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Solvent Extraction of Tetravalent Selenium

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Summary. A systematic study has been carried out on the extraction of SeI_4, by various water-immiscible organic solvents. Extraction has been investigated as a function of H_2SO_4 and KI concentrations. It has been found that the Se(IV) extraction is appreciably increased by addition of iodide ion to sulphuric acid solutions. In addition, the presence of water-miscible alcohols and acetone was found to enhance Se(IV) extraction from H_2SO_4–KI solutions. In the light of the obtained results an extraction mechanism is suggested.

Keywords. Selenium; Extraction; KI; Solvent.

Untersuchungen zur Extraktion von vierwertigem Selen

Zusammenfassung. Es wurde eine systematische Untersuchung zur Extraktion von SeI_4 mittels verschiedener mit Wasser nicht mischbarer organischer Lösungsmittel unternommen. Es wurde die Abhängigkeit der Extraktion von der Konzentration an H_2SO_4 und KI untersucht, wobei sich zeigte, daß die Se(IV)-Extraktion durch Zusatz von Iodid-Ionen zur schwefelsauren Lösung beträchtlich zu steigern ist. Weiters wurde gefunden, daß der Zusatz von wassermischbaren Alkoholen oder Aceton ebenfalls die Extraktion aus H_2SO_4–KI-Lösungen verbessert. Auf Basis dieser Resultate wird ein Extraktionsmechanismus vorgeschlagen.

Introduction

The addition of chloride, bromide or iodide ions to aqueous sulphuric acid solutions of certain metal ions has been found to enhance considerably the extraction of these ions by various organic solvents [1–5]. This has been attributed to the formation of metal halides which are extractable in the presence of sulphuric acid and/or water-miscible organic additives, both helping dehydration and association of ions in the polar phase. In this paper the behavior of tetravalent selenium in the presence of iodide ions is studied. Selenium has been selected because of its importance in semi-conductors. It is a typical semiconductor, used in semiconductor engineering for fabrication of rectifiers and photocells with a barrier layer.

Experimental Part

Reagent grade benzene, toluene, xylene, carbon tetrachloride, chloroform and nitrobenzene were used. The aliphatic alcohols (methanol, ethanol, isopropanol) and acetone were also reagent grade products of BDH, Fluka, Carlo Erba or Veb Laborchemie Apolda GDR. Acids of analytical grade BDH or Merck were used. Potassium iodide (Judex A. R.) was used for preparing the aqueous solutions.

The isotope ^{75}Se was prepared from high purity hydrated selenium dioxide by neutron irradiation in the reactor and dissolving in distilled water.

An EKCO scintillation counter, type N664c [having well type NaI (Tl) crystal], connected to an EKCO automatic scaler, type No. N610b, was used for gross activity measurements of the isotope. A Telefunken γ-ray spectrometer, type MS Str. 1104/1, connected to an MS Sz 831/2 NaI(Tl) detector, coupled optically to a multiplier phototube with silicon fluid was used for checking the purity of radioisotope.

The extraction experiments were carried out in stoppered glass tubes by shaking equal volumes (3 ml) of both organic and aqueous phases of the appropriate acid and organic additive (alcohol or acetone) concentrations. Mixing with concentrated sulphuric acid was done while cooling in an ice bath. The tubes were shaken for 30 min at room temperature (20 ± 4 °C). Fluctuations of temperatures in this range have practically no effect on the extraction in our experiments. Studying the influence of shaking time on the extraction equilibrium has shown that 5 min is sufficient for reaching equilibrium. After disengagement, aliquots of both phases were withdrawn for further analysis. The distribution ratio D was determined experimentally as the ratio of the activities of the tracer in the organic and aqueous phases.

Results and Discussion

Extraction of Se(IV) *from Pure* H_2SO_4

As a preliminary study for this work, the extraction of ^{75}Se with some non-polar solvents (benzene, toluene, xylene, chloroform, carbon tetrachloride and nitrobenzene) was investigated. It was found that the extraction of Se(IV) from H_2SO_4 solutions of all normalities gives values of E less than 0.1 for all mentioned solvents. Results on the extraction of Se from pure H_2SO_4 solutions are given in Table 1. Sulphuric acid does not play a dehydrating role as for Sb extraction [1], but in addition the acid acts as an extraction partner.

Effect of H_2SO_4 *and* KI *Concentrations*

As has been mentioned, in the absence of trace iodide ions the extraction of Se(IV) by all solvents studied is negligible from H_2SO_4 up to 12.5 M. The addition of KI

Table 1. Effect of H_2SO_4 concentrations on D of Se(IV)

H_2SO_4 M	D					
	Benzene	Toluene	Xylene	Chloroform	Carbon tetrachloride	Nitrobenzene
1.8	0.01	0.01	0.01	0.01	0.01	0.01
3.6	0.01	0.01	0.01	0.01	0.01	0.01
5.4	0.02	0.01	0.01	0.01	0.01	0.05
7.2	0.04	0.02	0.03	0.02	0.04	0.07
9.0	0.05	0.03	0.05	0.02	0.04	0.09
10.8	0.09	0.04	0.08	0.05	0.06	0.10
12.5	0.09	0.08	0.09	0.08	0.07	0.124

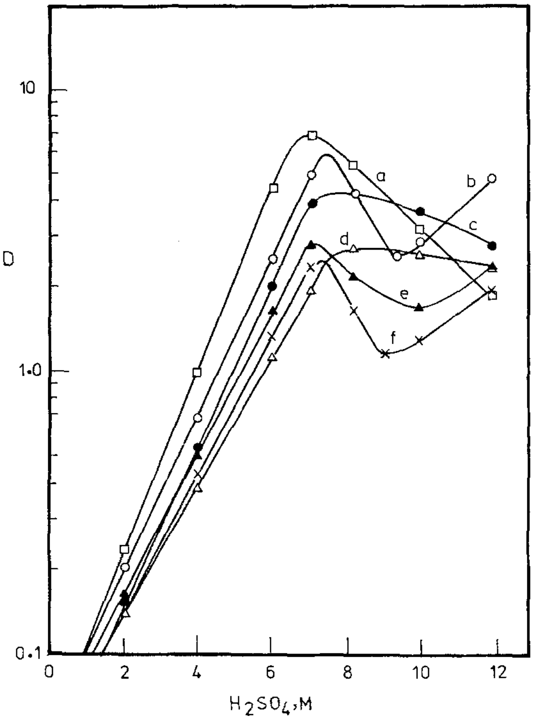

Fig. 1. Effect of the H_2SO_4 concentration on the extraction of Se(IV) from 8×10^{-3} KI; (a) nitrobenzene, (b) toluene, (c) xylene, (d) benzene, (e) CCl_4, (f) $CHCl_3$

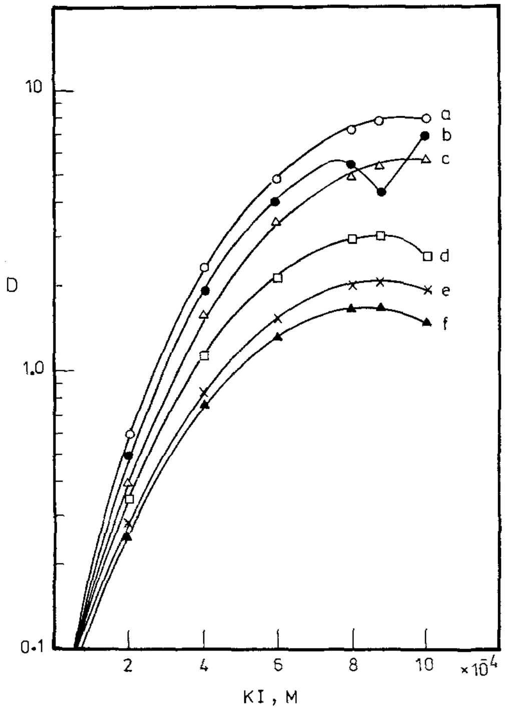

Fig. 2. Effect of the KI concentration on the extraction of Se(IV) from 5.4 *M* H_2SO_4; (a) nitrobenzene, (b) xylene, (c) toluene, (d) benzene, (e) chloroform, (f) carbon tetrachloride

in a concentration higher than the amount stoichiometrically required to yield SeI_4 changes the distribution picture for these solvents; extraction becomes high. This indicates that an iodide complex of selenium is preferentially produced in a solution containing a mixture of sulphate and iodide ions, even in the presence of a much higher ratio of the former ion. The extraction of selenium (10^{-4} *M*) has been investigated at a constant KI concentration (8×10^{-3} *M*) as a function of the H_2SO_4 concentration in the aqueous phase. The results are illustrated in Fig. 1. The log *E* vs. $[H_2SO_4]$ relations exhibit maxima, then minima, for the most solvents. High extraction is realized at around 7 *M* H_2SO_4, while a much higher sulphuric acid molarity is required for the chlorides and bromides of selenium to reach similar extraction levels [6]. The order of extractability of Se under the above conditions was not correlated with the properties of these solvents, due to the presence of more KI than the stoichiometric iodide concentration would afford. The maxima and minima observed in the presence of excess KI (Fig. 1) can be explained by the liberation of iodine at higher sulphuric acid concentrations.

On the other hand, the effect of KI concentration on Se extraction from 5.4 *M* H_2SO_4 was investigated for 10^{-4} *M* Se up to only 1×10^{-3} *M* KI. Extraction was found to increase in the order $CCl_4 \rightarrow CHCl_3 \rightarrow$ benzene $\rightarrow$ toluene $\rightarrow$ xylene $\rightarrow$ nitrobenzene (Fig. 2). Since nitrobenzene, with the highest dielectric constant (see Table 2), gives the best extraction, and since other donor-solvents extract Se better than inert and acceptor solvents, a donor–acceptor mechanism may also be

Table 2. Some physical properties of solvents used in the present study [2]

Solvent	Dielectric constant [at 25 °C]	*I* (V)	δ	Donor properties
Benzene	2.274	9.24	9.2	π-D
Toluene	2.24	8.82	8.9	π-D
Xylene	2.262	8.56	9.0	π-D
Nitrobenzene	34.82			π-D
$CHCl_3$	4.798	11.42	9.3	A
CCl_4	2.228	11.47	8.6	I
Water	78.54			
Methanol	32.63			
Ethanol	24.3			
Propanol	20.1			
Acetone	20.7			

Table 3. Effect of KI concentration on *D* of Se for extraction with xylene and nitrobenzene

KI, $M \times 10^{-4}$	–	0.2	0.6	0.8	1	2	4	6	8	10	20	40	60	80	100
Xylene	<0.01	0.01	0.02	0.06	0.1	0.4	1.8	8.6	20	16	12	10	8	7	7
Nitrobenzene	<0.01	0.01	0.07	0.09	0.2	0.9	2.4	10.6	20	25	28.2	30.5	32	32	32

tentatively proposed for the iodide extraction:

$$2\,\mathrm{Se}^{4+} + 8\,\mathrm{KI} + 4\,\mathrm{H_2SO_4} \rightleftharpoons 2\,\mathrm{SeI_4} + 4\,\mathrm{K_2SO_4} + 8\,\mathrm{H^+} \tag{1}$$

$$\mathrm{SeI_4} + nS \rightleftharpoons \mathrm{SeI_4}\cdot nS, \tag{2}$$

where n is the number of solvent (S) molecules in the extracted complex. The extraction of $\mathrm{SeI_4}$ with π-donors [2] can be correlated with the basicity of the solvent, which increases in the order: benzene → toluene → xylene. The extraction of $\mathrm{SeI_4}$ by π-donors from 5.4 M $\mathrm{H_2SO_4}$ was found to decrease if the KI concentration was increased considerably. This can be explained by the formation of a negatively charged iodide complex:

$$\mathrm{SeI_4} + m\,\mathrm{KI} \rightleftharpoons [\mathrm{SeI_{(4+m)}}]^{m-} + m\mathrm{K^+}. \tag{3}$$

For comparison the results of extraction with xylene ($\varepsilon = 2.262$) and nitrobenzene ($\varepsilon = 34.82$) are given in Table 3.

The produced iodoselenium anion is neither able to produce donor–acceptor complexes with xylene nor it is soluble in this non-polar solvent, while it is likely to be more soluble in the more polar nitrobenzene, and hence the continuous increase of D with increase of KI molarity for the latter solvent.

Extraction of Se(IV) *from Acidic-Alcoholic or Acetonic Solutions*

The addition of water-miscible alcohols and acetone to the aqueous phase was found to influence greatly the extraction of metal salts from acidic solutions. It was therefore interesting to investigate the effects of these organic additives in the present

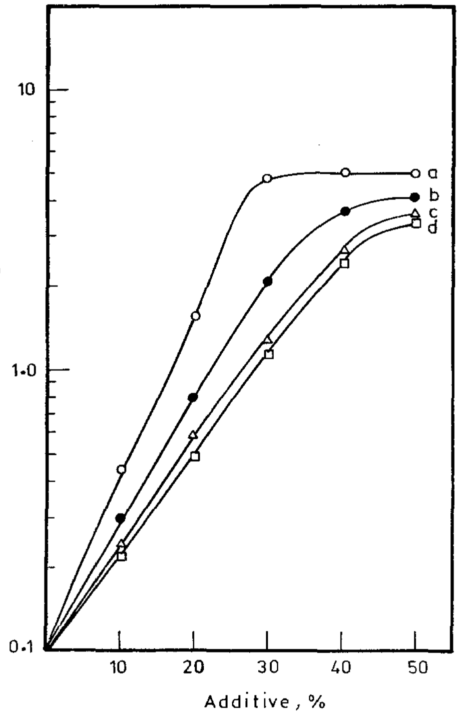

Fig. 3. Effect of alcohols and acetone on the extraction of Se(IV) by nitrobenzene from 2.7 $\mathrm{H_2SO_4}$ – 8×10^{-4} M KI; (a) acetone, (b) isopropanol, (c) ethanol, (d) methanol

Table 4. Calculated dielectric constants of water mixtures of water-miscible alcohols and acetone [2]

Additive	*v*/*v* (%)	Molarity	Dielectric constant
Methanol	0	0.00	78.54
	10	2.46	78.04
	20	4.92	71.54
	30	7.38	68.04
	40	9.84	64.54
	50	12.30	61.04
Ethanol	10	1.70	73.89
	20	3.40	69.24
	30	5.40	64.59
	40	6.80	59.94
	50	8.50	55.29
n-Propanol	10	1.33	72.78
	20	2.66	67.02
	30	3.99	61.26
	40	5.32	55.50
	50	6.65	50.00
Acetone	10	1.35	73.68
	20	2.70	68.82
	30	4.05	63.96
	40	5.40	59.10
	50	6.75	54.24

system. The effects of methanol, ethanol, isopropanol, and acetone on the extraction of selenium from 2.7 $H_2SO_4 - 8 \times 10^{-4}\,M$ KI were investigated for all the solvents. The effect of these additives in case of nitrobenzene was found to be more pronounced than that of the other solvents (Fig. 3). It is clear from this figure that D is markedly increased by increasing additive concentration. The highest effect is due to acetone.

The effect of water-miscible additives was found to increase in the order: methanol < ethanol < isopropanol < acetone. This behaviour is attributed to the decrease in hydration of selenium ions with the increase of organic additive concentration, which in turn provides a better chance for interaction with the iodide ions to form the extractable iodide complexes. From a physicochemical point of view the extraction of the element species into solvent solutions is governed by the difference of the dielectric constant between the two phases which decreases with the addition of alcohols and acetone to the aqueous phase. The dielectric constant (ε) decreases from 78.54 in pure H_2O to 55.29 in 50% *v*/*v* ethanol and to 54.24 in 50% *v*/*v* acetone (Table 4). The decrease of the electrical barrier between the phases should facilitate extraction, unless other opposing factors compete with the polarity factor [7].

References

[1] Alian A., El-Kot A., El-Bassiouny M., Haggag A. (1975) J. Radioanal. Chem. **24**: 271
[2] Alian A., Haggag A., El-Bassiouny M. (1974) J. Inorg. Nucl. Chem. **36**: 1629
[3] Olszer R., Siekierski S. (1968) J. Inorg. Nucl. Chem. **28**: 1991
[4] Alian A., Sanad W. (1972) Radiochim. Acta **17**: 158
[5] Mirza M. Y. (1967) J. Appl. Radiat. Isotopes **18**: 849
[6] Alian A., Sanad W., Khalifa H. (1968) Talanta **15**: 249
[7] Korkisch J., Janauer G. E. (1962) Talanta **15**: 262

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