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**LIQUID-LIQUID EXTRACTION OF ARSENIC FROM CONCENTRATED  
SULFURIC ACID SOLUTIONS**

Examiners: Professor Tuomo Sainio

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## TIIVISTELMÄ

Lappeenrannan teknillinen yliopisto  
School of Engineering Science  
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Niklas Jantunen

**Arseenin neste-nesteuutto väkevistä rikkihappoliuoksista**  
Diplomityö  
2017

55 sivua, 33 kuvaa, 16 taulukkoa ja 3 liitettä

Tarkastajat: Professori Tuomo Sainio  
TKT Sami Virolainen

Hakusanat: arseni, neste-nesteuutto, rikkihappo

Työssä tutkittiin arseenin neste-nesteuuttoa väkevistä rikkihappoliuoksista. Erotustehokkuuteen vaikuttavat uuttoreagenssin lisäksi erityisesti rikkihappopitoisuus ja arseenin hapetusaste. Käytetyin uuttoreagenssi teollisissa arseenin uuttoprosesseissa on tri-*n*-butyylifosfaatti (TBP). Tehokas erotus TBP:llä vaatii sekä latauksen että strippauksen toteuttamista useassa vastavirta-asteleessa. Julkaistut arseenin uuttoon liittyvät tutkimustulokset ovat pääosin rikkihappoliuoksille, joissa rikkihappoa on ollut 150–600 g dm<sup>-3</sup>. Tässä diplomityössä tutkittiin arseenin uuttoa vieläkin väkevämmistä liuoksista, joissa rikkihappopitoisuus oli yli 1000 g dm<sup>-3</sup>. Tutkittavat liuokset olivat teollisperäisiä, ja niistä toisessa arseni esiintyi pääasiassa hapetusasteella +V, ja toisessa vastaavasti +III. TBP:tä, di-butyyli-butyylifosfonaattia (DBBP), Cyanex 923:a sekä 1,2-oktaanidiolin ja 2-etyyli-1-heksanolin seosta käytettiin suorituskykytesteissä. Orgaanisten fosforihappojohdannaisten laimentaminen alifaattiseen Exxsol D80 –liuottimeen johti kolmannen nestefaasin muodostumiseen. Laimentamaton TBP sekä 1,2-oktaanidiolin ja 2-etyyli-1-heksanolin seos toimivat parhaiten tutkituista reagensseista, joten niiden suorituskykyä tutkittiin laajemmin. Tavanomaisella, TBP:tä hyödyntävällä uuttoprosessilla voidaan erottaa arseenia haposta, jossa arseni on hapetusasteella +V ja rikkihappopitoisuus 1015 g dm<sup>-3</sup>. 1,2-oktaanidiolin ja 2-etyyliheksanolin seokselle määritettiin hyvin samankaltaiset latausisotermit kuin TBP:lle, mutta TBP:n faasikäyttäytyminen oli huoneenlämmössä huomattavasti suotuisampaa kuin alkoholiseoksella. Arseenin ja rikkihapon erottuminen pesuvaiheessa oli tehokkaampaa TBP:llä. Trivalenttista arseenia ja rikkihappoa 1255 g dm<sup>-3</sup> sisältävästä liuoksesta voidaan myös erottaa arseni ja rikkihappo, mutta uuttoreagenssit olivat happopitoisuudeltaan väkevemmän liuoksen tapauksessa selektiivisempiä rikkihapolle kuin arseenille.

## ABSTRACT

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### **Liquid-liquid extraction of arsenic from concentrated sulfuric acid solutions**

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2017

55 pages, 33 figures, 16 tables and 3 appendices

Examiners: Professor Tuomo Sainio  
D.Sc. Sami Virolainen

Keywords: arsenic, liquid-liquid extraction, solvent extraction, sulfuric acid

Separation of arsenic from sulfuric acid solutions by liquid-liquid extraction was studied in this thesis. Separation efficiency is affected by the extractant, sulfuric acid concentration and oxidation state of arsenic. The most used extractant in industrial applications is tri-*n*-butyl phosphate (TBP). Efficient separation by extraction with TBP requires several counter-current stages both during loading and stripping. Results published earlier in the literature have mainly been given for solutions that have contained 150–600 g dm<sup>-3</sup> of sulfuric acid. In this thesis, extraction from even more concentrated solutions containing over 1000 g dm<sup>-3</sup> of sulfuric acid, was studied. Two industrial sulfuric acid solutions were used in the experiments. Another of these solutions contained mostly As(V), and the other As(III), respectively. TBP, di-butyl-butyl phosphonate (DBBP), Cyanex 923 and mixture of 1,2-octanediol and 2-ethyl-1-hexanol were used in performance tests. Diluting the organophosphorus extractants in aliphatic Exxsol D80 resulted in formation of a third liquid phase. Undiluted TBP and mixture of 6 % 1,2-octanediol in 2-ethyl-1-hexanol had the best performance among the studied extractants. Therefore, performance of TBP and mixture of 1,2-octanediol and 2-ethyl-1-hexanol was studied more extensively. An extraction process utilizing TBP can be used to separate arsenic from acid solution, in which arsenic is present in oxidation state +V and sulfuric acid concentration is 1015 g dm<sup>-3</sup>. The determined loading isotherms for 1,2-octanediol and 2-ethylhexanol were very similar to the ones for TBP but phase behavior of TBP in room temperature was significantly better. Separation of arsenic and H<sub>2</sub>SO<sub>4</sub> in scrubbing stage was more efficient with TBP. The separation of arsenic and sulfuric acid is possible also from the other acid solution, which contained mostly trivalent arsenic and 1255 g dm<sup>-3</sup> of sulfuric acid. The extractants were however more selective to sulfuric acid than to arsenic when this more concentrated acid was extracted.

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**LIST OF SYMBOLS**

$A/O$	initial aqueous to organic phase ratio, -
$c$	concentration, $\text{mol m}^{-3}$
$D$	distribution coefficient, -
$D'$	stripping coefficient, -
$E$	percentage extracted, %
$E_h$	oxidation-reduction potential, V
$E_{\text{SHE}}$	oxidation-reduction potential with respect to standard hydrogen electrode, V
$I$	ionic strength, $\text{mol m}^{-3}$
$M$	molar mass, $\text{kg mol}^{-3}$
$O/A$	initial organic to aqueous phase ratio, -
$R$	percentage removed, %
$T$	temperature, K
$t$	time, s
$V$	volume, $\text{m}^3$
$W$	percentage backextracted in scrubbing, %
$\alpha/\Omega$	aqueous to organic phase ratio in equilibrium, -
$\beta$	separation factor, -
$\Delta V$	change in volume, $\text{m}^3$
$\rho$	density, $\text{kg m}^{-3}$
$\Omega/\alpha$	organic to aqueous phase ratio in equilibrium, -

**Subscripts**

0	initial
aq	aqueous
eq	equilibrium, equilibration
org	organic
SHE	Standard hydrogen electrode
tot	total

**ABBREVIATIONS**

2-EHA	2-ethyl-1-hexanol
CCA	chromated copper arsenate
D2EHPA	di-(2-ethylhexyl) phosphoric acid
DBBP	di-butyl-butyl phosphonate
DPPP	di-pentyl-pentyl phosphonate
IARC	International Agency for Research on Cancer
IDLH	immediately dangerous for life and health
IUPAC	International Union of Pure and Applied Chemistry
LOD	limit of detection
LOQ	limit of quantification
NIOSH	The National Institute for Occupational Safety and Health
ORC	Outotec Research Center
TBP	tri- <i>n</i> -butyl phosphate
TISAB	total ionic strength adjustment buffer
TOC	total organic carbon
TOPO	tri-octylphosphine oxide

## 1 INTRODUCTION

Arsenic, As, is a metalloid that is found globally in the Earth's crust in concentrations of 1–2 mg kg<sup>-1</sup>. In sulfide minerals the concentrations are significantly elevated and may reach 126 g kg<sup>-1</sup> at maximum. (IARC, 2004) Ores containing sulfide minerals are important raw materials for metallurgical industry, and therefore small amount of arsenic is unavoidably fed into metallurgical processes. Arsenic is usually considered as an impurity and its accumulation might cause functional problems in industrial processes, or general health and safety risks. (Grund *et al.*, 2008)

Purification of copper by electrolysis is a common example of a process disturbed by arsenic. Arsenic, antimony, bismuth and iron in the impure copper anode dissolve in electrolyte and deteriorate quality of the cathode product. Impurities also reduce current efficiency which leads to increased energy consumption. (Szymanowski, 1998; Wiśniewski, 1998) There is also a risk of forming lethal arsine gas, AsH<sub>3</sub>, if concentration of copper gets low enough and the electrolysis is continued (Ballinas *et al.*, 2003). To prevent accumulation of impurity metals in sulfuric acid electrolyte, part of the electrolyte solution is removed, *i.e.* “bled off” from the electrolysis cell. The sulfuric acid containing impurities is then to be purified and eventually reused. (Szymanowski, 1998; Wiśniewski, 1998)

Arsenic sulfides, oxides and elemental arsenic evaporate during roasting and smelting in metal processing. Scrubbing of flue gas from these processes yields another type of sulfuric acid stream, again contaminated with arsenic. (Grund *et al.*, 2008) In order to reuse the acid, it must be purified. Arsenic can either be stabilized or processed to commercial products, such as arsenic trioxide, As<sub>2</sub>O<sub>3</sub> or metallic arsenic. In fact, most of the commercially produced arsenic is obtained from by-product streams (Grund *et al.*, 2008).

Several techniques exist for separation of arsenic from aqueous solutions. Adsorption, ion exchange, membrane filtration, precipitation and coagulation have been utilized for wastewater and drinking water purification. However, these techniques have mostly been tested with waters that have arsenic concentrations in ppb or ppm range and low acidities. (Leist *et al.*, 2000) Industrial streams may easily contain 10 g dm<sup>-3</sup> of arsenic, or more. Adsorbents or ion exchangers may saturate very quickly under such conditions, and coagulation or precipitation binds the chemicals to the formed agglomerates or precipitates. Solvent extraction is applicable for treating large volumes, separation is efficient with concentrated solutions and process configurations are usually

simple. Liquid-liquid extraction does not require elevated pressure during the separation and area of mass transfer can be manipulated by changing the shear rate applied to a system.

Removal of arsenic from sulfuric acid by liquid-liquid extraction has been previously demonstrated by several authors (Ballinas *et al.*, 2003; Iberhan & Wiśniewski, 2003; Demirkiran & Rice, 2002; Navarro & Alguacil, 1996; for more, see References) These publications summarize that the efficiency in extraction of arsenic depends on the extractant, sulfuric acid concentration and diluent. The aim of this thesis was to find the most attractive extractants from literature, study their performance experimentally and provide a foundation for designing a solvent extraction process for removing arsenic. For this purpose, experiments with two industrial sulfuric acid solutions were carried out.

## 2 ARSENIC

Elemental arsenic (CAS# 7440-38-2;  $M = 74.92 \text{ g mol}^{-1}$ ) exists usually as a brittle silver-colored metal. Other forms are yellow arsenic, and three amorphous forms, namely  $\beta$ ,  $\gamma$  and  $\delta$ . The  $\beta$ -form is the best known of these, and it is also known as black arsenic. Metallic arsenic converts to black arsenic in a few days under humid conditions and the amorphous forms convert back into metallic form when heated above  $270 \text{ }^\circ\text{C}$ . For yellow arsenic the conversion into metallic form happens already under gentle heating or exposure to light. (Carapella, 2002; Grund *et al.*, 2008)

Arsenic is present in numerous compounds, most often with oxidation states of  $-III$ ,  $+III$  and  $+V$ . The compounds can be classified as oxides, acids, sulfides, halides, arsenides and organoarsenics. The only well-known hydrogen compound is arsenic hydride,  $\text{AsH}_3$ . It is an extremely poisonous gas and also known as arsine. (Grund *et al.*, 2008)

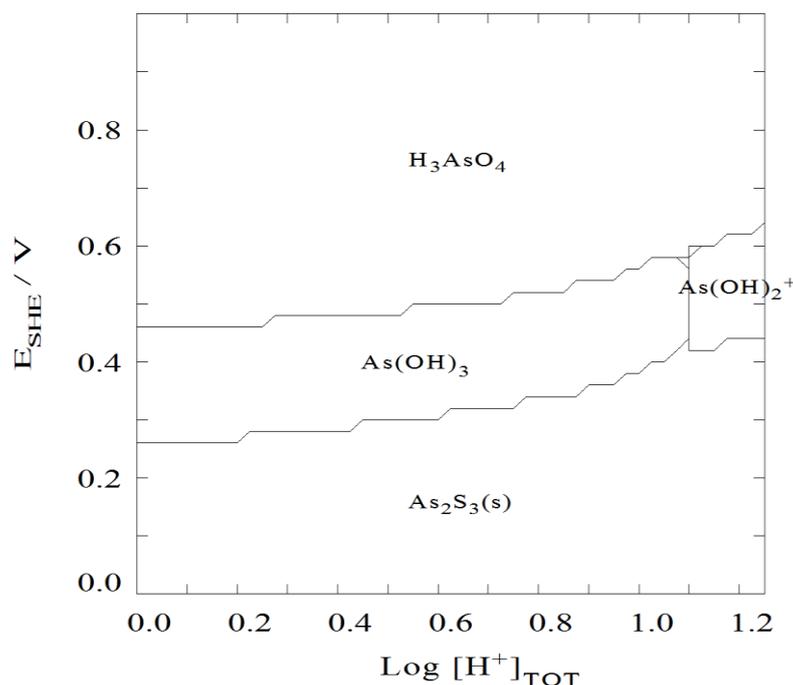
Heating of arsenic in air will oxidize it to arsenic trioxide,  $\text{As}_2\text{O}_3$ . It is a precursor for many other arsenic compounds and it is also economically the most important compound. Other two known oxides are arsenic pentoxide,  $\text{As}_2\text{O}_5$  and  $\text{As}_2\text{O}_4$ . Oxides  $\text{As}_2\text{O}_3$  and  $\text{As}_2\text{O}_5$ , are acid anhydrides that in aqueous solutions form arsenous acid and arsenic acid, respectively. Salts of these acids are called arsenates(III) (arsenites) and arsenates(V). (Grund *et al.*, 2008)

Despite being a known toxin and having limited demand, pure arsenic is still used in electronic and semiconductor industry. For a limited number of applications, gallium arsenide, GaAs, is the

preferred material choice over silicon. Arsenic can be found for instance in LEDs, infrared detectors, lasers, solar cells and lead-acid batteries. Other applications of arsenic compounds have been wood preservatives (chromated copper arsenate, CCA), herbicides, insecticides and glass colorants. (Grund *et al.*, 2008) Nowadays most countries have banned the use of herbicides and pesticides that contain arsenic, and also the use of CCA has been limited since 1998 (Metla, 2013).

## 2.1 Solution chemistry

Water, alkaline solutions or non-oxidizing acids do not react with metallic arsenic. As an example, arsenic and hydrochloric acid do not react without presence of a strong oxidizer. Concentrated nitric acid or aqua regia oxidize arsenic to arsenic acid,  $\text{H}_3\text{AsO}_4$ , where arsenic is present as As(V). Metallic arsenic can be oxidized to As(III) with dilute nitric acid and concentrated sulfuric acid solutions. (Carapella, 2002; Grund *et al.*, 2008) An industrial sulfuric acid solution containing arsenic most probably has the arsenic in both tri- and pentavalent form, but it depends on the oxidation-reduction potential,  $E_h$ , and  $\text{H}^+$  concentration (Fig. 1), which oxidation state is dominant.



**Figure 1** The predominance areas of arsenic species in acidic sulfate solution at 25 °C.  $c[\text{As}(\text{OH})_3] = 0.2 \text{ mol dm}^{-3}$ ,  $c(\text{SO}_4^{2-}) = 10 \text{ mol dm}^{-3}$  and  $I = 4 \text{ M}$ . Calculated and plotted with MEDUSA-software (KTH, 2016).

The presence of other ions, their concentrations and temperature have effect on speciation, and therefore the given predominance diagram (Fig. 1) is entirely a theoretical representation. Szy-

manowski (1998) and Iberhan & Wiśniewski (2003) have also mentioned that in highly concentrated sulfuric acid solutions As(III) is present as  $\text{AsO}^+$ , and As(V) is in the form of undissociated arsenic acid,  $\text{H}_3\text{AsO}_4$ . Hydration with water molecules makes it soluble (Szymanowski, 1998). These statements are in agreement with Fig. 1. Arsenic acid is an acid of pentavalent arsenic and its reported  $\text{pK}_a$  values are:  $\text{pK}_{a1} = 2.2$ ;  $\text{pK}_{a2} = 6.9$  and  $\text{pK}_{a3} = 11.5$  at 25 °C. These are comparable with phosphoric acid,  $\text{H}_3\text{PO}_4$  (Szymanowski, 1998).

As(III) forms arsenous acid, and it can be formulated in several ways, though formulas  $\text{H}_3\text{AsO}_3$ ,  $\text{As}(\text{OH})_3$  and  $\text{HAsO}_2$  are most commonly used. Arsenous acid is a weak acid ( $\text{pK}_{a1} = 9.1$ ) that can't be isolated because it is  $\text{As}_2\text{O}_3$  derivative, and it will precipitate if isolation is attempted.  $\text{H}_3\text{AsO}_3$  may also react like a weak base, thus it is amphoteric. (Szymanowski, 1998; Iberhan & Wiśniewski, 2003; Grund *et al.*, 2008) To avoid formation of poisonous arsine ( $\text{AsH}_3$ ), strong reducing agents must not get in contact with acidic solutions containing arsenic (Grund *et al.*, 2008).

## 2.2 Health effects

Practically all arsenic compounds are toxic for humans and most biological organisms. The most dangerous one is gaseous arsenic hydride (arsine),  $\text{AsH}_3$  (WHO, 2011). Immediately dangerous for life and health (IDLH) concentration for the gas is 3 ppm (NIOSH, 1994). In principle, toxicity of arsenic compounds then decreases in order  $\text{As}_2\text{O}_3$ , inorganic As(III) compounds, inorganic As(V) compounds and organic arsenic compounds. (WHO, 2011) Arsenic and inorganic arsenic compounds are listed as human carcinogens (IARC, 2017).

The likely routes of exposure to arsenic are inhalation of dusts or fumes containing an arsenic compound, or by ingestion of contaminated drinking water or food.  $\text{AsCl}_3$  may absorb through the skin. (Grund *et al.*, 2008) In Finland, municipal tap water is free from arsenic throughout the country and maximum legal concentration of arsenic in water is  $10 \mu\text{g dm}^{-3}$  (THL, 2015). Arsenic-contaminated drinking water is however a problem in several other countries around the world, for instance in Argentina, Bangladesh, Chile, China, India, Taiwan and the United States (IARC, 2004).

Acute arsenic poisoning results in gastrointestinal damage. Symptoms include vomiting, diarrhea, abdominal pain, muscle pain, cramps, weakness, flushing of the skin, edema, cardiac abnormalities and dehydration. Time between exposure and onset of the symptoms varies from minutes to sev-

eral hours. The development of symptoms and effects of chronic exposure are extensively described in the literature. (Grund *et al.*, 2008; WHO, 2011; IARC, 2004) Urine analysis provides information about recent exposure to arsenic, whereas hair and nails should be analyzed to reveal signs of chronic exposure (IARC, 2004).

### 3 SOLVENT EXTRACTION OF ARSENIC

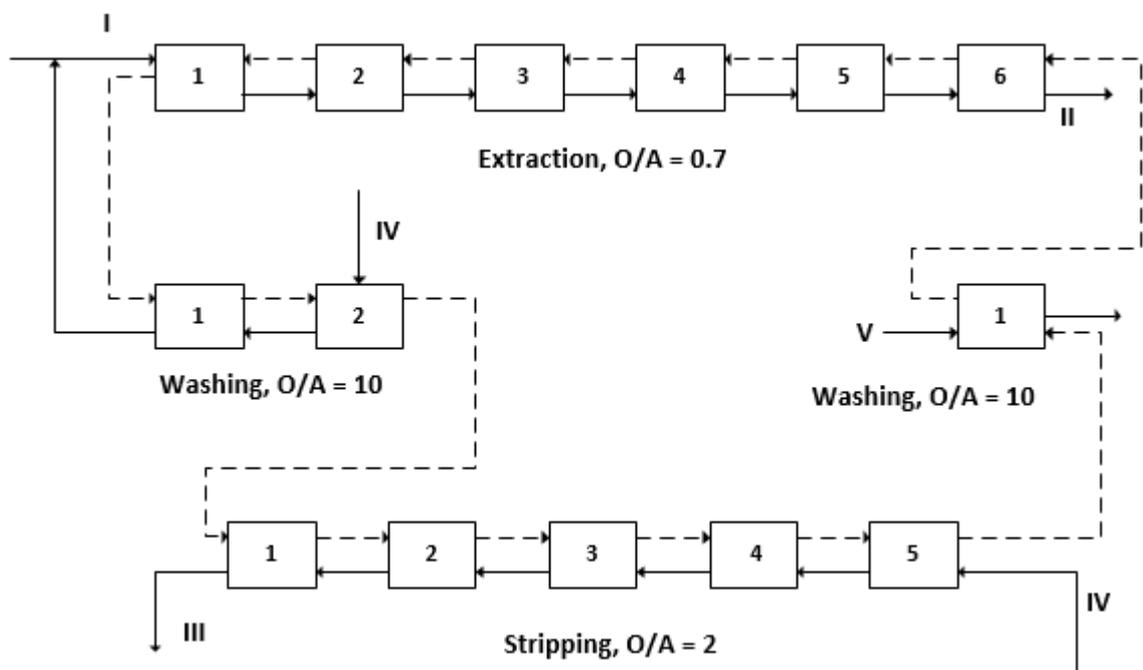
Solvent extraction is well-established and widely applied technique in the industry. The method involves mass transfer of a solute between two immiscible or partially miscible liquid phases. Usually the phases are aqueous and organic liquids. In reactive extraction, the solute is initially not soluble in both phases but only another of them. Let us consider solvents A and B, and phase A containing the solute. Molecules (extractants) that are soluble in B but not in A, and capable of forming complexes with the solute, can move the solute from phase A to B. Reversing the reaction by equilibrating loaded phase B with liquid C is called stripping, and it regenerates the extractant.

Several authors have had little emphasis on describing the fundamental reactions and phenomena behind arsenic extraction. Also the changes in physical properties – such as density, viscosity and interfacial tension – during extraction and stripping, have not been quantitatively reported in most publications. Instead, technical performance of various solvent extraction reagents has been studied, and discussion is focused on the practical issues. (Ballinas *et al.*, 2003; Bogacki *et al.*, 1998; Demirkiran & Rice, 2002; Gupta & Begum, 2008; Iberhan & Wiśniewski, 2003; Navarro & Alguacil, 1996)

Extractant choice has a direct effect on extraction equilibrium of arsenic and thus separation efficiency. It also affects the subsequent washing and stripping processes. The common difficulties in the extraction stage are relatively low distribution coefficients and formation of a third phase, which may be liquid or solid. Other unwanted phenomena in the process are emulsification, co-extraction of sulfuric acid and hydrolysis of the extractant. Many of these phenomena are extractant-specific and can be controlled with modifiers or for example by selecting composition for stripping liquor.

### 3.1 General process description

Traditional commercial processes that use tributyl phosphate (TBP) as extractant consist of six counter-current extraction stages, 1–2 washing stages and five stripping stages (Fig. 2). Additionally, there is a single washing step for the organic, where hydrolysis products of TBP are removed with 15 % NaOH (V). Trace, ppm-concentrations of TBP will be left in the raffinate (II) and stripping liquor (III), from where it is removed by adsorption on activated charcoal. The aqueous inputs for stripping and scrubbing are marked with IV. (Szymanowski, 1998; De Schepper & Van Peteghem, 1977) Phase ratios, and the required number of extraction, washing and stripping stages are process-specific and depend on feed solution (I) properties, target concentration and chemical equilibria.



**Figure 2** Block diagram of a traditional solvent extraction process to remove arsenic from sulfuric acid with TBP. Aqueous flows are marked with continuous lines and organic with dashed, respectively. (Szymanowski, 1998; De Schepper & Van Peteghem, 1977)

### 3.2 Solvating extractants

A solvating extractant is capable of replacing water molecules around a hydrated specimen, making it soluble in the organic phase. The extractant molecule contains an atom that can donate an electron pair, *i.e.* it can be considered as Lewis base. Usually the donor atom is oxygen or sulfur. (Szymanowski, 1998) Extraction may also proceed via hydrate-solvate mechanism, in which

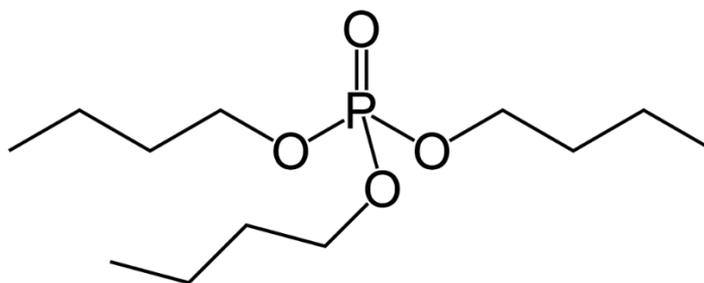
the hydrated specimen is extracted with its hydration shell. Hydrate-solvate mechanism is favorable with weakly basic extractants, such as alcohols, ethers and ketones. When basicity of an extractant increases, stability of the formed complexes increase and also the complex formation mechanism changes from hydrate-solvate mechanism to pure solvation. Acidity of the specimen also affects to sensitivity of transition between these mechanisms. The stronger the acid, the more likely pure solvation occurs with a given extractant. (Rozen & Krupnov, 1996) Travkin *et al.* (1993) have described extraction of arsenic acid with following equation



where S describes an extractant molecule,  $n$ ,  $h$ ,  $h_0$  and  $q$  are empirical constants that depend on the reaction conditions and extractant. When there is  $\text{H}_2\text{SO}_4$  in the feed solution, it is coextracted and may also be present in the complex. (Travkin *et al.*, 1993)

### 3.2.1 Tributyl phosphate

In the 1990's, TBP (Fig. 3) was the most popular extractant in industrial solvent extraction of arsenic. (Szymanowski, 1998) The later examined literature suggests no change regarding this matter.

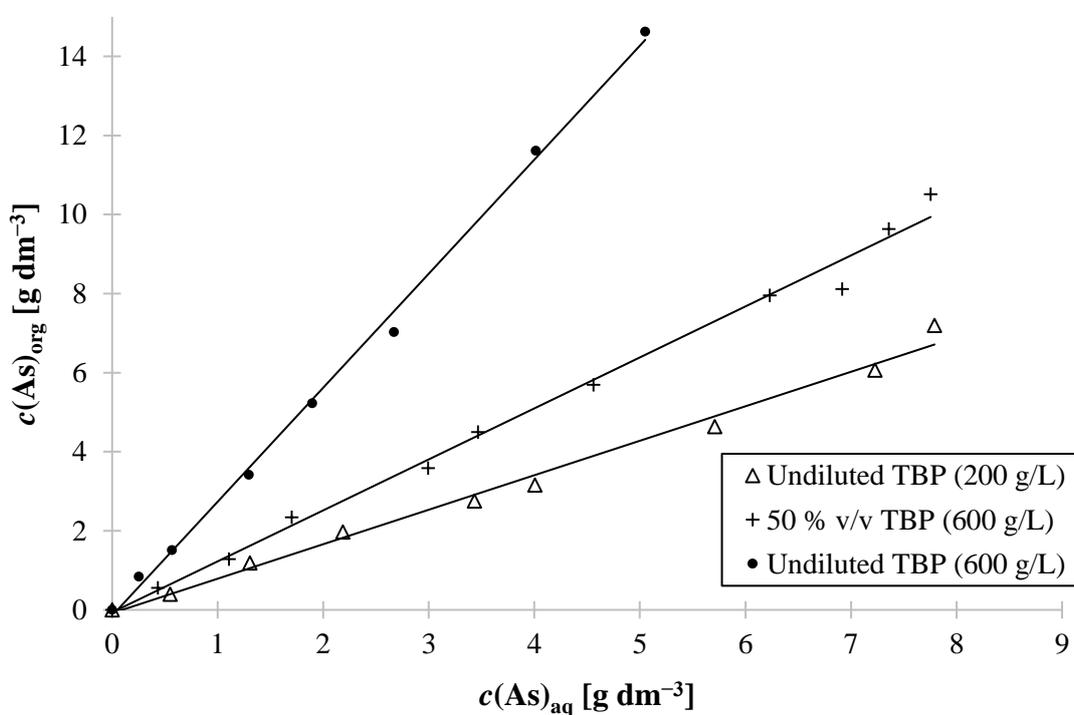


**Figure 3** Structure of tri-*n*-butyl phosphate.

Navarro and Alguacil (1996) have studied the performance of pure TBP and 50 vol-% TBP–tridecane extractant solutions. They have shown that equilibrium is reached approximately in one minute both in extraction and stripping. The higher the sulfuric acid concentration, the more arsenic will be transported to the organic phase (Fig. 4). On the other hand, also the amount of co-extracted  $\text{H}_2\text{SO}_4$  is proportional to its concentration in the feed. Co-extracted  $\text{H}_2\text{SO}_4$  should be washed from the loaded organic phase with water using high O/A phase ratio before stripping. (Navarro & Alguacil, 1996) When the loaded organic phase is washed from sulfuric acid, arsenic can then be

stripped with larger volume of water, dilute (0.5–1 %)  $\text{Na}_2\text{SO}_4$  solution, alkaline solution or dilute ( $15 \text{ g dm}^{-3}$ ) sulfuric acid. (Navarro & Alguacil, 1996; Demirkiran & Rice, 2002; Szymanski, 1998). Using dilute  $\text{H}_2\text{SO}_4$  or  $\text{Na}_2\text{SO}_4$  will make the phase separation faster (Szymanski, 1998; Iberhan & Wiśniewski, 2003).

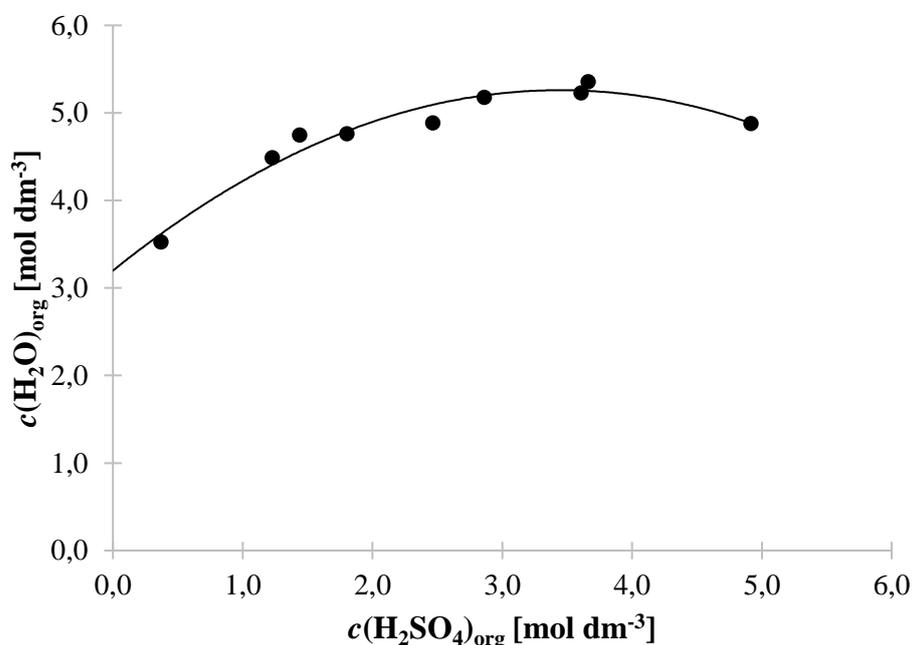
Demirkiran & Rice (2002) suggested that side-stream from stripping could be used for washing to prevent transportation of arsenic to the aqueous phase. The same authors preferred aromatic Shell-sol A -solvent in their studies, although aliphatic Shellsol T was found to give slightly better distribution of arsenic in 2 M  $\text{H}_2\text{SO}_4$ . The choice of aromatic solvent was justified by faster phase disengagement and easier dissolution of TBP. (Demirkiran & Rice, 2002).



**Figure 4** Extraction isotherms in extraction of As(V) from  $\text{H}_2\text{SO}_4$  solutions with TBP. Aqueous phase contained initially  $10.2 \text{ g dm}^{-3}$  of As(V). Bracketed concentrations are  $\text{H}_2\text{SO}_4$  concentrations. Re-produced from Navarro & Alguacil (1996).

Modifiers can be added to the organic phase to prevent third phase formation and speed up phase disengagement. The amount of modifiers ranges between 5–10 % and they can be alcohols (e.g. isodecanol), phosphinic acids, phosphate esters, tertiary carboxyl acids and quaternary ammonium salts. (Iberhan & Wiśniewski, 2003) TBP has been criticized due to requirement of high reagent concentration, low distribution coefficients, co-extraction of  $\text{H}_2\text{SO}_4$  and water (Fig. 5), and tendency to hydrolyze. (Ballinas *et al.*, 2008; Bogacki *et al.*, 1998; Iberhan & Wiśniewski, 2003) Even so, compared with other solvating organophosphorus extractants (DBBP, Cyanex 923

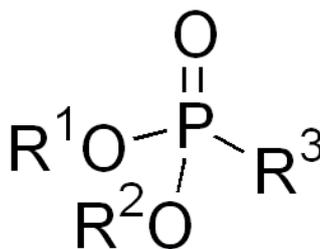
& 925), TBP has provided better separation of arsenic from sulfuric acid due to smaller extent of  $\text{H}_2\text{SO}_4$  co-extraction (Dreisinger<sup>b</sup> *et al.*, 1993).



**Figure 5** Effect of sulfuric acid on water content in TBP (Re-produced from Hesford & McKay, 1960).

### 3.2.2 Phosphonates

The general structure for a phosphonate ester is given in Fig. 6. The ones that have been used for extraction of arsenic are di-butyl-butyl phosphonate (DBBP), its branched isomer di-isobutyl-isobutyl phosphonate (HOSTAREX PO 212, Hoechst, Germany) and di-pentyl-pentyl phosphonate (DPPP) (Hiemeleers *et al.*, 1978; Dreisinger<sup>a</sup> *et al.*, 1993; Ballinas *et al.*, 2008). The only structural difference between TBP and DBBP is that DBBP has only three oxygen atoms, and therefore one alkyl group is directly bonded to phosphorus atom. The difference in structure is small but has significant effect on extraction performance. Dreisinger<sup>a</sup> *et al.* (1993) reported average distribution coefficients for arsenic to be around 1 for DBBP, 0.6 for DPPP and ca. 0.3 for TBP. Oxidation state was not mentioned but probably it has been mostly +V. The extractions were performed at 50 °C with undiluted extractants and phase ratio 1.



**Figure 6** General structure of an organophosphonate, where  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are alkyl or aryl groups.

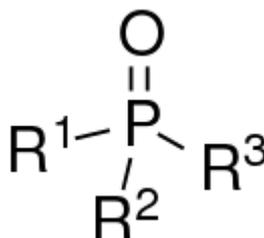
Formation of a third phase was not mentioned by Dreisinger<sup>a</sup> *et al.* (1993) or Ballinas *et al.* (2008) as  $\text{H}_2\text{SO}_4$  concentrations varied between 140–220  $\text{g dm}^{-3}$  and 160–220  $\text{g dm}^{-3}$  in their studies, respectively. However, Beyad *et al.* (1990) noticed that 20 vol-% solution of DBBP in kerosene forms a third phase in 10 N  $\text{H}_2\text{SO}_4$  solution at 22 °C. Weight concentration of DBBP in the original phase lowered from ca. 18.5 wt-% to 14 wt-% in less than five days. The effect was less pronounced in 10 N  $\text{H}_2\text{SO}_4$  at elevated temperature of 50 °C, and in 4 N  $\text{H}_2\text{SO}_4$  loss of extractant was not observed. 10 N HCl dropped the DBBP concentration from 18.5 to ca. 2 wt-% in one day. It was mentioned that the missing DBBP did not decompose, but all the missing reagent transported to third phase. (Beyad *et al.*, 1990)

10 N  $\text{H}_2\text{SO}_4$  corresponds roughly to 5  $\text{mol dm}^{-3}$  or 500  $\text{g dm}^{-3}$  solution. It can be concluded that third phase formation will be an issue with concentrated acid solutions when diluted DBBP is used, unless a modifier can keep the organic phase intact. Di-(2-ethylhexyl) phosphoric acid (D2EHPA) is proven to have synergism with DBBP (Ballinas *et al.*, 2008) but apparently DBBP-D2EHPA combination has not been tested in extremely concentrated sulfuric acid. D2EHPA has not shown signs of instability or third phase formation (Beyad *et al.*, 1990).

### 3.2.3 Phosphine oxides

Organophosphine oxides contain three alkyl or aryl groups, directly bonded to the phosphorus atom (Fig. 7). They extract both acids and metals (Flett, 2005). Trialkylphosphine oxides are the active constituents in commercial Cyanex 921, 923 and 925 extractants. Dziwinski & Szymanowski (1998) identified 18 compounds in Cyanex 923 of which 17 pointed out to be trialkylphosphine oxides. The mixture has four major phosphine oxides with *n*-hexyl [ $-(\text{CH}_2)_5\text{CH}_3$ ] and *n*-octyl [ $-(\text{CH}_2)_7\text{CH}_3$ ] groups as hydrocarbon substituents. These four compounds account for 92.4 % of the mixture. The smaller 7.3 % fraction consists of phosphine oxides with branched aliphatic chains. (Dziwinski & Szymanowski, 1998)

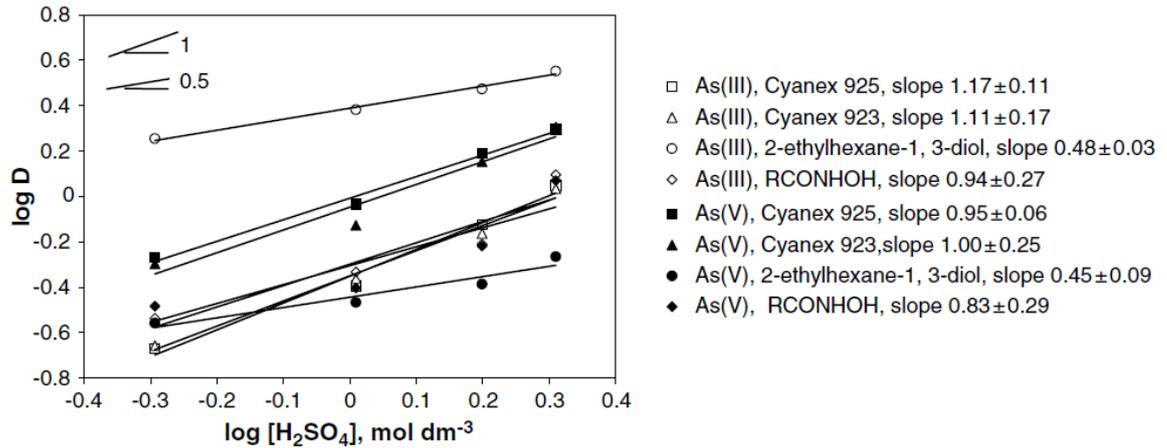
Cyanex 925 is somewhat similar to Cyanex 923 but it shows a more uniform distribution of its 19 compounds. 65.9 % of its components are trialkylphosphine oxides. Rest of the active compounds (26.8 %) are dialkyldithiophosphinic acids and trialkylphosphine sulfides. Alkyl chains in phosphine oxides of Cyanex 925 are more branched compared with Cyanex 923. Detailed description of both extractants is available in the cited literature. (Dziwinski & Szymanowski, 1998)



**Figure 7** General structure of organic phosphine oxide.  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  may be alkyl or aryl groups.

Both Cyanex 923 and 925 extract As(III) and As(V). Marginal difference in loading performance between these two extractants has been reported by Iberhan & Wiśniewski (2003) (Fig. 8, Table I). They extracted arsenic with 50 vol-% Cyanex solutions at 50 °C and did the performance comparisons with synthetic acid solutions containing 2.5 g dm<sup>-3</sup> of arsenic and 150 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. Stripping was tested with distilled water at 50 °C. Phase ratios were 1.

Similarly to TBP, extractability of arsenic with Cyanex 923 or 925 increases as H<sub>2</sub>SO<sub>4</sub> concentration in feed increases (Fig. 8). Trialkylphosphine oxides were reported to form As(V) complexes with 1:1:1 molar ratio of H<sub>3</sub>AsO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> and R<sub>3</sub>PO in the complex. (Iberhan & Wiśniewski, 2003)



**Figure 8** Effect of sulfuric acid concentration on distribution coefficient of arsenic for several extractants. (Iberhan & Wiśniewski, 2003)

Extraction is more efficient with aromatic diluent, whereas arsenic is easier to strip from loaded Cyanex 923 when aliphatic Exxsol D220/230 is used as diluent (Table I) (Iberhan & Wiśniewski, 2003). Similar behavior has been observed with trioctylphosphine oxide (TOPO, Cyanex 921). With *p*-xylene as diluent, TOPO has been reported to yield tenfold the efficacy of TBP. The efficiency, however diminishes significantly if aliphatic kerosene is used as diluent. (Marr *et al.*, 1985). Aromatic solvents are toxic and thus aliphatic diluents are more attractive.

**Table I** Extraction and stripping efficiencies for 50 vol-% solutions of Cyanex 923 and Cyanex 925.  $\text{H}_2\text{SO}_4$  concentration was  $150 \text{ g dm}^{-3}$  in the feed. Phase ratios were 1 both in extraction and stripping. Originally presented by Iberhan & Wiśniewski (2003).

Extractant	Step	As(III) [%]			As(V) [%]		
		Toluene	Octane	Exxsol D220/230	Toluene	Octane	Exxsol D220/230
Cyanex 923	extraction	40.4	–	34.3	57.4	–	43.4
	stripping	46.5	–	62.8	48.5	–	62.9
Cyanex 925	extraction	42.8	8	–	60.6	48	–
	stripping	11.8	8	–	39.6	30.2	–

Extractant performance on extraction of arsenic with Cyanex 923 and 925 was further compared by taking both extraction and stripping into account simultaneously, *i.e.* by comparing recoveries (Table II). Recovery percentages were calculated by multiplying percentages extracted with percentages stripped. It can be noticed that Cyanex 923 provided significantly better total recoveries than 925. Aliphatic Exxsol D220/230 is preferable diluent for Cyanex 923. It seems likely that dialkyldithiophosphinic acids and trialkylphosphine sulfides have stronger interactions with the

extracted arsenic species, resulting in lower back-extraction at stripping (Dziwinski & Szymanowski, 1998). Co-extraction of sulfuric acid is, however, more pronounced with Cyanex 923 and thus lower separation factors are achieved than with Cyanex 925 (Dreisinger<sup>b</sup> *et al.*, 1993).

**Table II** Arsenic recoveries calculated from extraction and stripping percentages reported by Iberhan & Wiśniewski (2003).

Diluent	Cyanex 923			Cyanex 925		
	As(III) [%]	As(V) [%]	Total [%]	As(III) [%]	As(V) [%]	Total [%]
Toluene	18.79	27.84	46.63	5.05	24.00	29.05
Octane	-	-	-	0.64	14.50	15.14
Exxsol D220/230	21.54	27.30	48.84	-	-	-

Even diluted, 50 vol-% Cyanex 923 has such high viscosity that extraction and stripping should be carried out at elevated temperature, for example at 50 °C. Equilibrium is reached within five minutes and phase disengagement occurs in few tens of seconds, providing clear phases. (Wiśniewski, 1997)

### 3.2.4 Alcohols

Aliphatic alcohols form solvates with arsenic in H<sub>2</sub>SO<sub>4</sub> solutions. Alcohols either substitute water molecules in hydrated arsenic compound or form hydrogen bonds with hydrated water molecules around the arsenic compound. Substitution of water with alcohols is partial but the degree of substitution will increase with increased H<sub>2</sub>SO<sub>4</sub> concentration, enhancing the extraction efficiency for both As(III) and As(V). Low distribution coefficients in extraction may be expected with monoalcohols, whereas stripping of arsenic from the organic phase is efficient. Alcohols have lower toxicity than other comparable extractants, they are stable and they can be used without modifiers. (Szymanowski, 1998)

2-ethylhexanol is an easily accessible extractant for arsenic. It is more selective towards As(III) than As(V). Yet for aliphatic alcohols, no relationships have been found between selectivity and type of branching, or hydrophobicity. Antimony, bismuth, iron or nickel don't interfere with arsenic extraction. 2-ethylhexanol works better undiluted, and extraction can be further improved by increasing temperature to 70 °C and adding quaternary ammonium salt, trioctylmethylammonium chloride (Aliquat 336). 5 % NaOH solution is suggested for stripping, because achievable peak loading in the strip is 5 g dm<sup>-3</sup> for As(III) when water is used for stripping. (Szymanowski, 1998)

Diols will offer significant improvement in extraction, because in addition to As(III) they extract also As(V) significantly. Szymanowski (1998) has compiled a table on performances of alcohol extractants (Table III). The table is based on data provided by Baradel & Guerriero (1988).

**Table III** Percentages extraction of As(III) and As(V) for various alcoholic extractant mixtures after one 10-minute equilibration. Phase ratio (O/A) was 2, initial concentrations  $200 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$ ,  $45 \text{ g dm}^{-1} \text{ Ca}$ ,  $6.1 \text{ g dm}^{-3} \text{ As(III)}$  and  $6.8 \text{ g dm}^{-3} \text{ As(V)}$ . Re-produced from Szymanowski (1998).

Extractant mixture	As(III) [%]	As(V) [%]
2-ethylhexanol	29.5	3.7
6 % tetradecane-1,2-diol in 2-ethylhexanol	68	38
6 % tetradecane-1,2-diol in 9:1 decane – isodecanol	81.5	60
6 % tetradecane-1,2-diol in 9:1 ISOPAR L – isodecanol	–	83
10 % octane-1,2-diol in SOLVESSO 100	85	84
10 % 2-phenylpropane-1,2-diol in 9:1 SOLVESSO 100 – isodecanol	67	56
10 % 2-methyl-2-propylpropane-1,3-diol in SOLVESSO 100	87	84
20 % 2-ethylhexane-1,2-diol in SOLVESSO 100	78	22

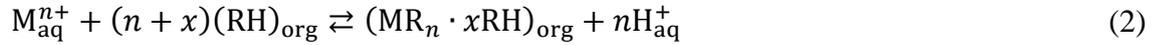
*ISOPAR L = Commercial mixture of isoparaffines (Esso)*  
*SOLVESSO 100 = Commercial mixture of aromatic hydrocarbons (Esso)*

Szymanowski (1998) mentioned that extractant mixture ENIM 100 is likely a mixture of alcohols similar to those mentioned in this chapter, *i.e.* diols. ENIM 100 was developed and patented by Baradel *et al.* (1986). They recommended to use the extractant in concentrations between 5–10 % with a phase modifier and aliphatic or aromatic diluent. It extracts both As(III) and As(V), and the affinity towards arsenic was characterized verbally as very good. (Baradel *et al.*, 1986)

Furthermore, pH was reported to have negligible effect on stripping of arsenic from ENIM 100 and thus water was stated to be suitable for stripping (Baradel *et al.*, 1986). This may be the case with As(V), but for As(III) this is uncertain considering Szymanowski's (1998) statement about saturation loading of As(III). In stripping tests, concentration of arsenic was varied from 1 to  $7 \text{ g dm}^{-3}$  in the organic phase, and equilibrium was reached in 10 min. Difficulties in phase separation occur at 20 °C but increasing temperature alleviates the problem. At 30 °C phase separation requires three minutes, and only 45 seconds are required at 50 °C. (Baradel *et al.*, 1986) Distribution coefficients of As(V) in similar extraction conditions have been mentioned to be 1.399 for ENIM 100, 0.520 for Cyanex 923, and 0.521 for TBP (Bogacki *et al.*, 1998). The extractants should however be tested at *precisely* similar solutions for fair comparison.

### 3.3 Acidic and chelating extractants

Acidic extractants are known to extract metal cations via cation exchange or chelation (Szymanski, 1998). A general reaction equation for cation exchange has been given by Flett (2005):

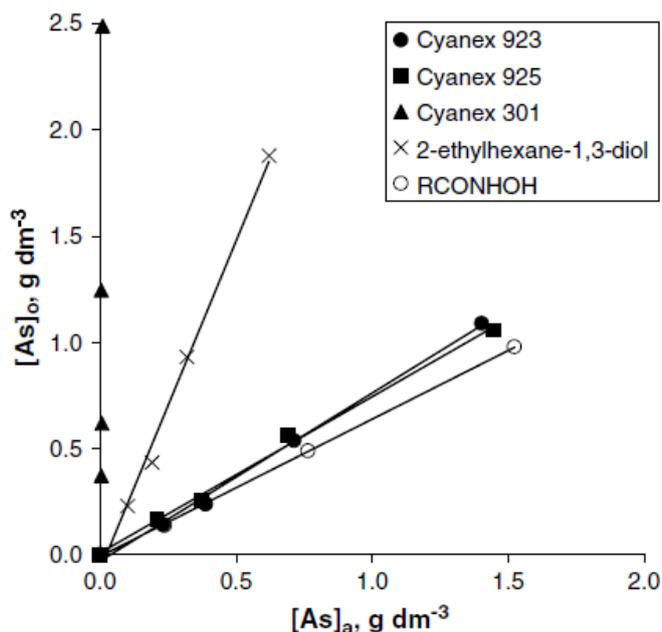


where M is a cation with valence  $n$ , R is a ligand, RH is an organic acid and  $x$  is the number of associated, non-protonated molecules. A general reaction equation for chelation is not discussed here as the mechanism is perhaps even less known than solvation in extraction of arsenic.

#### 3.3.1 Bis-(2,4,4-trimethylpentyl)-dithiophosphinic acid

Organic dithiophosphinic acids carry the functional group –PSSH, and complexation is explained by cation exchange mechanism (Reaction 2). Cation exchanger may work in extremely acidic ( $\text{pH} \leq 0$ ) conditions for As(III), because As(III) is found in cationic  $\text{AsO}^+$  form (Szymanski, 1998).  $\text{As}(\text{OH})_2^+$  is another possible formulation (Fig. 1). Since As(V) is mostly as undissociated  $\text{H}_3\text{AsO}_4$ , dithiophosphinic acids do not extract it effectively. If complete removal is desired, As(V) should be first reduced to As(III), which has been done by treating the feed solution with sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$  solution (Gupta & Begum, 2008).

According to Gupta & Begum (2008), only bis-(2,4,4-trimethylpentyl)-dithiophosphinic acid (Cyanex 301) of the phosphinic acid derivatives, extracts As(III) in significant amounts. Compared to solvating extractants, Cyanex 301 is superior in extraction of As(III) (Fig. 9) but it extracts also copper and it is extremely difficult to strip (Iberhan & Wiśniewski, 2003). Not even 18 M  $\text{H}_2\text{SO}_4$  strips any copper from loaded Cyanex 301 (Sole & Hiskey, 1995). If the co-extracted copper can't be stripped, it will accumulate in the organic phase and saturate the extractant.



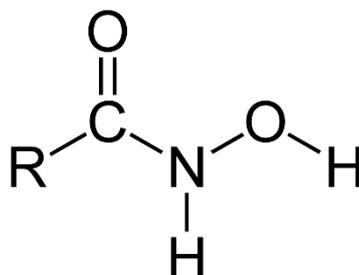
**Figure 9** Isotherms for As(III) liquid-liquid extraction from solution containing  $150 \text{ g dm}^{-3}$   $\text{H}_2\text{SO}_4$ . Extractant concentrations were  $1.2 \text{ mol dm}^{-3}$  for Cyanex 923,  $1.1 \text{ mol dm}^{-3}$  for Cyanex 925,  $3.2 \text{ mol dm}^{-3}$  for 2-ethylhexane-1,3-diol,  $0.2 \text{ mol dm}^{-3}$  for Cyanex 301 and  $0.1 \text{ mol dm}^{-3}$  for hydroxamic acids. (Iberhan & Wiśniewski, 2003)

Loaded Cyanex 301 stripped with alkaline solution, *e.g.* NaOH, forms a metastable emulsion (Iberhan & Wiśniewski, 2003; Gupta & Begum, 2008). Emulsion formation can be prevented by adding a significant excess of thiourea into the initial aqueous phase. Concentration of thiourea should be tenfold in relation to Cyanex 301 concentration, and acidity adjusted to 0.5–2 M. With thiourea copper forms water-soluble complexes that will not be transported to the organic phase. Furthermore, all arsenic could be stripped with a mixture containing one part of  $1 \text{ mol dm}^{-3}$  NaOH, and two parts of  $0.1 \text{ mol dm}^{-3}$   $\text{KBrO}_3$  in  $1 \text{ mol dm}^{-3}$  HCl-KBr. (Gupta & Begum, 2008)

The publication from Gupta & Begum (2008) lacks important details such as initial volume of the aqueous phase, where given volume of sodium thiosulfate was added. Initial metal concentrations were less than  $100 \text{ mg dm}^{-3}$ , and the reported results were obtained for HCl media. It was stated, though, that equal efficiency can be achieved also in  $0.5\text{--}2 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  as quantitative extraction of As(III) was observed (Gupta & Begum, 2008). Ratios and concentrations of the additives may change in more concentrated acid. Additionally, if thiourea is added to initial solution, it should be removed from the acidic aqueous phase if the acid was to be re-used.

### 3.3.2 Hydroxamic acids

LIX 1104, originally produced by German company Henkel, is a hydroxamic acid (Fig. 10) extractant specifically developed for purification of arsenic, antimony and bismuth from copper electrolyte solutions. Hydroxamic acids in LIX 1104 most likely contain highly branched alkyl groups with 6–22 carbon atoms. (Schwab & Kehl, 1989). Szymanowski (1998) suggests branched alkyl groups with at least 10–15 carbon atoms to provide adequate hydrophobicity and stability. Linear alkyl group in hydroxamic acid tends to make the acid more soluble in water and prone to hydrolysis, which are undesired properties for a solvent extraction reagent (Szymanowski, 1998). Alcohols with branched hydrocarbon chain, phenols and phenol esters are used as modifiers to prevent third phase formation and enhance phase separation (Iberhan & Wisniewski, 2003).



**Figure 10** Structural formula of a hydroxamic acid. R is alkyl or aryl group.

Iberhan & Wiśniewski (2003) have mentioned that complexation of arsenic with hydroxamic acids occurs via chelation but no further explanation of the mechanism was given. Szymanowski (1998) described complexation with a reaction equation analogous to reaction in Eq. 2, where  $x$  would be zero - similar to plain cation exchange.

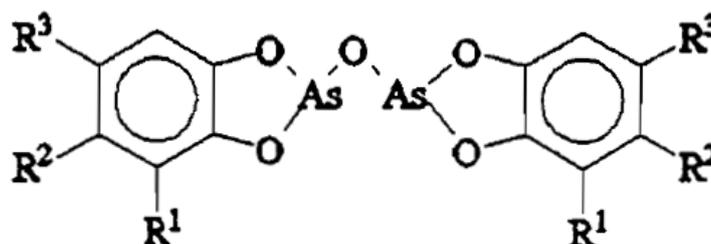
Hydroxamic acids are not selective to arsenic and are known to extract several metals in wide pH range, but in concentrated acids they extract arsenic, antimony, bismuth and iron. The metals are loaded simultaneously but can be separated in scrubbing and stripping stages. The recommended equilibration time in extraction is 10–20 minutes for arsenic. Iron and antimony equilibrate faster. Loaded organic phase can't be stripped from arsenic with alkaline solutions because hydroxamic acids would decompose. Instead, arsenic can be removed by precipitation as sulfides with gaseous  $\text{H}_2\text{S}$  at 2–3 bar pressure or alkali metal sulfide. Precipitation of As and Sb requires 15–25 minutes at 75–85 °C temperature. Iron can be stripped with *e.g.* 3–8 mol  $\text{dm}^{-3}$  HCl or 1 mol  $\text{dm}^{-3}$  oxalic acid. (Szymanowski, 1998; Schwab & Kehl, 1989). Some fundamental benefits of solvent extraction are lost with such flowsheet as pressure and temperature manipulations are mandatory. An

aqueous stream containing the arsenic would be more desirable considering further processing of arsenic.

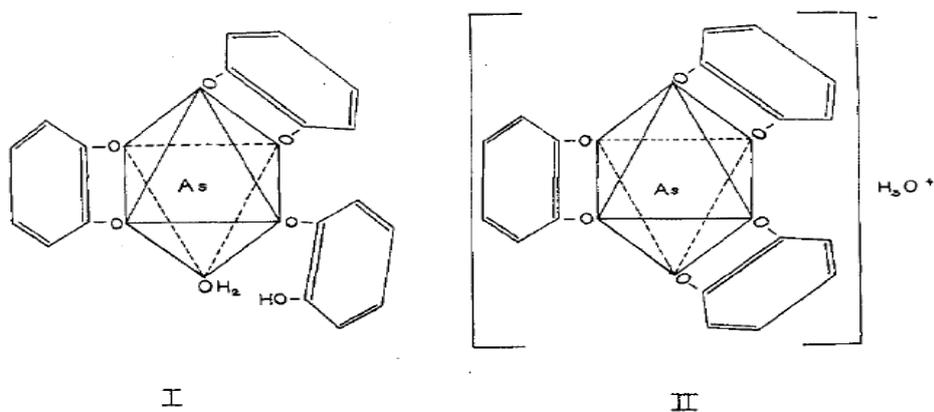
### 3.3.3 Polyphenols

Alkylated polyphenols that contain two or three hydroxyl groups in vicinal positions are suitable chelating ligands for both As(III) and As(V). 1,2-dihydroxybenzene (catechol) and 1,2,3-trihydroxybenzene (pyrogallol) are the structures responsible for chelation. Plain catechol and pyrogallol are hydrophilic, and therefore it is recommended to use di-alkyl derivatives in solvent extraction. (Baradel *et al.*, 1987; Szymanowski, 1998)

Figure 11 shows the As(III) complex suggested by Johanson (1969). Respectively, two possible structures for As(V) complex are shown in Fig. 12.



**Figure 11** As(III) complex with alkylated catechols. Structure suggested by Johanson (1969), picture from Szymanowski (1998).



**Figure 12** As(V)-catechol complexes suggested by Reihlen *et al.* (1925) and Rosenheim & Plato (1925). Picture from Larkins Jr. & Jones, 1963).

Alkyl derivatives of catechol and pyrogallol are viscous liquids and used as mixtures with aliphatic or aromatic solvents (Szymanowski, 1998). Baradel *et al.* (1987) reported in their patent about 88 % extraction yield for arsenic with *n*-hexylcatechol as extractant. Arsenic was extracted from a solution containing  $200 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$ ,  $45 \text{ g dm}^{-3} \text{ Cu}$  and  $5.9 \text{ g dm}^{-3} \text{ As}$ , and phase ratio was 1. The extractant was diluted to concentration of  $0.3 \text{ mol dm}^{-3}$  with ESCAID 100 solvent. Similar extraction procedure with di-octylcatechol as extractant resulted in 91 % extraction. Stripping yield with  $2 \text{ mol dm}^{-3} \text{ NaOH}$  solution was 93 %. Mixing times of 10 minutes were applied both in extraction and stripping, and phases were settled for 30 minutes. (Baradel, *et al.*, 1987) Long-term stability of alkylated catechols in highly acidic media is not discussed in the patent. Neither has been anything mentioned about co-extraction of copper, sulfuric acid or other possible elements present in a solution. These aspects should be further studied.

### 3.4 Literature review – summary

In addition to extractant choice, efficiency of arsenic extraction is enhancing with increasing sulfuric acid concentration. Travkin *et al.* (1993) have shown that increase in temperature decreases the extraction efficiency with neutral organophosphorus extractants. Alcohols have been reported to exhibit reverse behavior, as increase in temperature increases extraction of arsenic (Szymanowski, 1998). Significant improvements in extraction efficiency may be observed with aromatic diluents but they are much more hazardous than kerosene-based aliphatic solvents.

Selection of extractant mixtures for experiments was based on this literature review. Tributyl phosphate was an undisputed choice as it can be considered to be an “industrial standard”. Cyanex 301 and hydroxamic acids were omitted since difficulties in stripping were described in the literature for these extractants. 1,2-octanediol in 2-ethylhexanol was chosen to represent an alcohol mixture (Table III) used by Baradel & Guerriero (1988). 1,2-octanediol was chosen instead of 1,2-tetradecanediol, since latter was not available. Cyanex 923 was selected over Cyanex 925 because of slightly better overall recoveries (Table II).

## 4 MATERIALS AND METHODS

The aim was to recover arsenic from two industrial sulfuric acid solutions that had different compositions. To distinguish the solutions within the text, they are referred as ‘Acid 1’ and ‘Acid 2’. Sulfuric acid concentrations in the solutions were over  $10 \text{ mol dm}^{-3}$ , and thus they were significantly more concentrated acids than those described in the examined literature. The results pub-

lished earlier for the less concentrated, e.g. 2–6 M H<sub>2</sub>SO<sub>4</sub> solutions, are not guaranteed to be applicable in the process design for these more concentrated acids. Therefore, the main goal of the experimental work was to determine the equilibria with more concentrated sulfuric acids.

First the effects of extractant concentrations were studied, and loading isotherms were determined for the available and suitable extractants. Based on the loading isotherms, tests were continued by scrubbing and stripping experiments.

#### 4.1 Extractants and chemicals

The used extractants and tested concentration ranges are listed in Table IV. Aliphatic Exxsol D80 (CAS: 64742-47-8) solvent containing C11–C15 hydrocarbons was used as diluent with the organophosphorus extractants. Information on the chemicals is given in Table V.

**Table IV** The tested extractant mixtures and concentration ranges.

Extractant	Diluent	Concentration range
TBP	Exxsol D80	10–80 vol-%
DBBP	0.25 M D2EHPA + Exxsol D80	50 vol-%
Cyanex 923	Exxsol D80	10–80 vol-%
1,2-octanediol	2-ethyl-1-hexanol	2–20 wt-%

**Table V** List of extractant chemicals.

Extractant or diluent	CAS number	<i>M</i> [g mol <sup>-1</sup> ]	Supplier
TBP (97 %)	126-73-8	266.31	Sigma-Aldrich
DBBP (90 %)	78-46-6	250.31	Sigma-Aldrich
Cyanex 923	mixture	348 (approx.)	Cytec
D2EHPA (technical grade)	298-07-7	322.42	via Outotec Oyj
1,2-octanediol (98 %)	1117-86-8	146.23	Sigma-Aldrich
2-ethyl-1-hexanol (99 %)	104-76-7	130.23	Sigma-Aldrich

#### 4.2 Analytical methods and instrumentation

Metal and sulfuric acid concentrations were analyzed from all aqueous samples, and at the beginning concentrations in the organic phases were calculated from mass balance. This pointed out to be an unreliable method due to precipitation that occurred during the extractions, and consequently most of the organic samples were afterwards backextracted with pure water using *A/O* = 30, and the aqueous phases were then analyzed by ICP-MS. Samples were filtrated with syringe filters

( $d_p = 0.45 \mu\text{m}$ ) when it was necessary.  $\text{As}^{3+}$ , redox-potential and viscosity were measured only from Acid 1 and Acid 2.  $\text{As}^{3+}$  titrations and redox-potential measurements were performed by Outotec Research Center (ORC), Pori. Rest of the analyses were carried out at LUT.

Agilent 7900 ICP-MS was used to analyze concentrations of As, Sb, Bi, Cu, Cd, Ni, Zn, Hg and Pb from the aqueous samples. Calibration solutions were prepared from ROMIL's PrimAg (ICP Calibration Mix PA26) standard solution that contained 100 ppm of each of its 26 elements. Elevated helium flow rate was used for arsenic to minimize interference-related errors. Samples were diluted in two steps. First dilutions were weighed since viscosities and densities of the raw samples were significantly higher compared with water. Matrix solution used in dilutions contained 1 % HCl (34–37 %) and 1 %  $\text{HNO}_3$  (67–69 %) (Super Purity Acids, ROMIL-SpA™).

Fluoride concentrations were measured from the aqueous samples with Thermo Fisher Scientific 9609BNWP fluoride ion selective electrode (ISE). Samples were first diluted tenfold with pure water, and then buffered with 14.7 % sodium acetate and total ionic strength adjustment buffer (TISAB) to  $\text{pH} > 5$ . Buffering was necessary, since fluorine forms HF and  $\text{HF}_2^-$  in acidic solutions and these species can't be detected by the fluoride ISE (Thermo Fisher Scientific, 2011).

Anton Paar DMA 4500 density-meter was used to measure sample densities at 23 °C. Viscosities of Acid 1 & 2 were measured with an Ubbelohde capillary viscometer at 20 °C. The viscometer (Type 501 13/Ic) is manufactured by SCHOTT-GERÄTE GmbH, it is DIN-51562 compliant, and its capillary diameter is 0.78 mm.

All aqueous samples were titrated with Mettler Toledo T50 titrator using automatic burette and Mettler Toledo DG111-SC pH-electrode. 1 N and 0.1 N NaOH titrants were prepared from Titrisol® (Merck, Germany) and Fluka® (Sigma-Aldrich, Germany) concentrate ampoules, respectively. The electrode was calibrated before each titration set with pH 4 and 7 buffers, and a control sample with known acid concentration was titrated to verify titer of the titrant.

Precipitate from equilibration of 1,2-octanediol and 2-ethylhexanol with Acid 2 was stored overnight in an oven at 50 °C. Because of  $\text{H}_2\text{SO}_4$ , there was still residual moisture in the precipitate. This precipitate was weighed and dissolved in 5  $\text{cm}^3$  of reversed aqua regia (4:1  $\text{HNO}_3$ :HCl) by wet digestion. Wet digestion was carried out in UltraWAVE MA149-010 (Milestone Srl, Italy) microwave acid digestion system. Pressure of the vessel was initially set approximately to 40 bar,

and temperature was ramped up to 250 °C in 30 minutes. The system was maintained at 250 °C and 80 bar for 20 min before cooling and pressure release. All precipitate was dissolved, and the samples were immediately diluted to 50 cm<sup>3</sup> of pure water. ICP-MS analysis was later performed for the sample.

Total carbon was measured with Shimadzu TNM-L ROHS TOC-L analyzer. Synthetic air with 150 cm<sup>3</sup> min<sup>-1</sup> flow rate was used as carrier gas. Measurements were done for both Acid 1 and Acid 2, and raffinate samples from experiments with TBP and Acid 1.

### **4.3 Equilibrium experiments with varying extractant concentration**

Effect of extractant concentration on extraction efficiency was studied by batch extractions in 50 cm<sup>3</sup> separation funnels. Initial phase ratio (O/A) was 1:1 and temperature was 20 ± 1 °C in all experiments. Extractant concentrations were varied between the ranges given in Table IV. 20 cm<sup>3</sup> of both phases were equilibrated in the separation funnels, which were placed in an orbital shaker running at 250 rpm for 20 minutes. The phases were left to settle, and samples were taken from both phases when they visually looked clear.

DBBP was scarcely available and the idea was to first test D2EHPA as a synergistic phase modifier. If the problem of third phase formation would have been solved by D2EHPA addition for 50 vol-% solution, concentrations between 10–80 vol-% would have been tested in the same way as for TBP and Cyanex 923.

### **4.4 Equilibrium experiments with varying phase ratio**

Loading isotherms were determined for undiluted TBP and the mixture of 1,2-octanediol and 2-ethylhexanol. The alcohol mixture contained 6 wt-% 1,2-octanediol. Isotherm-related experiments were carried out in 50 cm<sup>3</sup> separation funnels at 21 ± 2 °C. The equilibration procedure was similar to that described in chapter 4.3 but now shaking rate was elevated to 275 rpm and total volume of the phases was 45 cm<sup>3</sup>. For loading isotherms, initial phase ratios (O/A) were first varied between 0.1–8 but higher end of the range was lowered, since with adequately large O/A ratios the aqueous phases became totally miscible with the organic phase.

In scrubbing experiments the loaded organic phases were washed with pure water, using phase ratios of 1, 2, 4, 8 and 10. The purpose of an intermediate washing step is to selectively remove

sulfuric acid from the loaded organic phase, and then strip arsenic from the arsenic-rich organic stream. This is the traditional approach, for which flowsheet is presented in Fig. 2. Washing experiments utilizing  $O/A = 1$  and 4 were repeated with 1 wt-%  $\text{Na}_2\text{SO}_4$  solution as washing solution.

Stripping isotherm was constructed for TBP, which was first loaded with Acid 1 at  $O/A = 0.1$  and consecutively washed with pure water at  $O/A = 4$ . The system of TBP and Acid 1 was selected for stripping experiments because of the best separation between arsenic and sulfuric acid (Figs. 23–26).

#### 4.5 Determination of phase volumes

Co-extraction of sulfuric acid and water result in phase volume changes. Changes in phase volumes had to be taken into account in the calculations, as otherwise the distribution coefficients and other characterizing parameters would have become distorted. To calculate phase volumes, their densities were measured and separation funnels were weighed after adding or removing a phase.

Phase ratio is the ratio of organic and aqueous phase volumes. Both organic-to-aqueous ( $O/A$ ) and aqueous-to-organic ( $A/O$ ) ratios are universally used. Changes in phase volumes during the extraction were expected, and thus for distinguishing equilibrium phase ratio from initial phase ratio, variable  $\Omega/\alpha$  was defined

$$\Omega/\alpha = \frac{V_{\text{org,eq}}}{V_{\text{aq,eq}}} \quad (3)$$

where  $\Omega/\alpha$  is the equilibrium phase ratio,  $V_{\text{org,eq}}$  is volume of the organic phase in equilibrium and  $V_{\text{aq,eq}}$  is volume of the aqueous phase in equilibrium. In this thesis,  $O/A$  is used to describe initial phase ratio, and  $\Omega/\alpha$  means equilibrium phase ratio.

#### 4.6 Performance-indicating quantities

There are certain fundamental parameters and illustration methods to describe extraction and stripping equilibrium. These parameters are useful in benchmarking the extractants and in process design, and most of them are found from *Nomenclature of Liquid-liquid Distribution (Solvent Extraction)* (IUPAC, 1993).

Distribution coefficients are used to indicate the tendency of a specimen to transfer from one phase to another. Distribution coefficient is defined as a ratio

$$D_A = \frac{c_{A,org}}{c_{A,aq}} \quad (4)$$

where  $D_A$  is the distribution coefficient of specimen A,  $c_{A,org}$  is the equilibrium concentration of A in the organic phase and  $c_{A,aq}$  is the equilibrium concentration of A in the aqueous phase. Respectively, stripping coefficient describes how easily a specimen is transferred to the aqueous phase and it is defined as inverse of distribution coefficient

$$D'_A = \frac{c_{A,aq}}{c_{A,org}} \quad (5)$$

where  $D'_A$  is the stripping coefficient of specimen A. (Habashi, 1999)

An extractant capable of providing high distribution coefficient is favorable, but a single distribution coefficient gives no information about selectivity of an extractant. For that purpose, separation factors are used. For species A and B separation factor  $\beta$  is defined by

$$\beta = \frac{D_A}{D_B} \quad (6)$$

where  $\beta$  is the separation factor. Like distribution coefficient, separation factor is specific for the certain given conditions.

As an extractant is loaded from a solution which contains multiple species, it is very likely that also other species get co-extracted with the target specimen. This is exactly the case in extraction of arsenic from sulfuric acid solutions. If separation factor equals 1, no separation will occur within the stage. (Habashi, 1999)

Both distribution coefficients and separation factors can be calculated from an extraction isotherm *i.e.* from plot of  $c_{org}$  versus  $c_{aq}$  (or vice versa). Distribution coefficients do not provide direct information about absolute amount of mass transfer if phase volumes change during extraction. Absolute mass transfer is better described by percentage extraction, which can be formulated

$$E(A) = 100 \% \cdot \frac{m_{A,org}}{m_{0,A,aq}} \quad (7)$$

where  $E(A)$  is percentage of A extracted,  $m_{A,org}$  is weight of A in the organic phase in equilibrium and  $m_{0,A,aq}$  is initial weight of A in the aqueous phase.  $E$  may be lower than percentage removed, for example when the solute precipitates during extraction. Percentage removed is calculated from

$$R(A) = 100 \% \cdot \frac{m_{0,A,aq} - m_{A,aq}}{m_{0,A,aq}} \quad (8)$$

where  $R(A)$  is percentage of A removed from the aqueous phase and  $m_{A,aq}$  is weight of solute in the aqueous phase in equilibrium.

## 5 RESULTS AND DISCUSSION

### 5.1 Sulfuric acid solutions

Measured compositions and physical properties of Acids 1 and 2 are given in Table VI. The table shows averages from the measurements. There was little variation in metal and acid concentrations between different samples from Acid 1 & 2 (Appendix I).

**Table VI** Compositions of Acid 1 and 2, and their physical properties.

Property	Acid 1	Acid 2	Analytical method
Colour	Light green	Brown	Visual inspection
$\rho$ in 23 °C [g cm <sup>-3</sup> ]	1.5912	1.6920	Anton Paar density meter
$\mu$ in 20 °C [mPa s]	8.87	16.84	Capillary viscometer
$c(\text{H}_2\text{SO}_4)$ [wt-%]	63.8	74.2	Acid-base titration
$c(\text{As})_{\text{tot}}$ [g dm <sup>-3</sup> ]	23.3	8.4	ICP-MS
$c(\text{As}^{3+})$ [g dm <sup>-3</sup> ]	2.2	7.1	Ce(SO <sub>4</sub> ) <sub>2</sub> titration
$c(\text{As}^{5+})$ [g dm <sup>-3</sup> ]	21.1	1.3	Mass balance
$c(\text{Cu})$ [mg dm <sup>-3</sup> ]	8.5	392.5	ICP-MS
$c(\text{Zn})$ [mg dm <sup>-3</sup> ]	0.9	335.6	ICP-MS
$c(\text{Ni})$ [mg dm <sup>-3</sup> ]	2139.4	111.3	ICP-MS
$c(\text{Cd})$ [mg dm <sup>-3</sup> ]	< 1	1030.7	ICP-MS
$c(\text{Sb})$ [mg dm <sup>-3</sup> ]	132.0	32.7	ICP-MS
$c(\text{Hg})$ [mg dm <sup>-3</sup> ]	8.5	10.2	ICP-MS
$c(\text{Pb})$ [mg dm <sup>-3</sup> ]	1.5	26.4	ICP-MS
$c(\text{Bi})$ [mg dm <sup>-3</sup> ]	21.3	1006.8	ICP-MS
$c(\text{F}^-)$ [mg dm <sup>-3</sup> ]	2	284.8	F <sup>-</sup> ion selective electrode
TOC [mg dm <sup>-3</sup> ]	580	30	TOC-L
Redox-potential [mV]	+500–525	+520–660	analyzed at ORC

## 5.2 Effect of extractant concentration

Using Exxsol D80 as an aliphatic diluent with the organophosphorus extractants resulted in third phase formation when the diluted extractants were contacted with Acid 2. For TBP and Cyanex 923, formation of third liquid phase was observed with all tested dilutions. Since DBBP was scarcely available and third phase formation was expected, it was tested only at 50 vol-% concentration, diluted by 0.25 M D2EHPA in Exxsol D80. D2EHPA didn't prevent third phase formation at the tested concentration. Respectively, a phase modifier was tested with 50 vol-% solutions of TBP and Cyanex 923. 10 vol-% of Aliquat 336 was added into the 50 vol-% extractant solutions but third phase formation still occurred.

Of the three liquid phases, top phase was totally clear and transparent. It was anticipated that this phase contained pure – or nearly pure – Exxsol D80 because of its look, smell and visually observed rheology. GC analysis was later performed for one of the top phases, and it further supported that the top phase contained only Exxsol D80. The bottom phase was obviously Acid 2 raffinate, and middle phase contained the loaded organophosphorus extractant. Some precipitation at the organic-aqueous interface, and at the bottom of the aqueous phase, was observed in all loading experiments. Precipitation was more pronounced with Acid 2.

Desired phase behavior during loading was obtained with undiluted TBP, and mixtures of 1,2-octanediol and 2-ethylhexanol. Undiluted Cyanex 923 has a viscosity of 50.5 mPas at +25 °C, and thus it was not used without dilution to Exxsol D80 (Cytec, 2008).

Major fraction of arsenic was removed from the aqueous phase with all tested 1,2-octanediol concentrations (Tables VII & VIII). Since arsenic was the metal to be separated, other metals are referred as impurities in this text. Because of precipitation in the extractions, percentages removed are reported instead of percentages extracted. Significance of these precipitates was discovered later, and thus concentrations in the organic phase were not determined by backextraction during these experiments, but from changes in aqueous phase concentrations and mass balance. Therefore, percentages extracted or concentrations in the organic phase are not known. Increase of 1,2-octanediol concentration in 2-ethylhexanol increased extraction of sulfuric acid (Fig. 13).

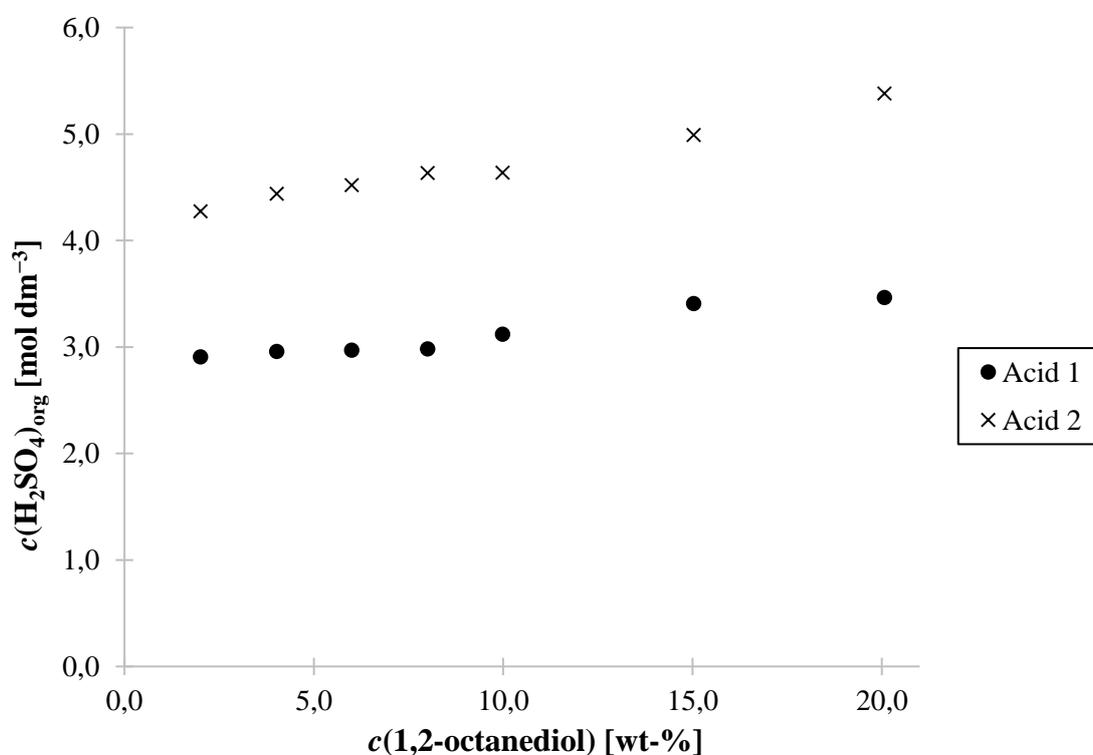
Nickel is clearly the most significantly removed impurity from Acid 1 in terms of absolute amount. Not as much nickel was removed from Acid 2, since its concentration in Acid 2 was only ca. 100 mg dm<sup>-3</sup>. Acid 2 contains more different impurities, and in higher concentrations compared with Acid 1. For instance, bismuth was almost quantitatively removed from Acid 1 since its concentration was only 30 mg dm<sup>-3</sup>. Bismuth was also the most significant impurity removed from Acid 2 by weight but percentages removed were lower than from Acid 1, probably due to presence of competitive species in Acid 2. Relatively high percentages of removal have been calculated for some impurity metals but their concentrations were so low that it is impossible to tell if the extractant mixture has had any specific affinity towards them. Extraction of arsenic is however certain, as shown and discussed later in this chapter.

**Table VII** Percentages of metals removed from Acid 1 in extraction with 1,2-octanediol in 2-ethyl-1-hexanol. O/A = 1,  $T = 20 \pm 1$  °C,  $t_{eq} = 20$  min.

<i>c</i> (1,2-octanediol) [wt-%]	2	4	6	8	10	15	20
<i>R</i> (Ni) [%]	56.03	33.08	71.40	63	36.27	17.84	25.64
<i>R</i> (Cu) [%]	57.95	37.44	71.26	64.15	39.33	36.56	41.67
<i>R</i> (Zn) [%]	56.14	57.10	76.47	81.97	57.95	58.10	48.72
<b><i>R</i>(As) [%]</b>	<b>75.54</b>	<b>66.18</b>	<b>86.86</b>	<b>85.59</b>	<b>82.99</b>	<b>85.63</b>	<b>90.35</b>
<i>R</i> (Cd) [%]	0	0	22.96	16.81	13.54	46.07	41.91
<i>R</i> (Sb) [%]	61.35	48.11	78.74	74.49	63.20	60.97	66.55
<i>R</i> (Pb) [%]	66.32	62	83.16	80.11	65.59	56.06	51.12
<i>R</i> (Bi) [%]	96.73	96.26	98.12	97.90	95.84	93.94	82.89

**Table VIII** Percentages of metals removed from Acid 2 in extraction with 1,2-octanediol in 2-ethyl-1-hexanol. O/A = 1,  $T = 20 \pm 1$  °C,  $t_{eq} = 20$  min.

$c(1,2\text{-octanediol})$ [wt-%]	2	4	6	8	10	15	20
$R(\text{Ni})$ [%]	45	38.10	28.61	24.67	4.65	29.10	52
$R(\text{Cu})$ [%]	45.18	38.59	29.18	25.28	4.14	29.31	50.66
$R(\text{Zn})$ [%]	48.72	41.47	34.29	28.78	9.43	26.37	47.30
<b><math>R(\text{As})</math> [%]</b>	<b>84.11</b>	<b>81.93</b>	<b>79.63</b>	<b>79.72</b>	<b>75</b>	<b>85.15</b>	<b>91.67</b>
$R(\text{Cd})$ [%]	44.55	37.78	28.33	22.33	1.91	25.42	44.12
$R(\text{Sb})$ [%]	41.56	36.20	25.91	24.86	4.33	30.53	48.58
$R(\text{Pb})$ [%]	74.87	71.92	65.95	65.97	56.70	35.74	54.05
$R(\text{Bi})$ [%]	56.29	46.84	39.81	40.80	19.66	46.28	66.58

**Figure 13** Extraction of sulfuric acid to mixtures of 1,2-octanediol and 2-ethylhexanol. Acids 1 and 2 contained  $10.4 \text{ mol dm}^{-3}$  and  $12.8 \text{ mol dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ , respectively.  $T = 20 \pm 1$  °C, O/A = 1,  $t_{eq} = 20$  min.

The results for 2–10 wt-% 1,2-octanediol were obtained with different ICP standard (Accustandard<sup>®</sup> ICS-05-5) than those for 15 and 20 wt-%. Accustandard<sup>®</sup> contained no bismuth, which was analyzed in a different run by using Fluka<sup>®</sup> Bismuth atomic spectroscopy standard from Sigma-Aldrich. Total concentration of arsenic in Acid 1 was measured to be  $15.9 \text{ g dm}^{-3}$  with Accustandard<sup>®</sup>, and this was not in agreement with the results obtained later with the new PA26 standard, nor with the titration results from ORC laboratory. The new multielement standard was used for

the rest of the analyses, and therefore the systematic error caused by ICP-standard is limited to results presented in this chapter.

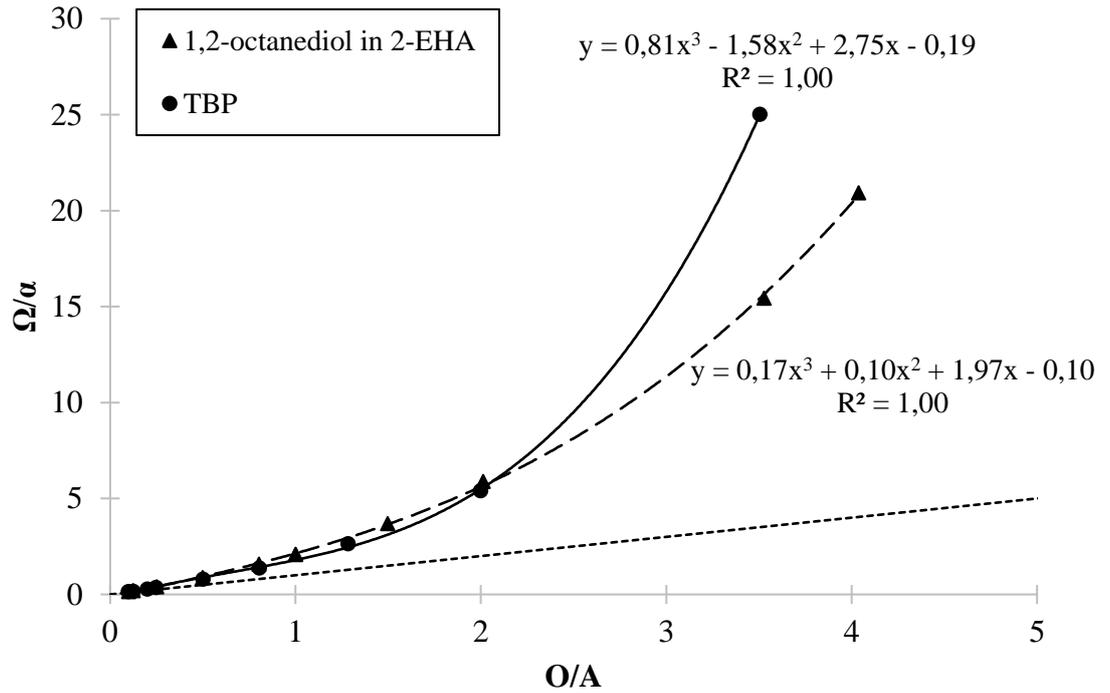
### 5.3 Changes in phase volumes

Co-extraction of sulfuric acid and water caused an increase in organic phase volume, and decrease in aqueous phase volume during loading. Densities of the phases changed simultaneously (Appendix II) so that total volume of the system remained practically constant (Table IX). Change in total volume was less than 1 % in most experiments, and minor leakages of acid from the funnels may have resulted in the values above 1 %.

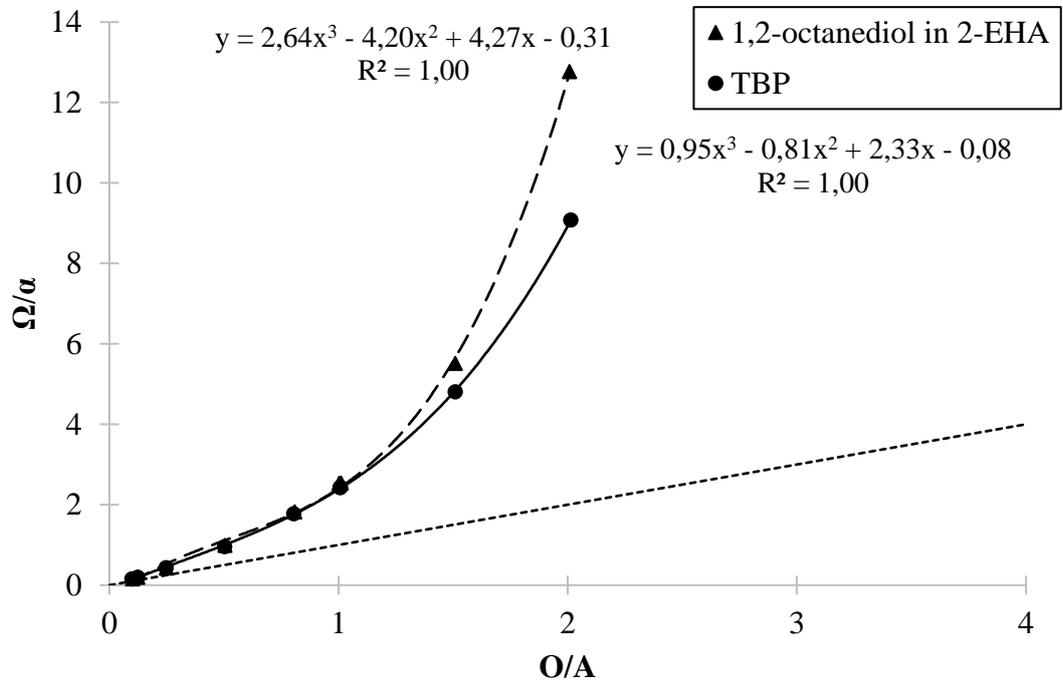
Third order polynomials can be used to interpolate phase ratio from given initial or equilibrium phase ratio (Figs. 14 & 15). The interpolation is decently accurate for at least single contact between fresh extractant and acid solution, when O/A is between 0–4 for Acid 1 and between 0–2 for Acid 2. This enables estimation of the phase volumes in equilibrium for given initial volumes (and vice versa) as total volume of the system can be assumed constant. Phase volume changes depend on amounts of extracted water and H<sub>2</sub>SO<sub>4</sub>, and thus the polynomials are system-specific.

**Table IX** Relative changes in the total liquid volume for the studied systems.

<b>Extractant-acid system</b>	<b><math>\Delta V_{\text{tot}}</math> [%]</b>
TBP + Acid 1	0.01–0.42
TBP + Acid 2	0.15–1.19
6 wt-% 1,2-octanediol in 2-ethylhexanol + Acid 1	0.14–1.99
6 wt-% 1,2-octanediol in 2-ethylhexanol + Acid 2	0.02–1.49



**Figure 14** Changes in phase ratios between initial state and equilibrium during loading of undiluted TBP and 6 wt-% 1,2-octanediol in 2-ethylhexanol with Acid 1. Dashed diagonal line represents a system without change in phase volumes.



**Figure 15** Changes in phase ratios between initial state and equilibrium during loading of undiluted TBP and 6 wt-% 1,2-octanediol in 2-ethylhexanol with Acid 2. Dashed diagonal line represents a system without change in phase volumes.

Acid 1 became totally miscible with undiluted TBP when initial phase ratio was increased to 5:1 and above. The mixture of 1,2-octanediol and 2-ethylhexanol was not tested above  $O/A = 4$ . Acid 2 became miscible with both extractants at  $O/A = 3.5$ .

## **5.4 Loading isotherms**

Loading isotherms were constructed for four extractant-acid pairs by varying  $O/A$  ratios while total volume of the liquid system was kept at  $45 \text{ cm}^3$ . Undiluted TBP and mixture of 1,2-octanediol (6 wt-%) in 2-ethylhexanol were tested for both Acids 1 and 2. Aqueous concentrations were directly determined from the raffinate samples, and concentrations in the organic phases were determined by the backextraction method as described in chapter 4.2.

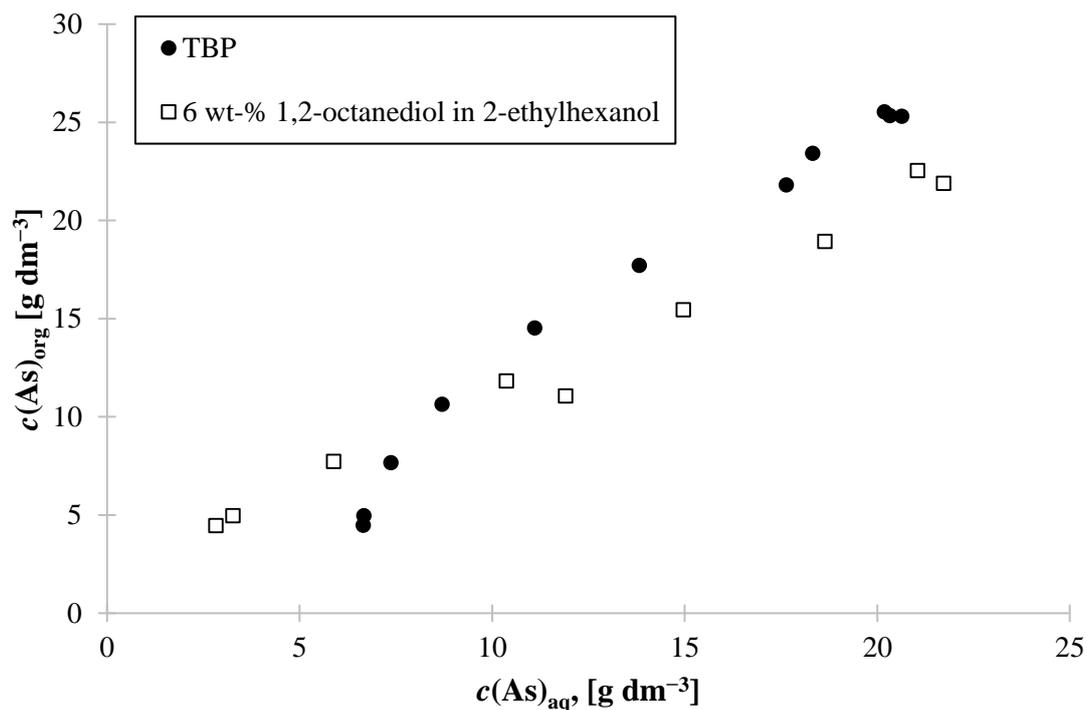
### **5.4.1 Acid 1**

TBP and alcohol mixture (6 wt-% 1,2-octanediol in 2-ethylhexanol) were loaded using  $O/A$  ratios between 0.1–4. Distribution coefficients and percentages extraction for arsenic are listed in Table X. Loading isotherms for arsenic are given in Fig. 16, and isotherms for sulfuric acid in Fig. 17.

**Table X** Percentages of arsenic extracted and distribution coefficients in extractions of Acid 1 which contained  $24.8 \text{ g dm}^{-3}$  of As and  $1015 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .

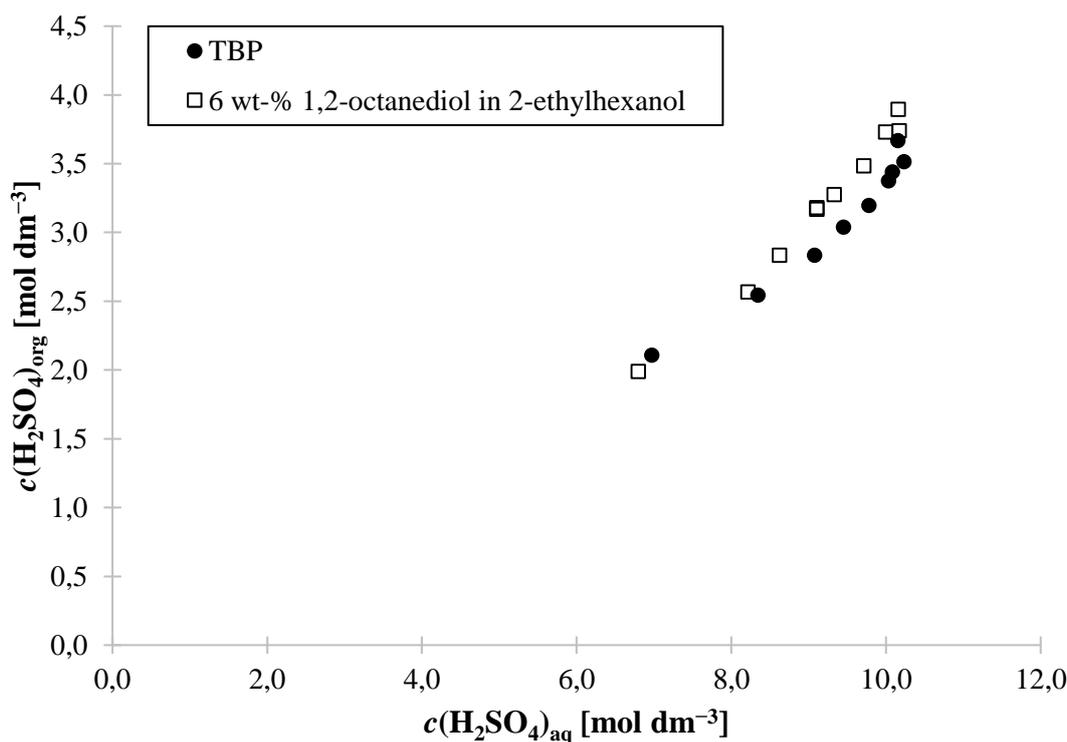
Extractant	O/A	$E(\text{As})$ [%]	$D(\text{As})$
TBP	0.1	13.72	1.07
	0.125	16.74	1.25
	0.2	25.04	1.27
	0.25	28.71	1.28
	0.5	47.41	1.24
	0.8	61.56	1.28
	1	70.90	1.31
	2	78.52	1.22
	3.5	87.02	1.04
1,2-octanediol in 2-ethylhexanol	4	88.87	0.74
	0.1	13.19	1.01
	0.125	17.37	1.07
	0.25	28.97	1.02
	0.5	46.80	1.03
	0.8	52.79	0.93
	1	69.01	1.14
	2	85.89	0.75
	3.5	90.13	0.64
4	91.21	0.76	

The determined isotherm for TBP from extraction of Acid 1 is not nearly as steep as reported by Navarro & Alguacil (1996) for their system containing  $600 \text{ g dm}^{-3}$  of sulfuric acid (Fig. 4). Earlier publications (Navarro & Alguacil, 1996; Demirkiran & Rice, 2002) report that extraction of arsenic is enhancing with increasing sulfuric acid concentration. However, the isotherm of arsenic for TBP in Fig. 16 suggests that there may exist a critical feed concentration for sulfuric acid between  $600\text{--}1000 \text{ g dm}^{-3}$ , above which the slope of extraction isotherm starts lowering with increasing sulfuric acid concentration. Acid 1 is chemically very different from the solution studied by Navarro & Alguacil (1996), and this difference can explain lower loading. See chapter 6 for more detailed explanation. Changes in phase volumes also lower and elevate concentrations in organic and aqueous phases, respectively. Also this effect is pronouncing with increasing acid concentration.



**Figure 16** Loading isotherms for extraction of arsenic from Acid 1 with undiluted TBP and 6 wt-% 1,2-octanediol in 2-ethylhexanol. Acid 1 contained  $24.8 \text{ g dm}^{-3}$  of As and  $1015 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .

Isotherms for TBP and 6 wt-% 1,2-octanediol solution (Fig. 16) are quite similar but phase behavior of TBP was better. The alcohol mixture required significantly longer settling time after equilibration. The times were not accurately recorded but settling of TBP and Acid 1 after equilibration required no more than couple of hours at maximum, after which the phases were clear. 1,2-octanediol and 2-ethylhexanol required at least a day of settling after loading, and severe phase separation problems were encountered during backextraction of the organic samples. The phases had to be separated with a centrifuge after backextraction, as the aqueous phases were still hazy four days after shaking. The phases could be separated after 20 min centrifugation at 4000 rpm.

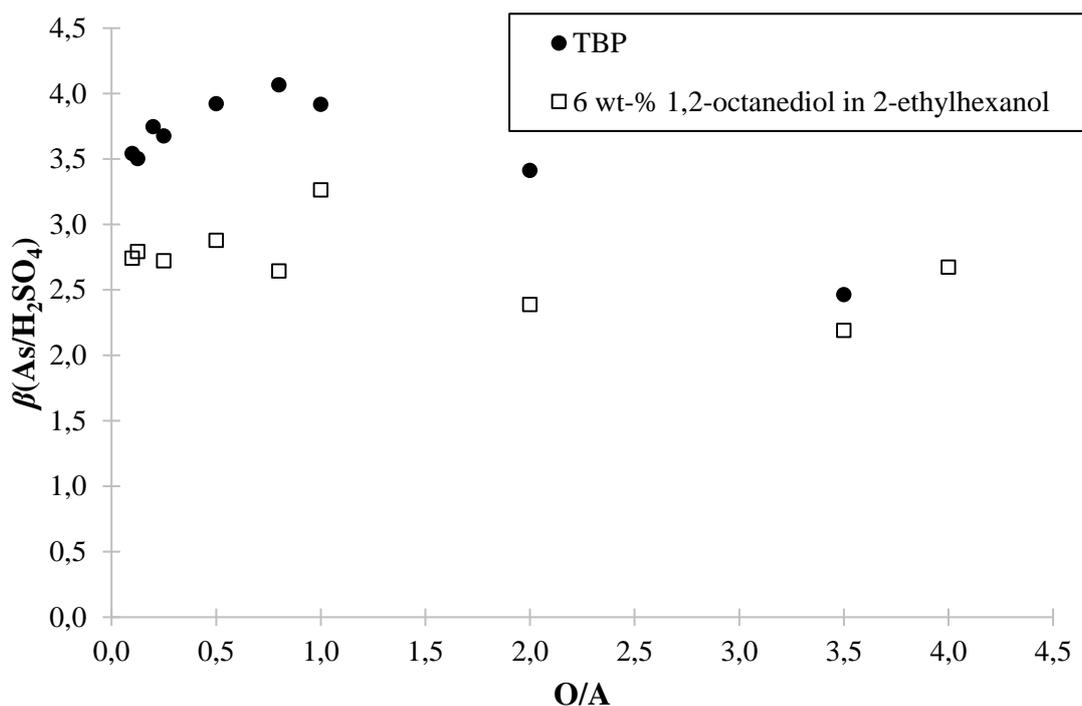


**Figure 17** Loading isotherms of sulfuric acid for undiluted TBP and mixture of 1,2-octanediol and 2-ethylhexanol as the extractants were loaded with Acid 1. Acid 1 contained  $24.8 \text{ g dm}^{-3}$  of As and  $1015 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .

TBP was slightly more selective towards arsenic over sulfuric acid (Fig. 18) than the alcohol mixture. Both extractants exhibited good selectivity over nickel (Table XI, Appendix III). Bismuth was not detected in loaded 1,2-octanediol and 2-ethylhexanol by backextraction but TBP extracted little Bi. Small amount of Sb was extracted by both extractants. Weight of arsenic with respect to total weight of metals in the organic phase ranged between 98.0–99.8 % for TBP, and 97.7–99.5 % for mixture of 1,2-octanediol and 2-ethylhexanol. The corresponding percentage in Acid 1 was initially 91 %.

**Table XI** Selectivity of the extractants during extractions with Acid 1 ( $24.8 \text{ g dm}^{-3}$  of As and  $1015 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ ).  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ . Values larger than 10 rounded to nearest integer.

	O/A	0.1	0.25	0.5	0.8	1	2	4
TBP	$\beta(\text{As}/\text{Bi})$	10	11	11	13	14	20	33
	$\beta(\text{As}/\text{Sb})$	5.15	6.41	6.57	9.05	12	16	15
	$\beta(\text{As}/\text{Ni})$	122	143	168	168	171	190	152
1,2-octanediol in 2-ethylhexanol	$\beta(\text{As}/\text{Sb})$	5.04	6.11	7.63	7	4.86	6.25	9.02
	$\beta(\text{As}/\text{Ni})$	70	169	168	185	140	94	209



**Figure 18** Separation of As from  $\text{H}_2\text{SO}_4$  when the extractants were equilibrated with Acid 1. Acid 1 contained  $24.8 \text{ g dm}^{-3}$  of As and  $1015 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .

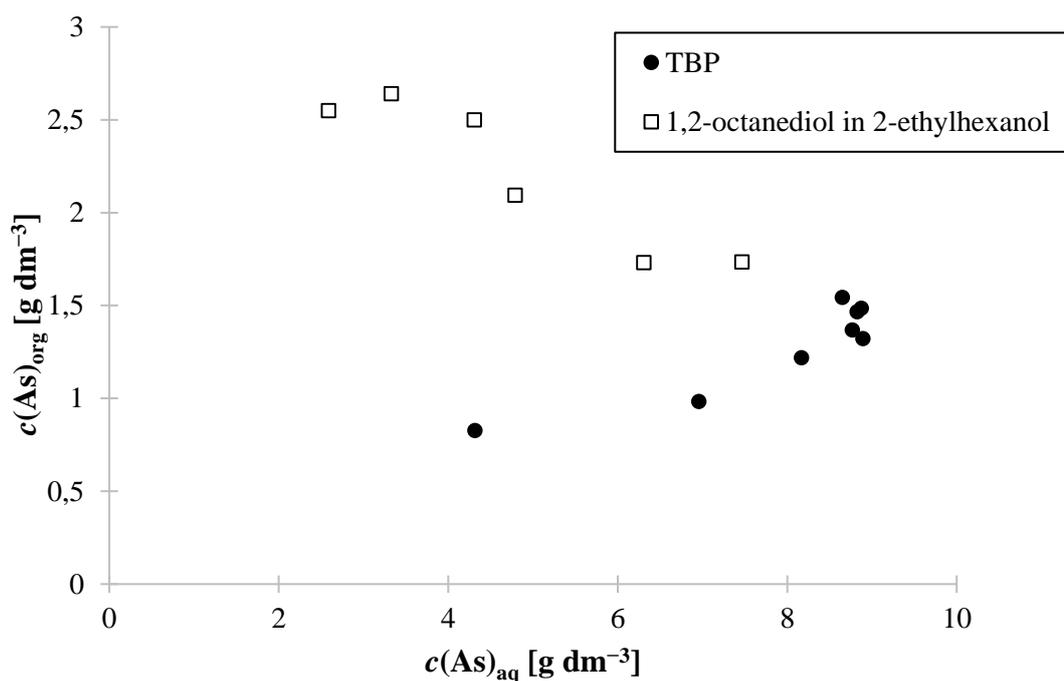
#### 5.4.2 Acid 2

Significantly lower distribution coefficients in organic phases were determined when the extractants were equilibrated with Acid 2 (Table XII, Fig. 19). In Acid 2 arsenic was present mostly as As(III) which explains the low arsenic loading in TBP, as TBP is known to extract mainly As(V).

Although the arsenic concentration is rather low ( $1.7\text{--}2.6 \text{ g dm}^{-3}$ ) also in loaded alcohol mixture, Table XII and Fig. 20 show that the percentage of extraction could be increased up to 81.2 % by increasing O/A to 2. TBP reached its peak at 26 %, which is higher than percentage of As(V) initially present in Acid 2. Extraction of more than initial amount of As(V) may occur due to changes in solution chemistry *i.e.* change in arsenic speciation during extraction. Speciation may shift from  $\text{As}(\text{OH})_2^+$  to  $\text{H}_3\text{AsO}_4$  as sulfuric acid is extracted and acid concentration in the aqueous phase is lowered simultaneously.

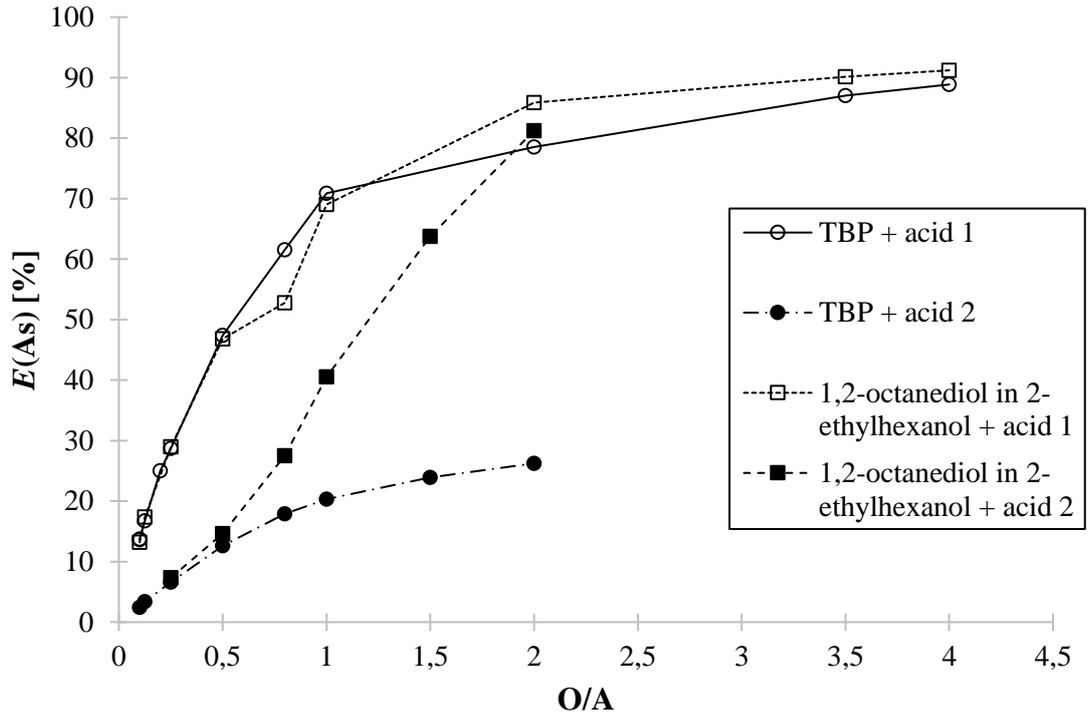
**Table XII** Performance of the tested extractants in equilibration with Acid 2 which contained  $8.6 \text{ g dm}^{-3}$  of As and  $1255 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .

Extractant	O/A	$E(\text{As})$ [%]	$D(\text{As})$
TBP	0.1	2.43	0.16
	0.125	3.38	0.18
	0.25	6.60	0.17
	0.5	12.63	0.17
	0.8	17.90	0.15
	1	20.30	0.15
	1.5	23.94	0.14
	2	26.24	0.19
1,2-octanediol in 2-ethylhexanol	0.25	7.34	0.44
	0.5	14.64	0.44
	0.8	27.53	0.59
	1	40.52	0.74
	1.5	63.78	0.88
	2	81.23	0.79

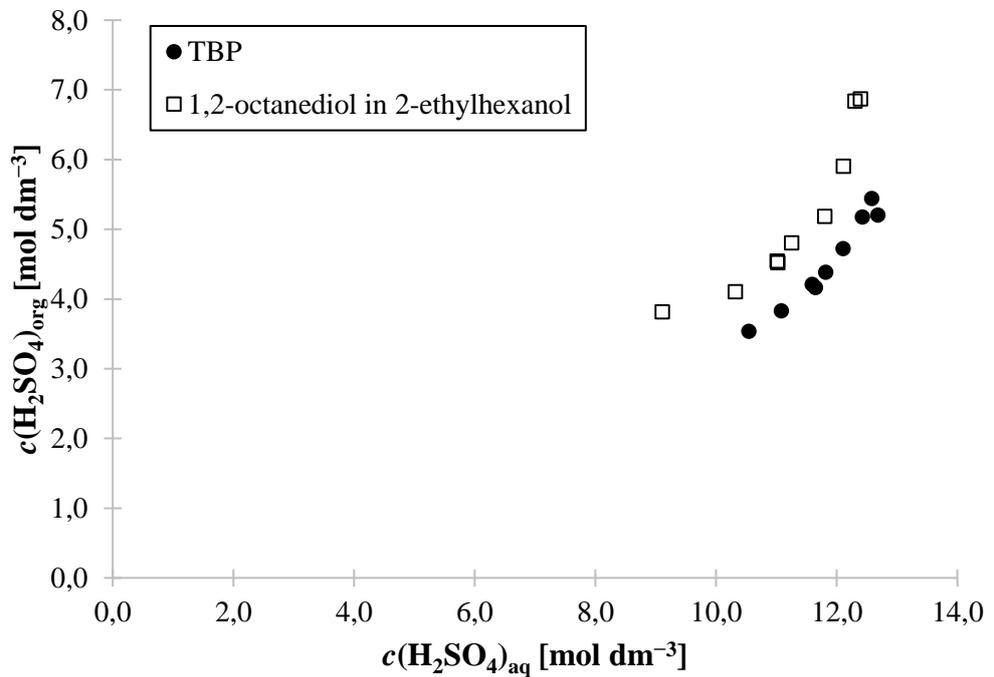


**Figure 19** Loading isotherms for extraction of arsenic from Acid 2 with undiluted TBP and 6 wt-% 1,2-octanediol in 2-ethylhexanol. Acid 2 contained  $8.6 \text{ g dm}^{-3}$  of As and  $1255 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .

The mixture of 1,2-octanediol and 2-ethylhexanol was loaded to higher  $\text{H}_2\text{SO}_4$  concentrations than TBP (Fig. 21). Difference in  $\text{H}_2\text{SO}_4$  extraction results in more intensive expansion of the organic phase (Fig. 15) compared with the systems containing Acid 1 (Fig. 14).



**Figure 20** Percentages of arsenic extracted during the loading experiments.



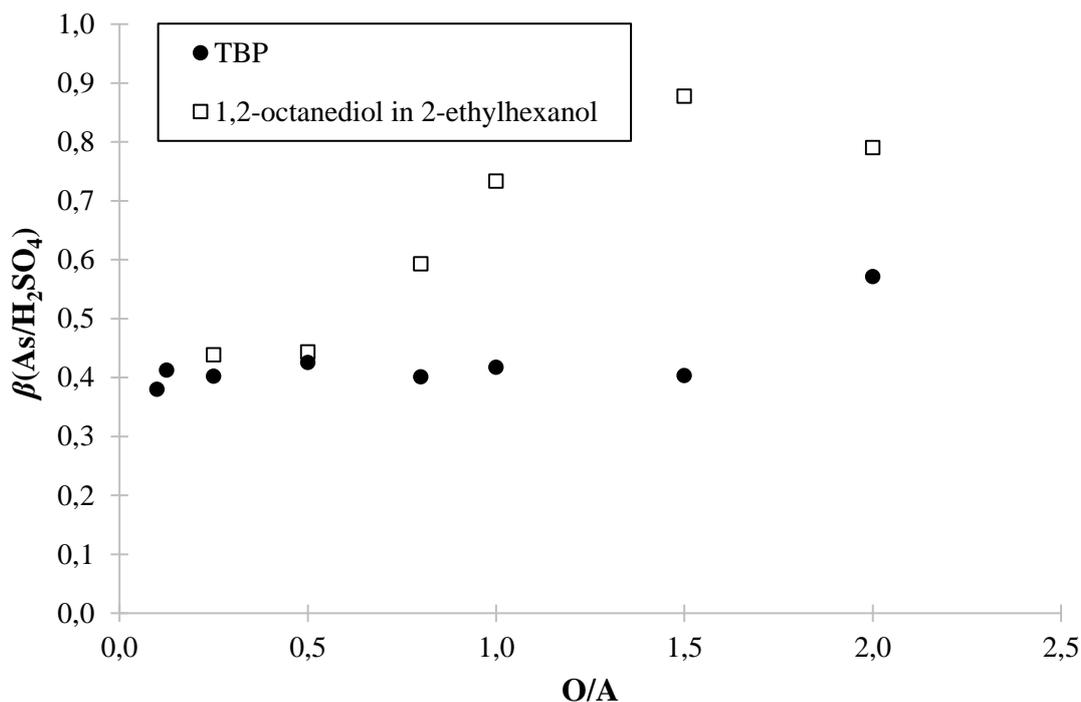
**Figure 21** Loading isotherms of sulfuric acid for undiluted TBP and mixture of 1,2-octanediol and 2-ethylhexanol when the extractants were loaded with Acid 2. Acid 2 contained  $8.6 \text{ g dm}^{-3}$  of As and  $1255 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .

1,2-octanediol solution extracted more  $\text{H}_2\text{SO}_4$ , and separation factors were quite close to 1 with O/A between 1–2 (Fig. 22). Both extractants can be used to separate arsenic and  $\text{H}_2\text{SO}_4$  during loading but with Acid 2 the extractants had better selectivity towards  $\text{H}_2\text{SO}_4$  with all tested phase ratios. According to these results, such equilibrium zones (O/A = 1.5) exist for the alcohol mixture that provide poor separation during loading. However, TBP provided separation with all tested O/A ratios.

Most impurity metals were present in ppm-level concentrations in the organic phase or their concentrations were below quantification limit (Appendix III). Deviations in concentrations led also to deviations in separation factors (Table XIII). Cd and Pb were determined from both loaded extractants by backextraction, and 1,2-octanediol and 2-ethylhexanol extracted also some Cu and Zn. Experiments with higher impurity concentrations would be required for better evaluation. Weight of arsenic with respect to total weight of metals in the organic phase ranged between 87.1–91.8 % for TBP, and 88.7–93.5 % for mixture of 1,2-octanediol and 2-ethylhexanol. Initially the percentage was 74 % in Acid 2.

**Table XIII** Selectivity of the extractants during extractions with Acid 2 ( $8.6 \text{ g dm}^{-3}$  of As and  $1255 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ ).  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ . < LOQ means that the concentration of impurity metal has been below LOQ. Values larger than 10 rounded to nearest integer.

Extractant	O/A	$\beta(\text{As}/\text{Ni})$	$\beta(\text{As}/\text{Cd})$	$\beta(\text{As}/\text{Sb})$	$\beta(\text{As}/\text{Bi})$	$\beta(\text{As}/\text{Cu})$	$\beta(\text{As}/\text{Zn})$
TBP	0.1	10	9.61	0.20	91	275	28
	0.125	11	21	1.10	132	< LOQ	< LOQ
	0.25	6.23	5.73	0.27	145	83	2.41
	0.5	8.01	5.31	0.38	128	1105	67
	0.8	3.38	4.67	0.72	145	< LOQ	6.76
	1	7.92	3.74	1.14	94	58	13
	1.5	3.63	4.35	2.47	190	< LOQ	14
	2	6.81	2.47	< LOQ	199	< LOQ	< LOQ
1,2-octanediol in 2-ethylhexanol	0.25	1.52	2.02	2.69	115	2.57	4.45
	0.5	2.34	3.02	< LOQ	223	7	4.16
	0.8	4.70	3.79	< LOQ	138	3.38	5.80
	1	3.47	3.13	6.22	220	3.03	2.94
	1.5	1.52	5.38	< LOQ	453	5.30	6.70
	2	6.46	5.30	36	1128	5.66	6.51



**Figure 22** Separation of As from  $\text{H}_2\text{SO}_4$  when the extractants were equilibrated with Acid 2. Acid 2 contained  $8.6 \text{ g dm}^{-3}$  of As and  $1255 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .

### 5.5 Scrubbing

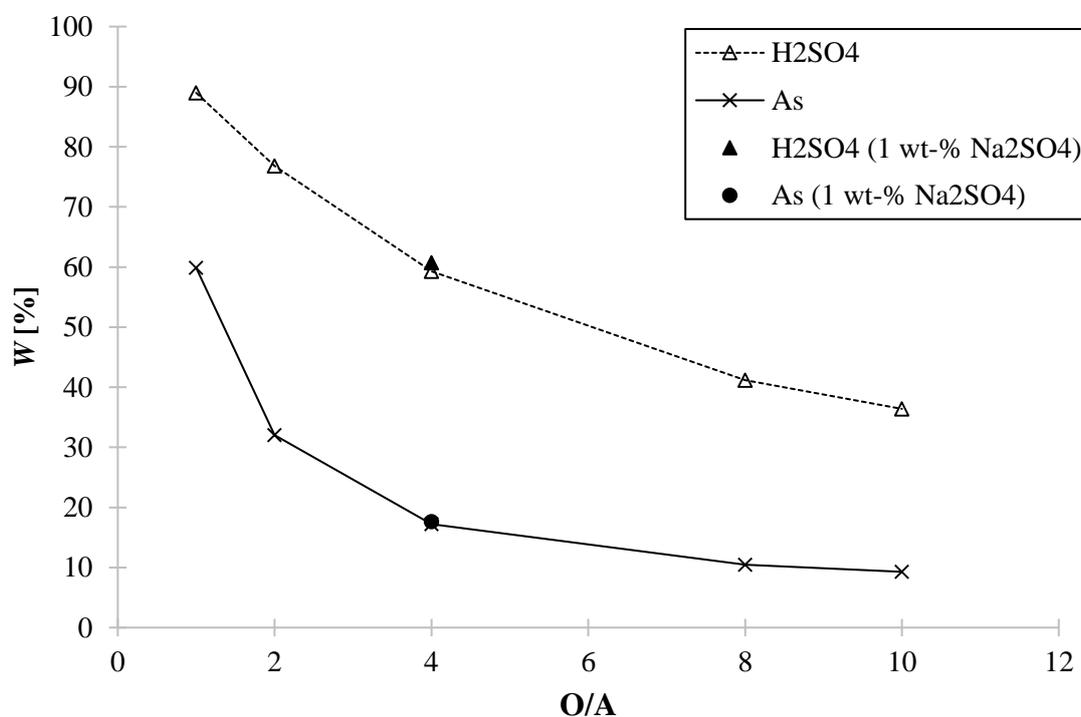
The extractants were loaded with the acids at  $\text{O/A} = 0.1$  before scrubbing. The raffinates were analyzed and percentages backextracted (Figs. 23–26) were calculated from mass balance. Arsenic concentration in the loaded organic phases were determined by backextraction method. Table XIV lists concentrations of arsenic and sulfuric acid in the loaded extractants. It is not known why TBP could be loaded to higher arsenic concentration than predicted by the loading isotherm (Fig. 19), as the equilibration and analyses were performed in the same way during both experiments. The loaded organic solutions were prepared in two batches, and arsenic concentrations in Acid 2-loaded TBP batches were determined to be  $2 \text{ g dm}^{-3}$  and  $2.3 \text{ g dm}^{-3}$  by the backextraction method.

For alcohol mixture and Acid 2, loading concentration corresponding  $\text{O/A} = 0.25$  was used, hence over 100 % of arsenic extracted in Fig. 26. Backextraction was not done from the sample loaded at  $\text{O/A} = 0.1$  because it had converted to dark purple, bitumen-like slurry and it contained precipitate. Mass balance calculation resulted in  $11 \text{ g dm}^{-3}$  concentration of As in the organic phase. Again, mass balance did not take precipitation into account and already small deviations can lead to large errors in such cases where weight and volume of the phase is small.

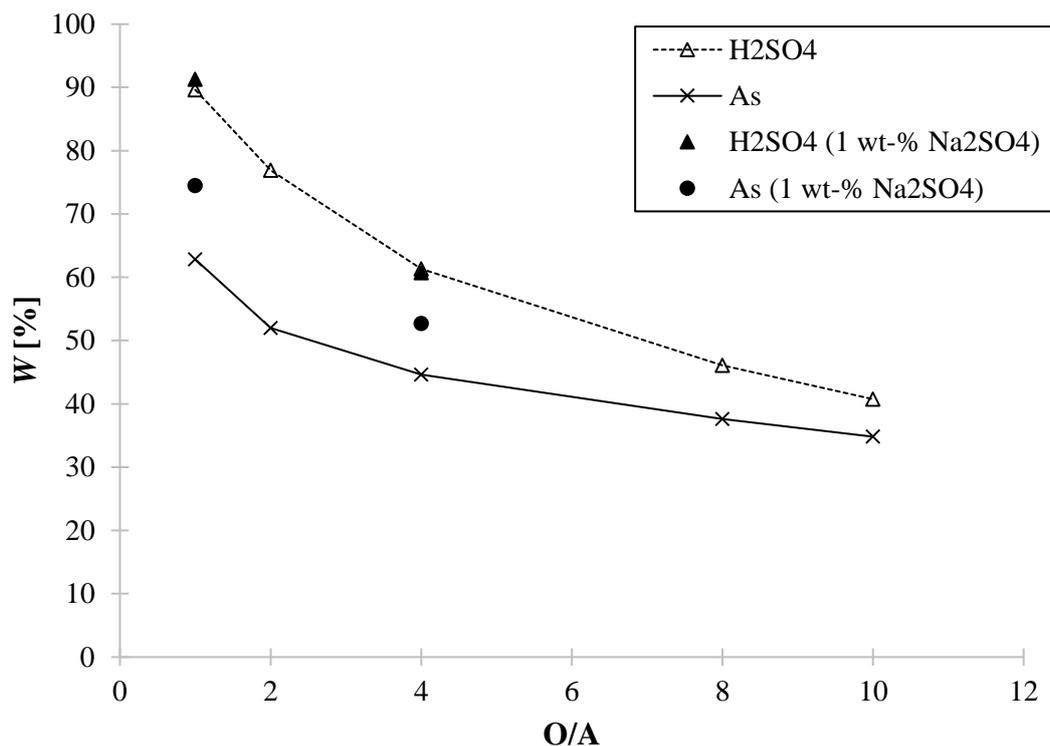
**Table XIV** Concentrations of arsenic and sulfuric acid in the loaded extractants.

Extractant	Acid	$c_0(\text{As})_{\text{org}}$ [g dm <sup>-3</sup> ]	$c(\text{H}_2\text{SO}_4)_{\text{org}}$ [g dm <sup>-3</sup> ]
TBP (97 %)	1	25.3	335
TBP (97 %)	2	2.3	560
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	21.9	367
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	1.7	647

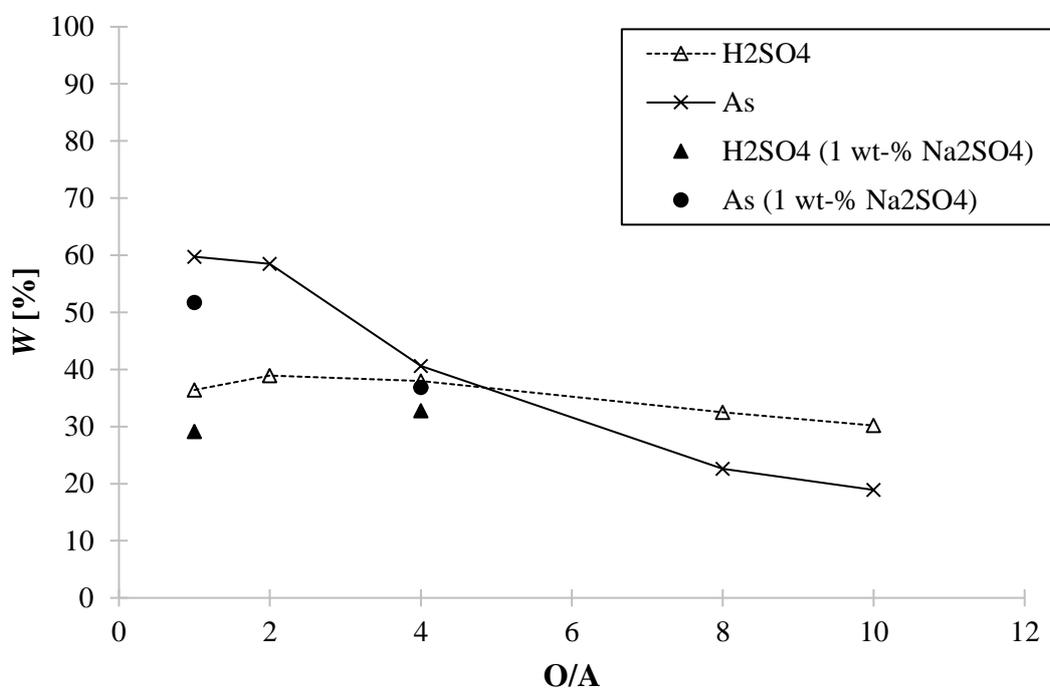
1 wt-% Na<sub>2</sub>SO<sub>4</sub> expectedly enhanced phase separation and it had relatively small effect on separation in Acid 1 systems. O/A = 1 could not be used in scrubbing of Acid 2-loaded alcohol mixture when pure water was used as washing solution. Equilibration resulted in single phase, and no phase separation occurred after centrifugation at 4000 rpm for 10 minutes. Addition of Na<sub>2</sub>SO<sub>4</sub> to washing solution provided two phases also with O/A = 1. The samples taken from scrubbed organic phases later pushed out another liquid phase to the bottom, suggesting that phase separation was not complete during sampling, or there were reactions proceeding (chapter 6). The loaded organic phase was virtually opaque and black-purple in color so it was impossible to visually observe possible water-in-organic emulsification (Fig. 27). The aqueous phases were clear during sampling but contained some precipitate in case of Acid 2.



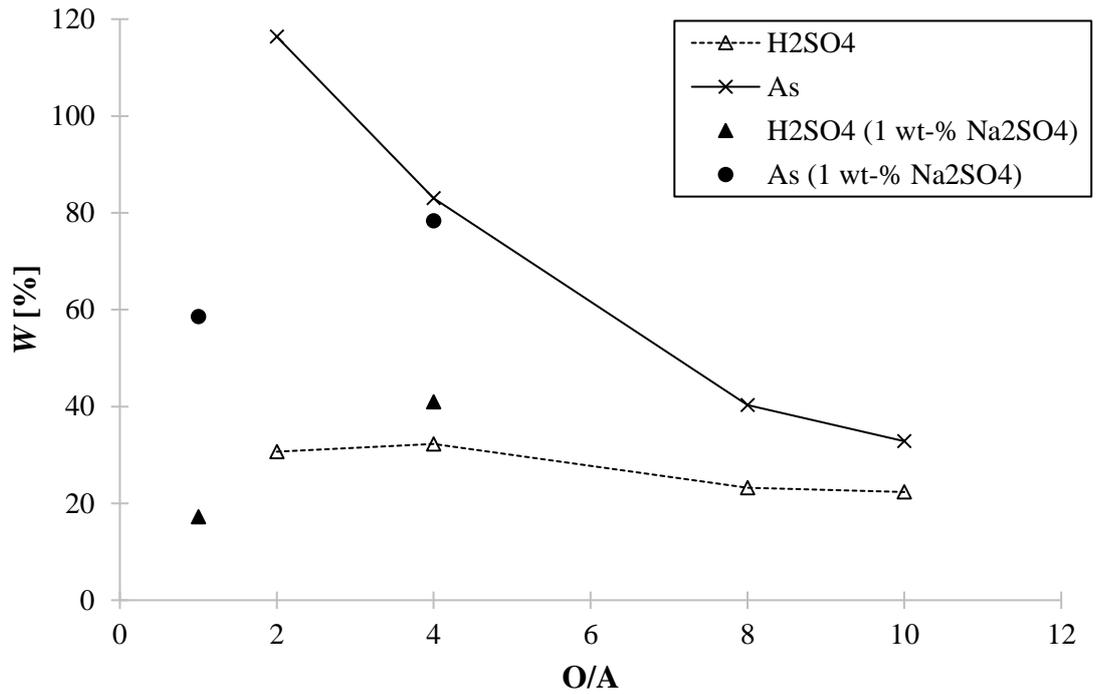
**Figure 23** Percentages backextracted in scrubbing of Acid 1-loaded TBP. Loaded TBP contained 23.5 g dm<sup>-3</sup> of As and 335 g dm<sup>-3</sup> of H<sub>2</sub>SO<sub>4</sub>.  $T = 21 \pm 1$  °C,  $t_{\text{eq}} = 20$  min.



**Figure 24** Percentages backextracted in scrubbing of Acid 2-loaded TBP. Loaded TBP contained  $2.3 \text{ g dm}^{-3}$  of As and  $560 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .



**Figure 25** Percentages backextracted during scrubbing of Acid 1-loaded mixture of 1,2-octanediol and 2-ethylhexanol. Loaded extractant mixture contained  $21.9 \text{ g dm}^{-3}$  of As and  $366 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .



**Figure 26** Percentages backextracted during scrubbing of Acid 2-loaded mixture of 1,2-octanediol and 2-ethylhexanol. Loaded extractant mixture contained  $1.7 \text{ g dm}^{-3}$  of As and  $647 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .



**Figure 27** Phase settling after scrubbing of Acid 2-loaded mixture of 1,2-octanediol and 2-ethylhexanol with pure water.

Results from washing of Acid 1-loaded TBP are relatively similar to those reported by Navarro & Alguacil (1996), and TBP + Acid 1 system had clearly the best overall performance.

Fig. 26 suggests that there is possibility to separate arsenic from Acid 2-loaded solution of 1,2-octanediol and 2-ethylhexanol by water scrubbing. Results in Fig. 26 are however inaccurate as loading concentrations describing another experiment ( $O/A = 0.25$ ) were used.

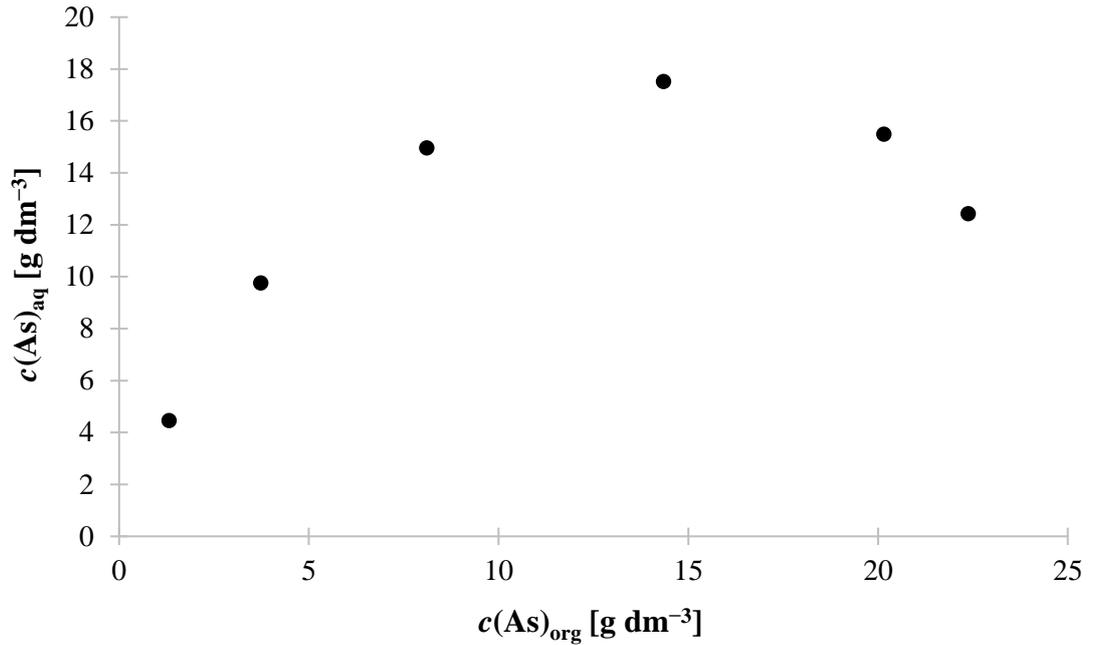
Phase behavior of the systems containing 1,2-octanediol and 2-ethylhexanol was unpredictable and it certainly does not allow efficient and smooth industrial operation under the tested conditions. Elevating temperature or switching the alcohol to another with longer aliphatic chain could enhance phase behavior and separation.

## 5.6 Stripping

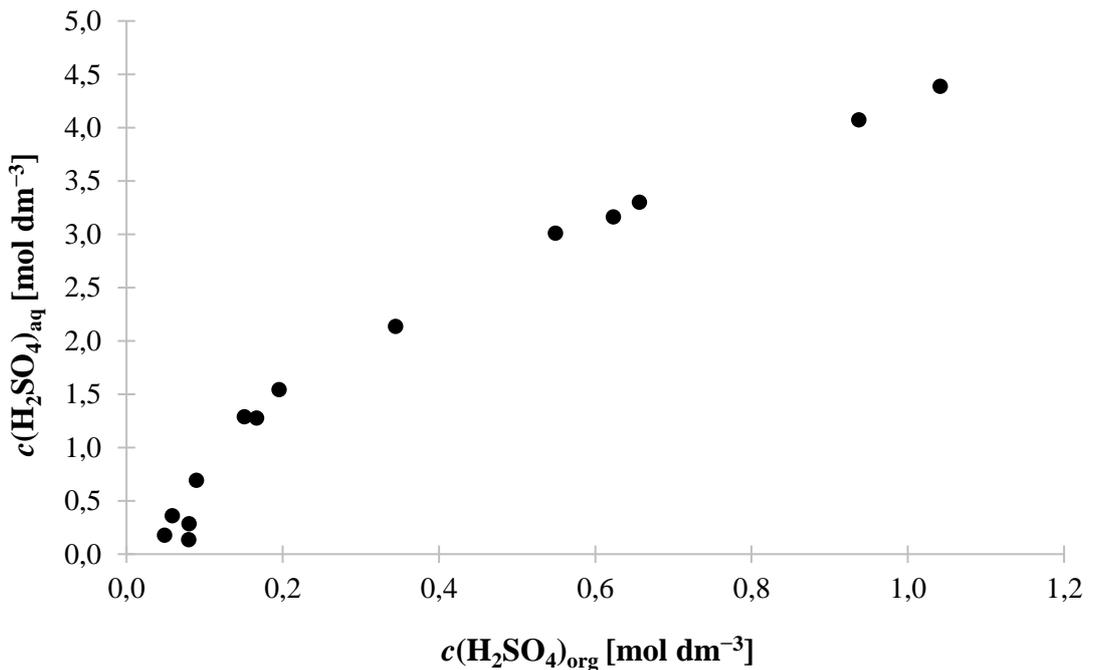
TBP was prepared for stripping by first equilibrating undiluted TBP (97 %) with Acid 1 using  $O/A = 0.1$ , and second by scrubbing the loaded TBP with pure water using  $O/A = 4$ . TBP containing  $23.5 \text{ g dm}^{-3}$  of As and  $151 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$  was obtained by the procedure. Performance indicating quantities for stripping are listed in Table XV, and Figs. 28 & 29 show the corresponding stripping isotherms.

**Table XV** Stripping coefficients and separation factors in stripping of Acid 1-loaded TBP. TBP contained initially  $23.5 \text{ g dm}^{-3}$  of As and  $151 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .

$A/O$	$D'(\text{As})$	$D'(\text{H}_2\text{SO}_4)$	$\beta(\text{As}/\text{H}_2\text{SO}_4)$
5	3.38	3.57	1.06
2	2.61	7.74	2.96
1	1.85	7.67	4.15
0.5	1.22	6.21	5.08
0.2	0.77	5.03	6.54
0.1	0.56	4.34	7.83



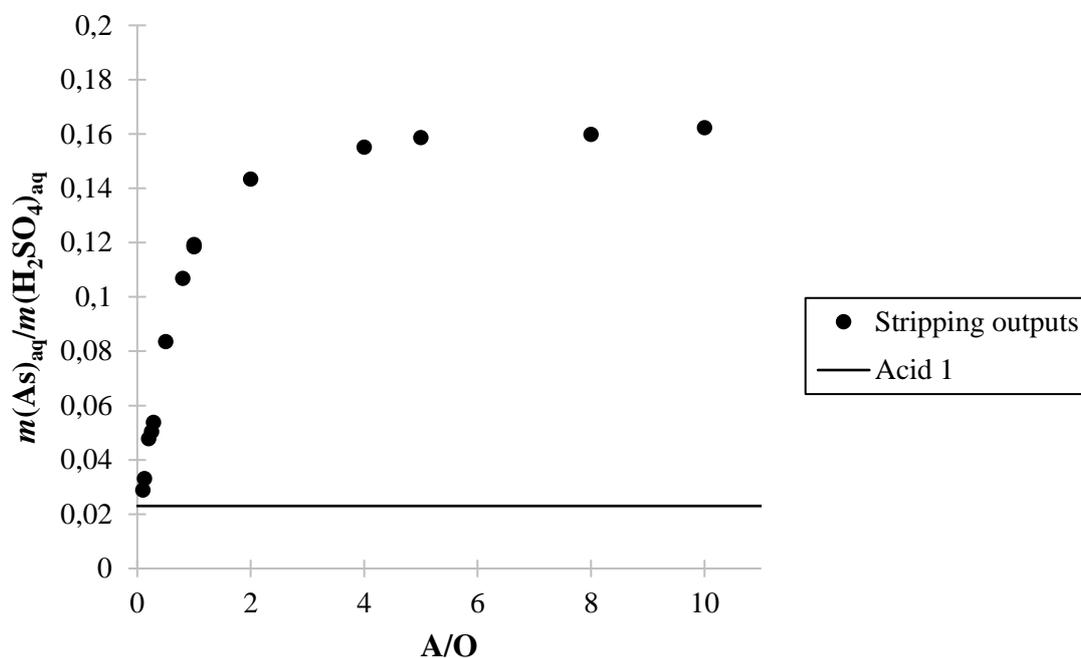
**Figure 28** Isotherm for stripping of As with pure water from Acid 1-loaded TBP which contained  $23.5 \text{ g dm}^{-3}$  of As and  $151 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .



**Figure 29** Isotherm for stripping of  $\text{H}_2\text{SO}_4$  from Acid 1-loaded TBP which contained  $23.5 \text{ g dm}^{-3}$  of As and  $5.8 \text{ mol dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .

The highest concentration of arsenic among the stripping raffinate was measured from strip produced by  $A/O = 0.5$ . Lowering  $A/O$  ratio further caused concentration of arsenic to drop in the stripping raffinate due to simultaneous change in equilibrium of sulfuric acid. Even if the stripping

raffinates have lower concentration of arsenic compared with the input Acid 1 ( $23.3 \text{ g dm}^{-3}$ ),  $m(\text{As})/m(\text{H}_2\text{SO}_4)$  ratio is higher for all stripping raffinates (Fig. 30).



**Figure 30** Ratio of As and  $\text{H}_2\text{SO}_4$  in the stripping raffinates compared with Acid 1.

Stripping with pure water at  $A/O = 2$  backextracted approximately 85 % of arsenic from loaded TBP. Concentrations of Ni and Cu were below limit of detection (LOD) in all stripping raffinates. Concentrations of all quantified impurity metals were in ppm-level (Table XVI), Sb and Hg being relatively the most abundant.

**Table XVI** Concentrations of impurity metals in stripping raffinates.

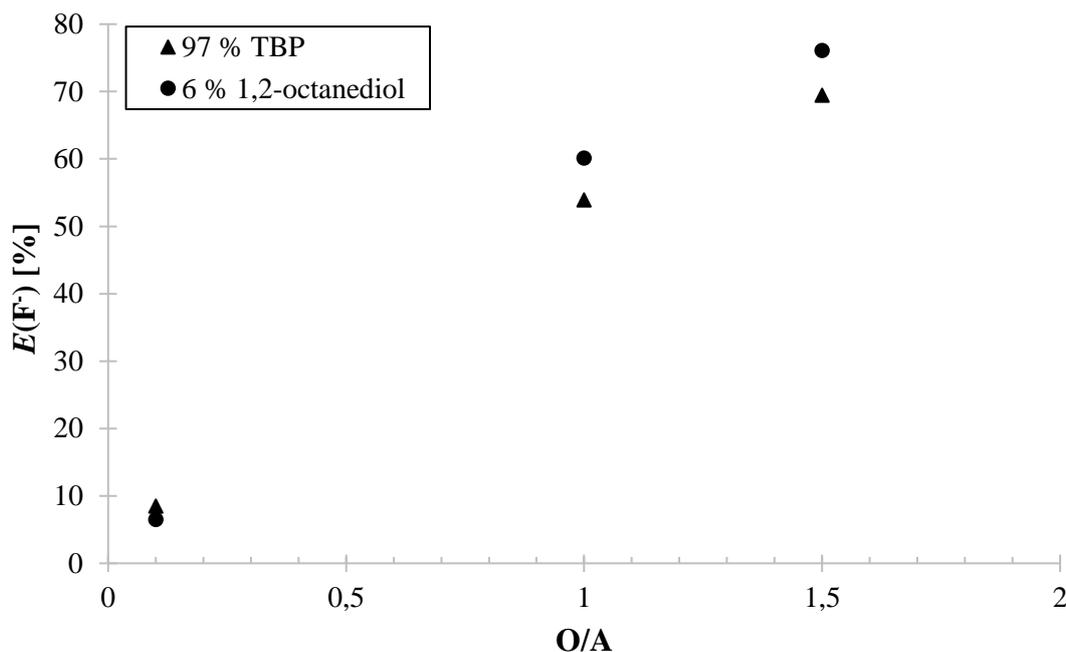
A/O	$c(\text{Zn})$ [mg dm <sup>-3</sup> ]	$c(\text{Cd})$ [mg dm <sup>-3</sup> ]	$c(\text{Sb})$ [mg dm <sup>-3</sup> ]	$c(\text{Hg})$ [mg dm <sup>-3</sup> ]	$c(\text{Pb})$ [mg dm <sup>-3</sup> ]	$c(\text{Bi})$ [mg dm <sup>-3</sup> ]
10	0.49	0.01	0.52	5.36	0.05	0.14
8	< LOQ	0.02	0.49	4.92	0.06	0.13
5	0.42	0.02	0.84	4.89	0.04	0.13
4	< LOQ	< LOQ	1.24	9.51	0.09	0.23
2	0.23	0.02	2.40	8.39	0.10	0.21
1	0.06	0.01	4.17	7.01	0.05	0.22
0.8	0.04	< LOQ	5.01	6.58	0.06	0.19
0.5	0.32	0.02	7.33	6.14	0.06	0.27
0.285	0.06	0.01	10.45	5.75	0.04	0.36
0.25	0.76	< LOQ	12.37	5.62	0.05	0.74
0.2	0.19	0.01	11.78	5.40	0.04	0.37
0.125	0.99	< LOQ	18.75	5.21	0.06	0.73
0.1	0.49	0.01	21.35	9.69	0.12	0.87

### 5.7 Description of precipitate

The precipitate from extraction of acid 2 with 1,2-octanediol and 2-ethylhexanol probably contained arsenic sulfide, arsenic trioxide and other inorganic salts of arsenic, since arsenic was the only element to exceed limit of detection in the ICP-MS analysis. Overnight storage in an oven at 50 °C did not dry the sample because of sulfuric acid leftover but this did not cause large error to the qualitative result as the impurity metals were not detected from the wet digested sample by ICP-MS.

### 5.8 Fluoride concentrations in Acid 2 raffinates

It is known that TBP extracts several acids, and possible extraction of hydrofluoric acid, HF, was evaluated for both extractants by analyzing the Acid 2 raffinates and calculating fluorine concentrations in the organic phase from mass balance. 2 mg dm<sup>-3</sup> of F<sup>-</sup> in Acid 1 was considered negligible, and therefore only Acid 2 raffinates were analyzed. Figure 31 shows that fluorine is extracted and/or precipitated.

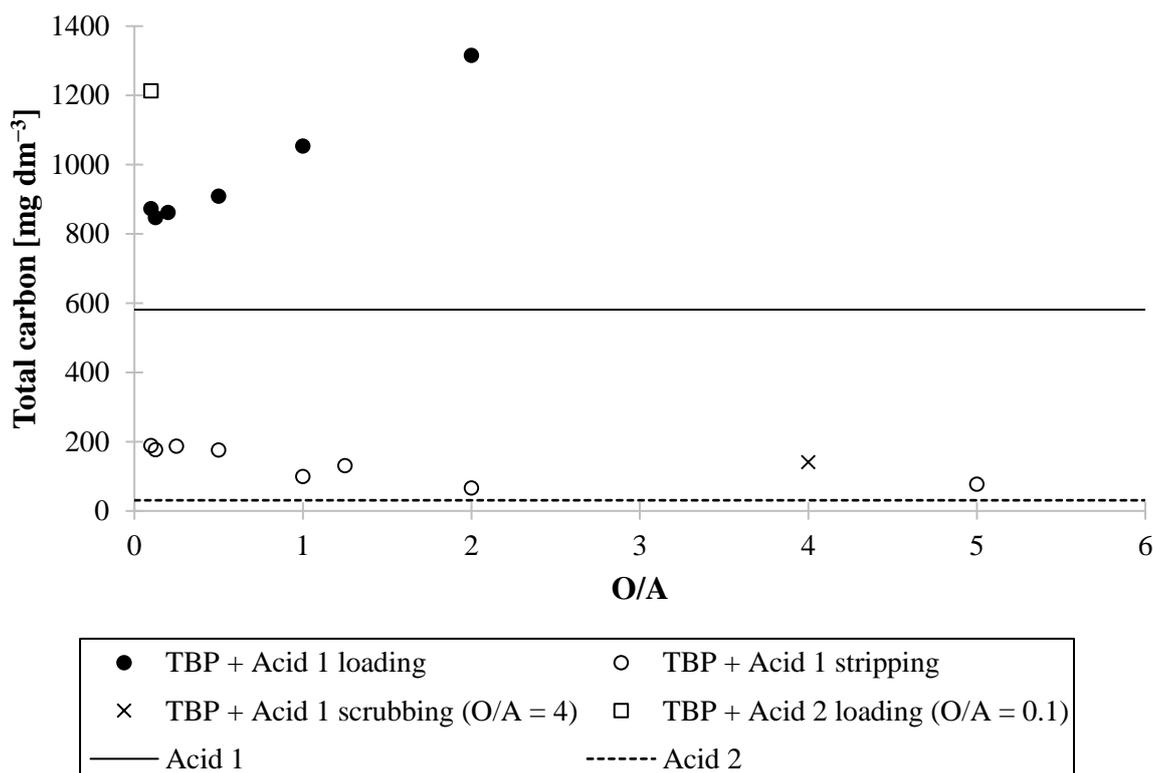


**Figure 31** Removal of fluoride from the aqueous phase in extraction of Acid 2. Acid 2 contained initially  $284.8 \text{ mg dm}^{-3}$  of  $\text{F}^-$  and  $1255 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ . Experimental conditions:  $T = 20 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ .

### 5.9 Total carbon in the raffinates

Total carbon measurements showed that organic molecules have dissolved into the raffinates during extraction (Fig. 32). Scrubbing and stripping raffinates contained carbon, although initially there was no carbon in the aqueous phases as pure water was used for scrubbing and stripping. The organic molecules in raffinates contained probably decomposition products of TBP, impurities in TBP and in case of Acid 1, unknown organic molecules from the feed acid.

Amount of organic matter in the aqueous phases is probably negligible in terms of sizing a solvent extraction process. The organic molecules may, however, cause problems during later processing of the raffinates. Further studies are suggested for determining the composition of organic matter in the raffinates. It is also recommended to study the performance of TBP - or any other chosen extractant - after several contacts with highly concentrated sulfuric acid.

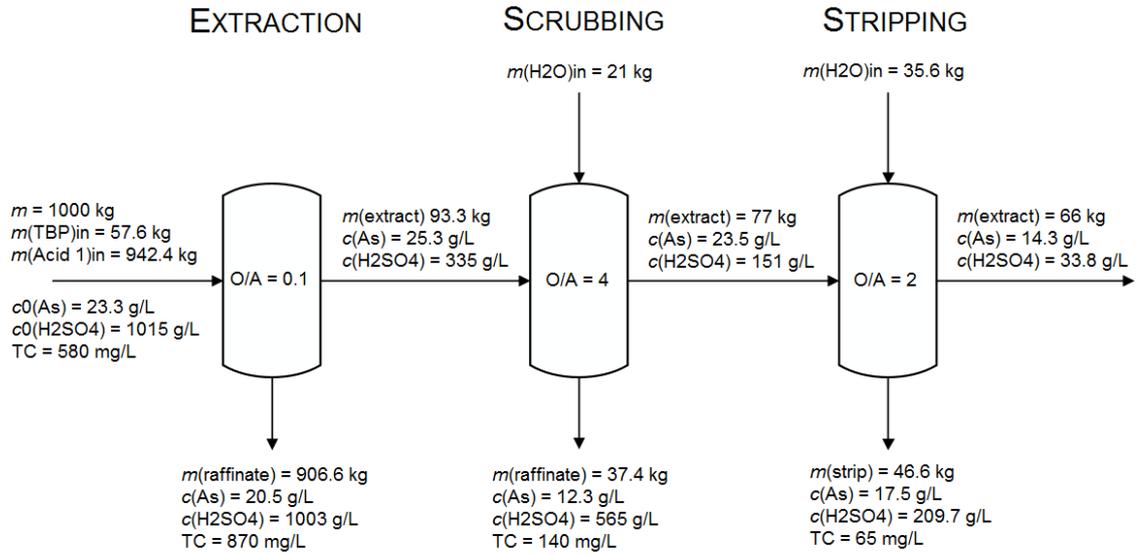


**Figure 32** Total carbon in Acids 1 and 2, and the raffinates.

Total carbon was not measured from the raffinates that were produced during extractions with 1,2-octanediol and 2-ethylhexanol. The alcohols have some mutual solubility with water, for why it would be better to select a diol with longer hydrocarbon chain for testing. To minimize water solubility and for better phase separation, another diluent is also recommended.

### 5.10 Single-pass flowsheet

Mass-balance calculations were carried out for extraction of arsenic with TBP from Acid 1 by single-pass extraction ( $O/A = 0.1$ ), scrubbing ( $O/A = 4$ ) and stripping ( $O/A = 2$ ). This system was chosen due to its better performance over other tested systems. Figure 33 indicates that good separation can be achieved.  $m(\text{As})/m(\text{H}_2\text{SO}_4)$  ratio is 0.023 in Acid 1 and 0.083 in the stripping raffinate (Fig. 30). Extraction-scrubbing-stripping cycle with chosen phase ratios provides a stream which is impoverished from sulfuric acid but still quite rich in arsenic. Scrubbing of sulfuric acid using high  $O/A$  ratio is particularly recommended. Overall yield of arsenic is poor, only 5.17 % but efficiency of all process steps could be further improved by utilizing counter- or crosscurrent equilibrations and by optimizing phase ratios. Figure 33 does not represent a process but it is rather an illustration of the experimental results.



**Figure 33** Material balance over single-pass separation of arsenic and  $\text{H}_2\text{SO}_4$  from Acid 1. TC = Total carbon.

## 6 CONCLUSIONS

Extraction of arsenic from two industrial sulfuric acid solutions was studied. Equilibrium data was collected from four extractant-acid systems, and performance of applicable extractants was compared. The use of aliphatic diluent with the studied organophosphorus extractants resulted in formation of a third liquid phase when sulfuric acid concentration was  $1255 \text{ g dm}^{-3}$  in the feed acid. The extraction systems remained in two liquid phases when extractions were performed with undiluted TBP or binary mixtures of 1,2-octanediol (2–20 wt-%) and 2-ethylhexanol. TBP and mixture of 6 wt-% 1,2-octanediol in ethylhexanol showed similar loading performance during extraction of Acid 1. Since Acid 1 contained mostly As(V), TBP could be loaded up to  $25.3 \text{ g dm}^{-3}$  of As, and alcohol mixture respectively to  $22 \text{ g dm}^{-3}$ . TBP exhibited significantly better separation of As and  $\text{H}_2\text{SO}_4$  during scrubbing of Acid 1-loaded TBP, and better phase behavior.

Acid 2 systems contained mostly trivalent arsenic, and maximum of 26 % of total arsenic could be extracted with TBP, whereas the alcohol mixture could extract 81 %. Peak concentrations of arsenic were  $1.7 \text{ g dm}^{-3}$  in TBP and  $2.6 \text{ g dm}^{-3}$  in mixture of 1,2-octanediol and 2-ethylhexanol. TBP can be used to extract sulfuric acid from Acid 2 leaving most arsenic in the raffinate. It is another question, whether this would be economically feasible.

The observations in extractions of Acid 1 and 2 can be explained by the predominance area diagram (Fig. 1). It can be seen that  $\text{H}_3\text{AsO}_4$  is predominant in oxidizing solutions with high sulfuric acid concentrations, and the speciation borderline is descending towards lower acidity. Therefore, increasing sulfuric acid concentration in the aqueous phase probably increases the proportion of As(V) in solution until the borderline is approached again. Increasing concentration of  $\text{H}_2\text{SO}_4$  in the solution without increasing redox-potential probably causes speciation to shift from As(V) to As(III). With Acid 2, reverse shift likely explains the observed increase in extraction of arsenic with TBP using higher O/A ratios.

Severe phase separation problems were encountered during scrubbing of Acid 2-loaded 1,2-octanediol and 2-ethylhexanol, and centrifugation was required to separate the phases. Alcohols may undergo several reactions in sulfuric acid media. Primary alcohols form ethers (condensation), and primary alcohols can also react with any carboxylic acid present to form esters (Fischer esterification). Carboxylic acids required for esterification can be produced from primary alcohols by oxidation. Oxidation of a secondary alcohol yields ketones. It was not evaluated whether solutions such as Acid 1 or Acid 2 would be oxidizing enough to initiate these mechanisms. The mentioned

reaction products may also act as extractants. Further research on stability and performance of alcohols with preferably longer hydrocarbon chains is required to answer this question. Research on effects of temperature and diluent choices would also be useful.

Precipitation was observed in all extraction experiments. Precipitate from extraction of the less pure Acid 2 was analyzed and arsenic was the only element that could be quantified from it. The precipitate contained probably arsenic sulfides,  $\text{As}_2\text{O}_3$  and/or other inorganic metal compounds. Solubilities of these compounds are likely exceeded as sulfuric acid and water is extracted to the organic phase, leading to decrease in aqueous phase volume and acidity. Precipitation may disturb extraction processes and tolerances should be evaluated by continuous test runs in industrial type reactors.

The traditional flowsheet – in which TBP is loaded near to saturation, scrubbed with water at relatively high O/A ratio and then stripped – is applicable for TBP and Acid 1 system. Single extraction (O/A = 0.1), scrubbing (O/A = 4) and stripping (O/A = 2) provided a strip solution with  $17.5 \text{ g dm}^{-3}$  of As and  $209 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ . The acidity in this stream and scrubbing raffinate are similar to those solutions that have been used in feed solutions of many published experiments. There are plenty of options to treat the resulting aqueous streams from scrubbing and stripping stages. For these solutions, also diluted organophosphorus extractants could be used to further enrich and separate arsenic. Changes in arsenic and  $\text{H}_2\text{SO}_4$  concentrations in the aqueous phase are relatively little during single loading. A raffinate with  $20.5 \text{ g dm}^{-3}$  of arsenic and  $1000 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$  was produced. Although yield of arsenic is low and only small fraction of Acid 1 is treated in the given illustration (Fig. 33), a flowsheet utilizing optimized separation cascades and recycle streams could provide significant improvement to overall recovery. Kinetics and phase separations are, however, relatively fast.

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**APPENDIX I: Standard deviations for measured concentrations in the feed acids**

<b>Element/compound</b>	<b>Acid 1</b>	<b>Acid 2</b>
Ni	0.08 g dm <sup>-3</sup>	6.45 mg dm <sup>-3</sup>
Cu	2.21 mg dm <sup>-3</sup>	14.41 mg dm <sup>-3</sup>
Zn	1.24 mg dm <sup>-3</sup>	26.15 mg dm <sup>-3</sup>
As	0.87 g dm <sup>-3</sup>	0.27 g dm <sup>-3</sup>
Cd	0.04 mg dm <sup>-3</sup>	31.99 mg dm <sup>-3</sup>
Sb	5.70 mg dm <sup>-3</sup>	1.86 mg dm <sup>-3</sup>
Hg	4.11 mg dm <sup>-3</sup>	2.18 mg dm <sup>-3</sup>
Pb	0.12 mg dm <sup>-3</sup>	0.92 mg dm <sup>-3</sup>
Bi	8.68 mg dm <sup>-3</sup>	33.23 mg dm <sup>-3</sup>
H <sub>2</sub> SO <sub>4</sub>	0.23 wt-%	0.36 wt-%

**APPENDIX II: Densities of the phases and phase ratios**

Densities of extractant solutions at 23 °C.

<b>Extractant</b>	<b>Diluent</b>	<b>Extractant concentration [wt-%]</b>	<b><math>\rho</math> [g cm<sup>-3</sup>]</b>
TBP (97 %)	Exxsol D80	11.89	0.819
TBP (97 %)	Exxsol D80	17.48	0.828
TBP (97 %)	Exxsol D80	22.49	0.835
TBP (97 %)	Exxsol D80	27.89	0.844
TBP (97 %)	Exxsol D80	33.10	0.852
TBP (97 %)	Exxsol D80	43.03	0.869
TBP (97 %)	Exxsol D80	52.95	0.886
TBP (97 %)	Exxsol D80	62.31	0.903
TBP (97 %)	Exxsol D80	71.52	0.920
TBP (97 %)	Exxsol D80	80.38	0.939
TBP (97 %)	None	97.00	0.979* (lit.)
1,2-octanediol (98 %)	2-ethylhexanol (99 %)	2.00	0.8326
1,2-octanediol (98 %)	2-ethylhexanol (99 %)	4.02	0.834
1,2-octanediol (98 %)	2-ethylhexanol (99 %)	6.00	0.836
1,2-octanediol (98 %)	2-ethylhexanol (99 %)	8.00	0.8377
1,2-octanediol (98 %)	2-ethylhexanol (99 %)	9.98	0.8354
1,2-octanediol (98 %)	2-ethylhexanol (99 %)	15.03	0.8439
1,2-octanediol (98 %)	2-ethylhexanol (99 %)	20.07	0.8478
Cyanex 923	Exxsol D80	10.83	0.8105
Cyanex 923	Exxsol D80	16.23	0.8144
Cyanex 923	Exxsol D80	21.04	0.817
Cyanex 923	Exxsol D80	26.84	0.8226
Cyanex 923	Exxsol D80	31.80	0.8264
Cyanex 923	Exxsol D80	42.19	0.8345
Cyanex 923	Exxsol D80	52.84	0.8428
Cyanex 923	Exxsol D80	62.16	0.8505
Cyanex 923	Exxsol D80	71.99	0.8586
Cyanex 923	Exxsol D80	81.51	0.8666
Cyanex 923	None	mixture	0.877** (lit.)

\* at 20 °C; \*\* at 25 °C

Equilibrium phase densities and ratios from loading experiments.

Extractant	Acid	O/A	$\Omega/\alpha$	$\rho(\text{raffinate})$ [g cm <sup>-3</sup> ]	$\rho(\text{extract})$ [g cm <sup>-3</sup> ]
TBP (97 %)	1	0.10	0.14	1.5844	1.1751
TBP (97 %)	1	0.12	0.17	1.5833	1.1764
TBP (97 %)	1	0.20	0.28	1.5769	1.1733
TBP (97 %)	1	0.25	0.35	1.5745	1.171
TBP (97 %)	1	0.50	0.79	1.5595	1.1597
TBP (97 %)	1	0.80	1.38	1.5428	1.1516
TBP (97 %)	1	1.28	2.63	1.5324	1.1458
TBP (97 %)	1	2.00	5.41	1.4885	1.1248
TBP (97 %)	1	3.51	24.99	<i>1.4055</i>	1.101
TBP (97 %)	1	4.01	46.12	<i>1.3792</i>	1.0937
TBP (97 %)	2	0.10	0.16	1.684	1.2557
TBP (97 %)	2	0.12	0.20	1.6825	1.252
TBP (97 %)	2	0.25	0.44	1.6739	1.2408
TBP (97 %)	2	0.50	0.96	1.6606	1.2231
TBP (97 %)	2	0.81	1.78	1.6446	1.2078
TBP (97 %)	2	1.01	2.44	1.6342	1.1983
TBP (97 %)	2	1.01	2.43	1.6342	1.1983
TBP (97 %)	2	1.51	4.81	1.6106	1.1807
TBP (97 %)	2	2.01	9.08	1.5878	1.1669
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	0.10	0.15	1.575	1.0816
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	0.13	0.19	1.5792	1.0777
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	0.25	0.40	1.5691	1.0722
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	0.50	0.88	1.5514	1.0552
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	0.80	1.57	1.5321	1.039
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	1.00	2.09	1.5197	1.0412
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	1.00	2.07	1.5197	1.0412
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	1.50	3.69	1.4926	1.0144
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	2.01	5.88	1.4764	1.0022
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	3.53	15.43	1.3452	0.9779
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	4.04	20.92	<i>1.3236</i>	0.9683
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	0.10	0.16	1.6795	1.1888
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	0.12	0.20	1.6775	1.1863
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	0.25	0.43	1.6664	1.1742
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	0.51	0.99	1.6473	1.1551
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	0.81	1.82	1.6238	1.1361
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	1.00	2.53	1.6113	1.1183
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	1.01	2.54	1.6113	1.1183
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	1.51	5.51	1.5837	1.089
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	2.01	12.77	1.5589	1.0684

*Extrapolated values in italic print.*

Equilibrium phase densities and ratios from water-scrubbing experiments.

Extractant	Acid	O/A	$\Omega/\alpha$	$\rho(\text{raffinate})$ [g cm <sup>-3</sup> ]	$\rho(\text{extract})$ [g cm <sup>-3</sup> ]
TBP (97 %)	1	0.98	0.72	1.1672	1.0126
TBP (97 %)	1	1.88	1.34	1.246	1.0467
TBP (97 %)	1	3.77	2.54	1.3349	1.0835
TBP (97 %)	1	7.62	4.85	1.4175	1.1154
TBP (97 %)	1	9.45	5.86	1.4401	1.1229
TBP (97 %)	2	0.97	0.61	1.2272	1.0246
TBP (97 %)	2	1.97	1.15	1.3403	1.0714
TBP (97 %)	2	4.02	2.10	1.4568	1.1174
TBP (97 %)	2	7.92	3.61	1.5479	1.1581
TBP (97 %)	2	9.88	4.35	1.5718	1.1694
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	0.96	1.97	1.1377	1.0107
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	1.84	2.54	1.2265	1.0025
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	3.77	3.68	1.3344	1.0063
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	7.54	5.47	1.4194	1.0203
6 wt-% 1,2-octanediol in 2-ethylhexanol	1	9.23	6.25	1.4408	1.0272
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	1.93	3.13	1.318	1.0425
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	3.91	3.69	1.4347	1.0287
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	7.81	5.35	1.53	1.082
6 wt-% 1,2-octanediol in 2-ethylhexanol	2	9.87	6.44	1.5539	1.0985

Equilibrium phase densities and ratios from stripping of pre-treated TBP with pure water.

Extractant	Acid	A/O	$\alpha/\Omega$	$\rho(\text{raffinate})$ [g cm <sup>-3</sup> ]	$\rho(\text{extract})$ [g cm <sup>-3</sup> ]
TBP (97 %)	1	10.68	11.64	1.0093	0.9795
TBP (97 %)	1	8.27	9.18	1.0125	0.9799
TBP (97 %)	1	5.05	5.77	1.0207	0.9807
TBP (97 %)	1	4.05	4.66	1.0261	0.9812
TBP (97 %)	1	2.01	2.39	1.0505	0.9844
TBP (97 %)	1	1.01	1.20	1.0902	0.9925
TBP (97 %)	1	1.00	1.20	1.0902	0.9925
TBP (97 %)	1	0.81	0.97	1.1084	0.9967
TBP (97 %)	1	0.50	0.62	1.1453	1.0087
TBP (97 %)	1	0.29	0.36	1.1932	1.0269
TBP (97 %)	1	0.25	0.32	1.2022	1.0306
TBP (97 %)	1	0.23	0.29	1.2098	1.0335
TBP (97 %)	1	0.13	0.16	1.2516	1.0504
TBP (97 %)	1	0.10	0.12	1.2686	1.0573

**APPENDIX III: Percentages of impurity metals extracted and their concentrations**

Percentages of impurity metals extracted, and their concentrations in loaded extractants after equilibration with Acid 1, which contained  $24.8 \text{ g dm}^{-3}$  of As and  $1015 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1$  °C,  $t_{\text{eq}} = 20$  min. All concentrations given in  $\text{mg dm}^{-3}$ .

Extractant	O/A	$E(\text{Sb})$ [%]	$c(\text{Sb})_{\text{org}}$ [ $\text{mg dm}^{-3}$ ]	$E(\text{Bi})$ [%]	$c(\text{Bi})_{\text{org}}$ [ $\text{mg dm}^{-3}$ ]	$E(\text{Ni})$ [%]	$c(\text{Ni})_{\text{org}}$ [ $\text{mg dm}^{-3}$ ]
TBP	0.1	2.82	26.64	2.65	2.42	0.11	17.94
	0.125	3.13	24.24	1.90	1.42	0.12	16.09
	0.2	5.10	24.23	3.36	1.54	0.24	19.39
	0.25	6.07	23.43	3.97	1.48	0.25	16.23
	0.5	9.73	18.49	7.26	1.33	0.57	18.16
	0.8	12.66	15.18	11.31	1.31	1.01	20.30
	1	15.81	12.07	13.66	1.01	1.60	20.45
	2	19.36	9.61	18.75	0.90	2.90	24.17
	3.5	35.46	10.28	31.59	0.88	9.75	47.39
4	45.47	11.64	43.27	1.07	14.80	63.58	
1,2-octanediol in 2-ethylhexanol	0.1	2.79	27.28	< LOQ	< LOQ	0.21	33.70
	0.125	4.76	36.47	< LOQ	< LOQ	0.27	33.71
	0.25	7.44	28.67	< LOQ	< LOQ	0.24	14.74
	0.5	10.66	20.76	< LOQ	< LOQ	0.53	16.59
	0.8	11.88	14.68	< LOQ	< LOQ	0.75	15.07
	1	18.83	19.04	< LOQ	< LOQ	1.61	26.40
	2	33.80	17.95	< LOQ	< LOQ	2.94	25.29
	3.5	37.16	12.09	< LOQ	< LOQ	3.70	19.53
4	34.20	9.85	< LOQ	< LOQ	3.36	15.69	

Concentrations of impurity metals in loaded extractants after equilibration with Acid 2, which contained  $8.6 \text{ g dm}^{-3}$  of As and  $1255 \text{ g dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .  $T = 21 \pm 1 \text{ }^\circ\text{C}$ ,  $t_{\text{eq}} = 20 \text{ min}$ . All concentrations given in  $\text{mg dm}^{-3}$ .

Extractant	O/A	$c(\text{Ni})_{\text{org}}$	$c(\text{Cu})_{\text{org}}$	$c(\text{Zn})_{\text{org}}$	$c(\text{Cd})_{\text{org}}$	$c(\text{Sb})_{\text{org}}$	$c(\text{Pb})_{\text{org}}$	$c(\text{Bi})_{\text{org}}$
TBP	0.1	1.79	< LOQ	2.05	17.06	27.12	152.31	1.79
	0.125	1.91	< LOQ	0.00	8.93	5.51	127.75	1.43
	0.25	3.31	< LOQ	26.59	31.65	17.62	104.37	0.98
	0.5	2.57	< LOQ	0.96	33.78	11.59	81.37	1.06
	0.8	5.77	< LOQ	8.71	35.81	4.97	76.96	0.73
	1	2.51	< LOQ	4.63	45.03	2.70	68.47	0.89
	1.5	5.02	< LOQ	3.75	33.89	1.05	60.07	0.32
	2	2.81	< LOQ	< LOQ	60.43	< LOQ	60.33	0.27
1,2-octanediol in 2-ethylhexanol	0.25	15.23	31.28	16.18	101.74	2.24	52.69	1.75
	0.5	9.86	11.40	16.97	66.77	< LOQ	54.78	0.89
	0.8	5.60	28.56	13.28	69.12	< LOQ	115.45	1.82
	1	9.00	37.40	30.89	98.31	1.53	60.83	1.34
	1.5	24.69	25.42	15.71	67.74	< LOQ	85.70	0.73
	2	5.57	22.87	15.64	65.73	0.26	66.40	0.28