	4.4	6.9	43.4
ether	phenetole	2.29	18.4	4.5	4.0	28.4
ether	dipentyl ether	3.94	15.6	3.1	3.0	36.4
ether	butyl phenyl ether	3.31	17.5	3.7	4.3	26.3
ether	DBC	3.11	15.8	4.7	4.4	29.4
ether	diphenyl Ether	3.62	19.4	3.4	4.0	8.2
ether	dibenzyl ether	3.77	19.6	3.4	5.2	16.7
hydrocarbon	cyclohexane	2.82	16.8	0	0.2	2.0
hydrocarbon	*n*-heptane	3.77	15.3	0	0	11.0
hydrocarbon	methylcyclohexane	3.08	16	0	1.0	1.9
hydrocarbon	toluene	2.57	18	1.4	2.0	1.1
hydrocarbon	*p*-xylene	3.08	17.8	1.0	3.1	11.0
hydrocarbon	*n*-nonane	4.71	15.7	0	0	6.1
hydrocarbon	cumene	3.31	18.1	1.2	1.2	21.1
hydrocarbon	1,3,5-trimethylbenzene	3.59	18	0.6	0.6	11.9
hydrocarbon	butylbenzene	3.98	17.4	0.1	1.1	3.1
hydrocarbon	*n*-dodecane	6.12	16	0	0	8.7

ketone was low (Extraction=24.2%) nonetheless the HSPs is located in the sphere (wrong in). As the HSPs of most hydrophobic dicyclohexyl ketone was outlier, the current Hansen sphere seem not to be complete. These results suggest that the extractability of Se(IV) using most solvents can be predicted based on HSPs but some exceptions are also present.

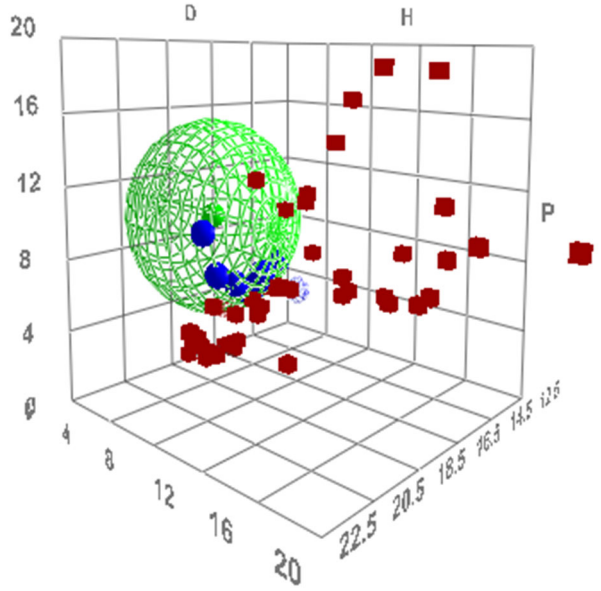

Figure 5. Three-dimensional Hansen solubility parameter (HSP) diagrams of solvents based on the Se(IV) extractability in 8.0 mol/dm^3 HCl. The blue and red symbols indicate valid and invalid solvents for Se(IV) extraction, respectively.

3.4 Stripping of Se(IV)

In the previous study [14,15], Ga(III) and As(III) extracted using 2-NON was quantitatively stripped by contacting the organic phase with distilled water or aqueous solutions with a low HCl concentration. Following the precedents, stripping of Se(IV) using 2-NON and DBC was examined (Table 2). The forward extraction percentages of Se(IV) were 84 – 94% for DBC and 95 – 98% for 2-NON. The higher extraction using DBC compared with the results in above sections is probably due to the greater O/A ratio (O/A = 1.0).

Table 2. Stripping of Se(IV) from DBC and 2-NON. O/A = 1.0, $[Se(IV)]_{init} = 1.0 \times 10^{-3}$ mol/dm^3.

Stripping solution	Stripping [%]	
	from DBC	from 2-NON
Distilled water	17.7	0.5
0.010 mol/dm^3 HCl	26.1	0.0
0.10 mol/dm^3 HCl	20.8	0.0
1.0 mol/dm^3 HCl	23.8	0.0
5.0 mol/dm^3 HCl	19.3	0.0
0.10 mol/dm^3 HNO_3	36.3	1.0
1.0 mol/dm^3 HNO_3	43.6	0.0
0.10 mol/dm^3 NaOH	17.0	3.0
0.10 mol/dm^3 EDTA·2Na	10.1	0.5

Se(IV) was not stripped from 2-NON by contacting distilled water and hydrochloric acid solution. Stripping of Se(IV) from DBC was also low. Sodium hydroxide and EDTA were also not suitable as stripping reagents. Se(IV) in 2-NON, which should be present as $SeCl_4$, should be hydrolyzed for the stripping. In a previous study, Se(IV) extracted using cyclopentyl methyl ether (CPME) was quantitatively stripped using 1.0 mol/dm^3 HNO_3 [7]. Similarly, the stripping from DBC showed the highest value using 1.0 mol/dm^3 HNO_3. However, nitric acid was not effective for the stripping of Se(IV) from 2-NON. The conditions for stripping Se(IV) from 2-NON have not yet been found, and further investigations are required.

4. Conclusion

Most of the ketones showed high extractability for Se(IV) in 8 mol/dm^3 HCl. As the extraction using dicyclohexyl ketone was exceptionally low, excessively hydrophobic ketones might not be suitable for the extraction. On the other hand, the extraction using ethers was relatively low. However, the extraction would not be evaluated adequately in the extraction test for 1.0 h. According to the results of extraction tests using various solvents and exclusion of hydrophilic solvents, the extractability for Se(IV) using various organic solvents was partly classified using HSPs. The relationships between solvent HSPs and extractability for Au(III), Ga(III), and As(III) have also been suggested [13-15]. However, additional factors must be considered to explain the exceptions. Conditions for quantitative stripping of Se(IV) extracted from 2-NON and DBC have not been found. In a future study, the conditions for extraction operations as well as the extraction mechanism should be investigated.

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