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Diplomarbeit

Elimination of Mercury from Wastewater by Emulsion Extraction

Elimination du mercure de l'eau polluée par extraction emulsionée

erstellt für

École Centrale Paris

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Kurzfassung

Abtrennung von Quecksilber aus Abwässern mit flüssigen Membranen

Elimination of mercury from wastewater by emulsion extraction

Diese Arbeit beschäftigt sich mit der Entfernung von Quecksilber aus Abwässer mit Hilfe der Flüssig Membran Permeation. Hierbei wird der Schadstoff mit einer im Abwasser verteilten W/O-Typ-Emulsion entfernt. Dieser Prozess ist sowohl mit der Flüssig-Flüssig Extraktion, als auch dem Membran Verfahren verwandt und erlaubt eine Extraktion und Reextraktion in derselben Stufe. Das Verfahren ist besonders für stark verdünnte Lösungen geeignet, insbesondere aufgrund des hohen Konzentrierungsfaktors in der internen Phase und der Möglichkeit den Grossteil des Metalls schon in einer einzigen Stufe zu entfernen.

Da Hg normalerweise nur als Spurenmetall im Abwasser vorliegt und einen niedrigen Grenzwert (0,01 mg/l in Österreich) hat, wurde dieses Verfahren ausgewählt.
Der Ablauf der Arbeit selbst kann in drei Teile unterteilt werden:
(1) Diskontinuierliche Flüssig-Flüssig Extraktionsversuche, die der Untersuchung des Mechanismus der Extraktion dienen. (2) Danach wurden diskontinuierliche Versuche zur Optimierung einer Emulsion zur Entfernung von Hg aus dem Abwasser durchgeführt. (3) Letztendlich wurde die Emulsion in kontinuierlichen Versuchen Mischer-Abscheider getestet. Hier konnte eine 95% Effizienz der Extraktion erreicht werden.

Abstract

Elimination of Mercury from Wastewater by Emulsion Extraction

Elimination du mercure de l’eau polluée par extraction emulsionée

Object of this study was the extraction of mercury from wastewater using the Emulsion Liquid Membrane (ELM) process.
This technique is related to solvent extraction and membrane techniques and allows to perform extraction and stripping of the metal in only one stage, with a “water in oil”-emulsion.
Because of its high concentration factors in the internal phase of the emulsion, this process is preferred for very diluted solutions and allows also extracting to very low concentration levels in this one stage.
This are the main reasons for choosing this process for the extraction of mercury, which appears normally only as trace metal and has a limit value of 0.01 mg/l in Austria.

This work can be distinguished in three parts. (1) First the mechanism of the extraction was examined in solvent extraction experiments. (2) Then an emulsion for the extraction of mercury was optimised. (3) And finally the optimised emulsion was tested in a mixer-settler system. In the continuous experiments, an efficiency of 95 % for the extraction of mercury was achieved.

Résumé

Elimination du mercure de l'eau polluee par extraction emulsionee

Elimination of Mercury from Wastewater by Emulsion Extraction

L'objectif de cette étude est de réaliser l'extraction du mercure dans une eau polluée par le procédé de Membrane Liquide Emulsionnée.
Cette technique est apparentée à l'extraction liquide-liquide et à la technique des membranes. Ceci permet d'améliorer l'extraction et la désextraction du métal en une seule étape.
Ce modèle est valable pour les solutions très diluées en ce qui concerne la phase externe car on obtient une concentration très élevée dans la phase interne.
Pour ces raisons, ce procédé concernant l'extraction du mercure a été choisi car, en général, le métal est sous forme de traces et a une valeur limite de 0,01 mg/l en Autriche.

Ce travail peut être divisé en trois parties. (1) Premièrement, le mécanisme de l'extraction a été examiné par des expériences en extraction liquide-liquide. (2) Puis, une émulsion pour l'extraction du mercure a été optimisée. (3) Et finalement, l'émulsion optimisée a été testée dans un mélangeur décanteur. L'extraction du mercure en continu est quasi totale, car il est extrait à 95 %.

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1 Introduction

1.1 Problem

Industrial wastewater typically contains a multiplicity of pollutants and heavy metals.
These heavy metals usually appear as trace metals and even in low concentration they cause problems for wastewater treatment.

Among these heavy metals mercury, a natural occurring element, appears in several inorganic and organic forms in the nature. In surface water, mercury is normally found only in small concentrations.
Even in small concentration levels, inorganic mercury is naturally transformed to methyl-mercury. This form of mercury quickly enters the aquatic food chain and accumulates in biological tissues.
If ingested into the human body, mercury especially affects the nervous system. Mercury was therefore ranked third on the CERCLA1) priority list of hazardous substances on rank three, after arsenic and lead, during the last six years.

Solvent extraction is an established process for removing heavy metals, but to reach the permissible limits, for example 1µg/l for drinking water in the EU or 2µg/l in the US [30, p 221] a multiplicity of extraction stages are necessary.
An alternative to this process is the Liquid Membrane Technique (LMP) respectively Emulsion Liquid Membrane Process (ELM). This technique is a combination of a solvent extraction and a membrane process [8, p 8], whereas the extraction and stripping is performed in only one stage.
Li made the first technical application of this process [14] in the 1960s [8, p 1]. In the beginning, LMP was used for production of metals and in the 1980s this technique was tested for applications in the wastewater treatment. [8, p 1–4]
A major advantage of this kind of treatment is the good separation efficiency for metal ions in very diluted solutions.

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1) The Comprehensive Environment Response, Compensation, and Liability Act (CERCLA) oblige the Agency for Toxic Substances and Disease Registry (ATSDR) and the US Environmental Protection Agency (EPA) to prepare a list of hazardous substances. This list is published every two years. The ranking is based on the frequency of the substance in the environment, the possibility of human exposure and the toxicity.
www.atsdr.cdc.gov

1.2 Objective

This work now is engaged with the extraction of mercury from wastewater by the emulsion liquid membrane process, a form of the liquid membrane technique where the aqueous stripping phase is emulsified in the organic phase.

The experiments of this work can be distinguished into three parts:
First the extraction of mercury with solvent extraction process, with Trioctylamine (TOA) as extracting agent and sodium hydroxide (NaOH) and Ethylen-di-amin-tetra-acetate (EDTA) as stripping agents was tested.
In these experiments the optimal parameters for the solvent extraction were sought and the stoechiometric complex for the extraction were determined.

Secondly an emulsion with the same components as in the solvent extraction experiments was produced; and in several discontinuous experiments, optimised concerning the usage of surfactant, extracting agent and stripping agent. And also the stability of the emulsion in consideration of the efficiency of the extraction and concentration of the mercury in the internal phase.

Finally, this optimised emulsion was tested in continuous experiments in a mixer-settler system.

2 Theory

2.1 General Context

2.1.1 Mercury – A Danger for Humans and Nature

Mercury is a chemical element, which occurs naturally in our environment, but environmental mercury levels have significantly increased since the dawn of the industrial age [11, p 1–2].

2.1.1.1 Forms of Mercury

In nature mercury may appear in several different forms; one example is, metallic mercury [Hg^0], which is a silver-white, shiny metal and liquid at room temperature (melting point: -38.87°C). Because of its high vapour pressure (0.0016 mbar at 20°C, 0.3684 mbar at 100°C), elemental mercury evaporates easily. Mercury vapours are colourless, inodorous and highly toxic. Mercury forms also inorganic compounds with chlorine, sulphur or oxygen, such as mercuric(II)chloride [$HgCl_2$], mercuric(II)sulphide [HgS], mercurous(I)chloride [Hg_2Cl_2], etc. These salts appear normally as white powder or crystals, except mercuric sulphide (cinnabar), which is a red powder that blackens on exposure to light. There exist also a large number of organic mercury compounds, for example: methyl-mercury, phenyl-mercury and di-methyl-mercury. di-methyl-mercury occurs as an achromatic liquid, whereas methyl-mercury and phenyl-mercury exist as white crystalline solids [28, p 2]; [30, p 364-377].

In the nature mercury is normally found as cinnabar (mercuric sulphide HgS), which is an insoluble and stable compound [28, p 2]. It occurs in the earth crust at an average level of 0.5 ppm, depending on the location [30, p 371].

”Major mercury producing countries include mainly: Algeria, China, Finland, Czech Republic, Slovakia, Kyrgyzstan, Mexico, Morocco, Russia, Slovenia, Spain, Turkey and the Ukraine.” [23, p 274]

Main uses of mercury include, among other things, electrolytic production of chlorine and caustic soda, manufacturing of wiring devices and switches, measuring and control instruments and dental equipment. But because of the high toxicity of mercury many applications have been now banned [30, p 374-375].

2.1.1.2 Sources of Mercury

As already mentioned, mercury is distributed to the environment by natural as well as anthropogenic processes. Mercury is primarily released to the atmosphere (approximately 80 %), while the remaining is released to the land (15%) and to water (5%) [28, p 4].

According to the UNEP [27, p 86], mercury releases can be grouped in four categories:

- Natural sources – discharging as a result of natural mobilisation of naturally occurring mercury
- Anthropogenic releases from the mobilisation of mercury impurities in raw material such as fossil fuel or other extracted, treated and recycled minerals.
- Anthropogenic releases resulting from mercury used in products and processes
- Remobilisation of historic anthropogenic mercury already previously deposited.

Natural sources of mercury include for example evaporating from geological mineral deposits, emissions from volcanic activities, photo reduction of divalent mercury in natural waters, volatilisation from soil, seismic activities, and geothermal sources [27, p 11; p 86-92]. The major anthropogenic sources of mercury discharges into the environment imply, among other things, mining and smelting and industrial processes involving the use of mercury, such as Chlor - alkali electrolysis, textile production, pulp and paper production. Also includes combustion of fossil fuels (primarily coal), production of cement and medical and municipal waste incinerators [24, p 11]. Other examples of industrial sources of mercury releases are steel and coke production, lime manufacturing, primary copper smelting, crematories, plastic materials and resin manufacturing, landfills and gold mining.
Consumer products containing mercury include batteries, paint, measuring instruments, catalysts and pigments, electric switches, dental amalgams, fungicides, laboratory reagents, medicines, cosmetics, fluorescent lamps and mercury vapour lamps [27, p vi, p 9-14, p 88]; [30, p 377-395].

Mercury disposal to surface water involves direct discharges from industry and homes to water receptors, indirect discharges via wastewater treatment systems, deposition of mercury from the atmosphere, and surface run-off and leachate from mercury contaminated soils and landfills [27, p 98].

The estimation of the total mercury emission and the quotient of anthropogenic releases are very difficult, because of the complexity of the bio-geochemical cycle of mercury in the nature.
Nriagu and Pacnya (1988) estimate that the anthropogenic mercury emission is more than 50 % of the global emission, whereas the WHO (World Health Organisation) reported that the natural emission is 1 to 1.3 times the anthropogenic emission. The OECD (Organisation for Economic Co-operation and Development) estimates natural emissions of mercury to air, water and land in a range from 2500 to 15000 t/y. Most recently Pirrone (1996) estimated the worldwide emission of mercury to 2200 t/y where the natural sources, industrial sources and

recycling each contribute for 1/3 [30, p 389].[2]

Generally, the discharge of mercury from anthropogenic sources is decreasing worldwide due to limited use, stricter regulations due to use and disposal, and better off-gas and wastewater treatment processes. So the release of Hg to the environment in the US in 1994 was 14 % less than in 1991 [30, p 378][3] and is still decreasing. In Austria the total emission of mercury between 1985 and 1995 has decreased about 65 % [26, p 1]. In Europe the emission of mercury has decreased approximately 85 % between 1988 and 1998 [5, p 5]. Besides these positive developments, the worldwide emission of mercury is still high and has toxious levels in many areas.

2.1.1.3 Effect for Human and Nature

The natural bio-geochemical cycle of mercury, which can be seen in **Figure 1**, is very complex. The cycle is characterised by degassing of the element from soils and surface waters, followed by atmospheric transport (often over long distances), deposition of mercury back to soils and surface water, and sorption to soil or sediment particles. And finally mercury, deposited on land or surface water is revolatilised into the atmosphere [30, p 379].

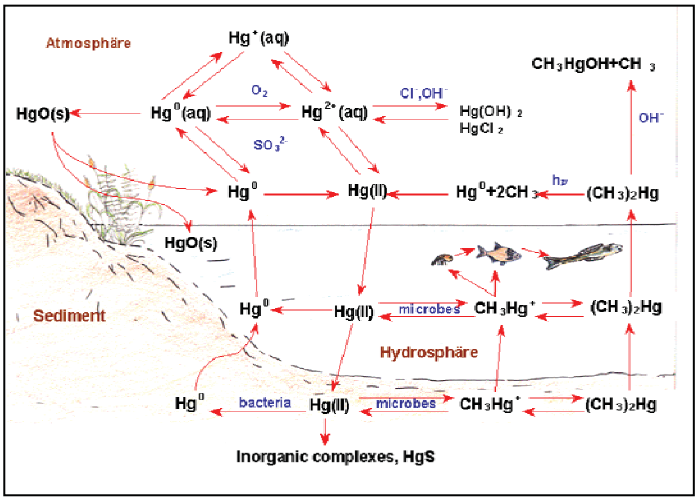

Figure 1: Bio-geochemical mercury cycle [30, p 407]

In the atmosphere over 95 % of the mercury is in the form Hg^0. In this form mercury can be transported over long distances. Wet deposition is the main method of removal of mercury

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[2] US ATSDR, 1999 [30] according to

Quantitative assessment of worldwide contamination of air, water and soils by trace metals. J.O Nriagu and J.M. Pacyna, Nature 333 (1988) 134 – 139

Historical trends of airbone trace metals in Detroit from 1971 to 1992. N. Pirrone, G.J. Keeler, J.O. Nriagu, et al., Water Air Soil 88(1-2) (1996), 145 - 165

[3] US ATSDR, 1999 [30] according to

TRI94, 1996, Toxic Chemical Release Inventory, National Library of Medicine, National Toxicology Information Program, Bethesda, MD from the atmosphere [23, p 398-406]. In soils and surface waters, mercury exists normally in the states Hg^{2+} (mercuric) and Hg^{1+} (mercurous). In the soil, in fresh and salt-water inorganic mercury can be methylated by microorganisms. This biotransformation is the most important and most effective process of mercury-transformation in the nature [30, p 399-405].

Methyl-mercury is the most common form of organic-mercury. This form is soluble, very mobile and swiftly enters into the aquatic food chain. And there it is accumulated to a far greater level in biological tissues than any of the inorganic forms [11, p 2]; [30, p 401]. In the terrestrial food chain, mercury can be found especially in mushrooms, but also in the roots of higher plants [28, p 5]; [30, p 404]. The bio-magnification of methyl-mercury has a most significant impact on human beings and wildlife.

Potential sources of general exposure to mercury to animals and humans involve inhalation of mercury vapours, ingestion of contaminated drinking water and food, or exposure to mercury through dental and medical treatments [30, p 379].
The effects to animals and human beings are multiple; the nervous system is generally very sensitive to all forms of mercury. Long-term exposure to metallic, inorganic or organic mercury can permanently damage the brain, kidneys and developing foetus. Effects on brain functions may appear in memory problems, irritability, changes in vision or hearing, and shyness. Short-term exposure to high levels of metallic mercury vapours may result, among other things, in lung damage, sickness, diarrhoea, and increases in blood pressure or heart rate [29, p 3]. The US EPA (Environmental Protection Agency) has declared that mercuric chloride and methyl-mercury are possible human carcinogens [28, p 12].4)

2.1.2 State of Art for Wastewater Treatment [10, p iii-ix, p 84-110]

Wastewater treatment techniques include: [10, p iii-iv]

- Separation or clarification techniques, which are normally used in combination with other operations, either as a first step to protect other treatment facilities or as a final clarification step. Among these techniques are grit separation, sedimentation, air flotation, filtration, microfiltration/ultrafiltration, and oil-water separation.

- Physico-chemical treatment techniques are basically used for inorganic or barely biodegradable organic contaminants, such as precipitation/sedimentation/filtration, crystallisation, chemical oxidation, wet air oxidation, chemical reduction, hydrolysis,

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4) US ATSDR, 1999 [28] resp. [30] according to
US EPA, 1984, Mercury health effects update: Health issue assessment. Final report. Washington DC: US Environmental Protection Agency, Office of health and Environmental Assessment. Document no. EPA 600/8-84-019F

nanofiltration/reverse osmosis, adsorption, ion exchange, extraction, distillation/rectification, stripping, and incineration

- Finally biological treatment techniques for biodegradable waste water comprehend techniques such as anaerobic digestion processes, aerobic digestion processes, and nitrification/denitrification processes. Example for anaerobic digestion processes are: fixed-bed process, biological removal of sulphur compounds and heavy metals. Aerobic digestion processes include processes such as: complete-mix activated sludge process, membrane bioreactor process, trickling filter process, and biofilter fixed-bed process.

A "traditional" wastewater treatment normally includes a combination of a physico-chemical process, such as precipitation or filtration and a biological process [5, p 6]. Although such a treatment however often fails to reduce heavy metal concentrations below permissible limits.

Adequate techniques for heavy metal removing are: [10, p ix]

- Precipitation/sedimentation/filtration
- Crystallisation
- Solvent Extraction
- Nanofiltration or Reverse Osmosis

2.1.2.1 Precipitation [10, p 84-87]

In the precipitation process solid particles are formed via chemical reagents. This is followed by a separation of these particles by an additional process, such as sedimentation, air flotation or filtration.

Typical chemicals, which are used for precipitation, are:

- Lime, dolomite, sodium hydroxide, soda for heavy metals,
- Calcium salts for sulphates or fluorides, and
- Sodium sulphide and polyorganosulphides for mercury.

The main disadvantage of this process is that the resulting sludge has to be treated as a solid chemical waste, from which a recovery of the metal is hardly possible.

2.1.2.2 Crystallisation [10, p 87-90]

Crystallisation is a process related to the precipitation process, except that the precipitate is formed on seed material for example sand or minerals, in a fluidised-bed reactor. The driving force for this process is the reagent concentration and pH.

All types of wastewater with a concentration of the pollutant in range between 10 – 100000 ppm can be treated. For good results, however, the reagents must be added in an overdose, which results in the addition of extra compounds in the wastewater. Therefore, this process is restricted to non-toxic reagents.

2.1.2.3 Reverse Osmosis and Nanofiltration [10, p 105-110]

In general, “a membrane is a semi-permeable barrier through which only selected chemical species may diffuse.” [17, 150] The pressure difference across the membrane is the driving force of this process. The membrane normally holds back all particles down to the size of organic molecules and even ions.

Nanofiltration and reverse osmosis have different applications. Whereas reverse osmosis is used to separate down to ionic species and nanofiltration is adequate for removing larger organic molecules and multivalent ions.

Fouling and high-energy costs are the major disadvantages and limitation factors of these techniques [17, p 151].

2.1.2.4 Solvent Extraction [10, p 118-120]; [16, p 53-73]; [17, p 149-150]

Solvent extraction is normally used for large-scale operations where a heavy contamination appears (typical range 100 – 200 ppm). This technology can be used for the selective removal of heavy metals.

During this process, an extracting agent diluted in an organic solvent is contacted with the wastewater. The metal ion in the aqueous feed is transferred into the organic phase by forming a complex with the extractant. Afterwards, the organic solution is contacted with an aqueous stripping solution. There a back-transfer of the metal ion into the strip solution occurs [17, p 50].

Heavy metals are either present in wastewater as anion or cations. Anions can be removed for example by long chain alkyl amines as extracting agents only if acids are present in the feed. Cations are extracted by acidic or chelating extractants. Examples of this kind of reagents are: oxime molecules or organophosphate (e.g. di(2-ethylhexyl)phosphoric acid (D2EHPA), dithiophosphoricacid (DTPA)) [17, p 150].

The advantages of this process are the efficiency, the selectivity of the extraction and the possibility of operating continuous process.

The main disadvantages are: rather expensive equipment and large amount of solvent. Besides that, the process is not very effective for trace amounts of metals. There is also a potential for cross-contamination of the wastewater with the organic solvent, which can be avoided by using long chain organic compounds.

2.1.3 Non-state of Art Technologies [17, p 151-155]

2.1.3.1 Adsorption and Ion-Exchange Processes [17, p 155]

The problem of the loss of solvent into the wastewater stream observed in the solvent extraction can be overcome with the use of a solid matrix for adsorption and ion-exchange, though this technique is only economic for low concentrations, compared to solvent extraction. Up to now activated carbon or synthetic ion exchange resins have been used, but the great disadvantage for these materials are the lack of selectivity, which is, however, in the wastewater treatment normally an advantage. Experimental and pilot scale research is now working on the use of new ion-exchange resins and zeolite materials for selective removal of specific heavy metals.

The biological variant of this process is the biosorption, where biological materials, such as marine algae, fungi or bacteria, are used as chelating ion-exchange media. These materials are more selective than traditional ion-exchange resins. Another possibility is the combination of solvent extraction to extract the major part of the metal and ion exchange to eliminate its last traces.

2.1.3.2 Liquid Membrane Technique

Liquid membrane technique is a combination of a solvent extraction and a membrane process. Unlike solvent extraction, the liquid membrane process is performed in only one stage.

An organic solution (liquid membrane) acts as a barrier between two aqueous phases: one is the continuous (external) phase, which contains the heavy metal and the other is the stripping (internal) phase. The organic phase consists of a solvent, an extractant, which acts as a carrier for the heavy metal, and a surfactant for the emulsion membrane technique. The stripping phase contains a stripping agent.

In the emulsion liquid membrane process an emulsion is formed by dispersing the internal aqueous phase into the organic phase. The emulsion is then dispersed into the external aqueous phase.

Mass transfer occurs between the outer continuous phase and the intern aqueous phase. The metal ions diffuse in the external to the outer interface and react there with the extracting agent by forming a complex. This complex is transported through the organic phase to the internal interface, where the stripping agent breaks the complex and releases the extractant. At the same time the metal is concentrated in the internal aqueous solution.

Another kind of operating the liquid membrane technique is the supported liquid membrane. Here the organic phase is impregnated in a solid porous membrane between the two aqueous phases.

Applications of this technology are environmental protection (waste water treatment), chemical analysis, chemical technology, medicine and cosmetics.

The liquid membrane technique has many advantages, such as especially good separation efficiency for metal ions in very diluted solutions. This has been the main reason of the choice of this process for the extraction of mercury from wastewater. The next section contains a more precise description of this technique.

2.2 Liquid Membrane Technique (LMP)

A liquid membrane is a homogeneous, non–porous membrane, where the solute is dissolved at the one side and released at the other side.
The liquid membrane technique (also liquid membrane process or liquid membrane permeation) is a combination of a membrane technique with a solvent extraction process. The chemical reaction is the same as for solvent extraction, but a multiplicity of stages are necessary for solvent extraction to extract to very low concentration levels. The liquid membrane process is therefore preferred for extreme diluted solutions, as only one stage is needed.

2.2.1 Methods

There exist several different methods for carrying out the liquid membrane process, but only two seem adaptable: the supported liquid membranes and the emulsion liquid membranes. [6, p 320]

2.2.1.1 Supported Liquid Membranes [8, p 4-7]

Here a rigid porous substrate, normally with a microporous structure, is filled with organic solution of an extracting agent. The external aqueous phase and the stripping phases are passing the membrane on either side. The transport can be accelerated by the use of facilitated or carried transport [17, p 152]. The advantage of this method (no need to prepare or split an emulsion) indicates high reduction of costs. The disadvantage is the lifetime of such membrane, approximately two weeks [8, p 4], which is due to an elution of the organic phase during the process. A scheme of this method, see **Figure 2 (right side)**.

2.2.1.2 Emulsion Liquid Membranes (ELM) [8, p 4-7]

In this process the stripping phase is emulsified in the organic phase with a surfactant as stabiliser with high shear stress. Afterwards this emulsion is dispersed at a weaker shear stress in the external aqueous phase [21, p 107]. The organic phase of the emulsion acts as a liquid membrane and the emulsified aqueous phase as the receiving phase [6, p 320]. The organic phase consists normally of an extracting agent, a surfactant and the solvent. The internal aqueous phase comprises the stripping agent. A prerequisite for the efficiency of this method is a good stability of the emulsion during the contacting with the wastewater, in order to avoid a pollution of the aqueous feed with the solvent and a back transfer of the metal in the feed. A sheme of this method, see **Figure 2 (left side)**.

This process is the method of choice for this work; therefore a detailed description of it is ensued in the following sections.

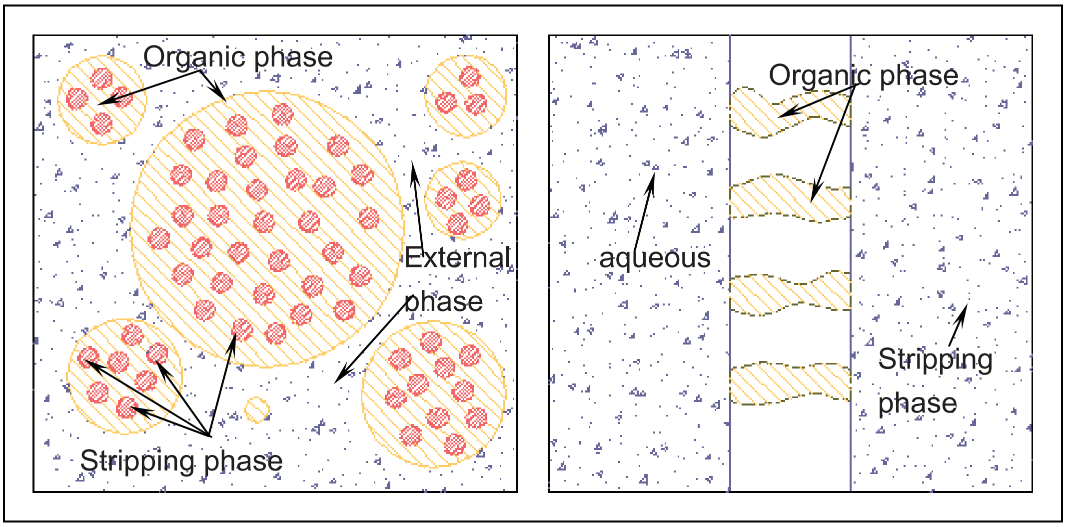

Figure 2: Emulsion liquid membrane and supported liquid membrane

2.2.1.3 Other Membrane Designs [17, p 153-154]

Hollow fibres containing liquid membranes (HFCLMs) are an alternative to the supported liquid membranes. Here “two sets of hollow fibres are packed together into a microporous hollow fibre permeator. The organic phase is packed between the two sets of fibres and the aqueous feed and the stripping solution pass through the hollow space of the fibres on either side of the organic phase.” [17, p 153]

Another possibility is to trap an emulsion within the hollow fibres permeator. According to Wiencek, 1993 and 1998 [13, p 153]5), this arrangement allows for the performance of an emulsion liquid membrane process without stability problems. The major drawback as well in this method is the lifetime of the membrane.

2.2.2 Mechanism

As already mentioned, and the liquid membrane process (LMP) is related to the membrane technique as well as to the solvent extraction process [8, p 8]. Unlike solvent extraction,

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5) According to Kentish, 2001 [17]
Emulsion-liquid-membrane extraction of copper using a hollow-fibre contactor.
S.Y.B. Hu, J.M. Wiencek, AIChE J 44 (3) (1998) 570 – 591
Extraction with emulsion liquid membranes in a hollow-fiber contactor.
B. Raghuraman, J. Wiencek, AIChE J. 39 (1993) 1885.

extraction and stripping of the metal are carried out in one single stage or more precisely for the ELM in one single emulsion drop [19, p 59].

As previously mentioned, emulsion droplet consist normally of two phases:
An organic phase, which build the membrane and thus acts as a barrier between the internal aqueous phase and the wastewater stream, which is normally also an aqueous phase. This organic phase is composed of an extracting agent (ion exchanger (anionic, cationic)), a surfactant, which is necessary to stabilise the emulsion and a solvent (aliphatic or aromatic organic compound; for example dodecane, kerosene, toluene). The (internal) aqueous phase contains a stripping agent; in this phase the concentration of the metal is carried out.

The actual extraction is carried out in three steps (see also **Figure 3**).
(1) First the metal diffuses from the aqueous feed (external aqueous phase, continuous aqueous phase) to the outer interface of the emulsion drop. At this interface the solute reacts with the extracting agent by forming a complex.
(2) Afterwards the extractant acts as a carrier and transports the metal to the internal interface.
(3) At this second interface the complex reacts with the stripping agent and releases the metal. The metal is then concentrated in the stripping phase whereas the extracting agent is available for a new complexing reaction at the outer interface [19, p 59].

The main driving force is given by the difference in concentrations of the metal in the membrane at both interfaces [6, p 320].

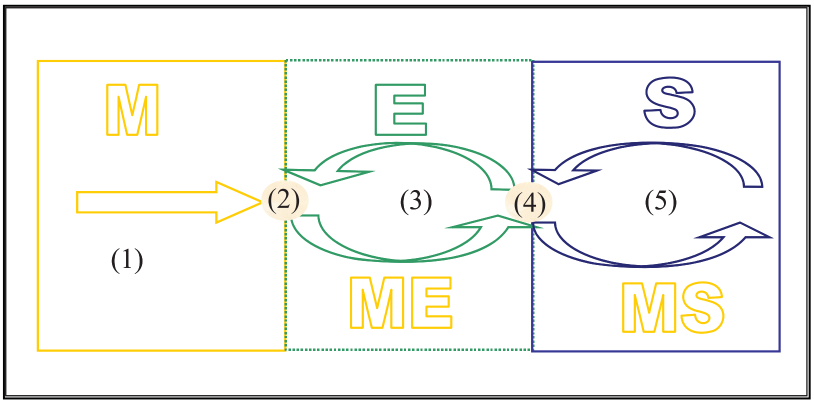

Figure 3: Mechanism of mass transfer

(1) Transfer of the metal to the outer interface of the emulsion
(2) Forming of a complex with the extracting agent at the interface
(3) Transport of the complex through the organic phase to the inter interface
(4) Reaction with the stripping agent at the inter interface
(5) Concentration of the metal in the internal phase
]]>

2.2.3 Emulsion Liquid Membranes

The composition and the mechanism of this technique are already explained in the section (**page 14** - **16**) above. In this section the preparation, the actual mass transfer and splitting of the emulsion are described in detail.

Generally the ELM processes are composed of three steps: (1) the preparation of the emulsion, (2) afterwards the mass transfer of the metal from the aqueous feed to the intern aqueous phase (stripping phase) (i.e. extraction/stripping) and (3) finally the splitting of the emulsion in order to recover the metal and recycle the organic phase [18].

2.2.3.1 Preparation of the Emulsion

As aforementioned, emulsions are produced by emulsifying an aqueous stripping phase in an organic stripping phase. At lab scale there are normally no difficulties to produce emulsions, dynamic homogenisers are usually used (ULTRA TURRAX). In pilot scale plants the production of emulsion is much more complicated, especially because of corrosion problems [18].

Apparatus that are typically used are, high-pressure homogeniser, where both phases are pumped through small holes, rotor-stator-systems, colloid-mills and static low pressure homogenisers, which have the advantage of a low pressure and a simple construction. There is also the possibility of emulsion producing by an ultrasonic or electric field [8, p 46-50].

2.2.3.2 Mass Transfer

The ELM processes are related to solvent extraction and also to the membrane process. The mass transfer is carried out in four steps:

(1) A transfer of the metal and back-transfer of the extractant to the outer interface. (2) A reaction occurs with the extractant at the outer interface surface and (3) diffusion of all components in the membrane phase. This step can be compared with an extraction, but for the ELM only the velocity of the reaction is mattering and not equilibrium.

Diffusion in the membrane is the result of difference in concentrations of the metal on both sides of the membrane. Diffusion is normally spontaneous, irreversible and temperature-sensitive.

The diffusion flux (**Equation (1)**) is derived from the first law of Fick: [6)]

$$J_i = D_i * \frac{c_i^{III} - c_i^{I}}{d} \tag{1}$$

J_i	*diffusion flux [mol/sm^2]*
D_i	*diffusion coefficient [m^2/s]*
d	*thickness of the membrane [m]*
c^{III}	*Concentration in the internal phase [mol/m^3]*
c^{I}	*Concentration in the external phase [mol/m^3]*

(4) Finally the stripping reaction occurs at the internal interface to free the metal into the internal phase and regenerate the surfactant.

There are different mechanisms of transfer through a membrane; these are described in the next sections [8, p 33-37].

2.2.3.2.1 Facilitated Diffusion

A system, which is not in equilibrium, tries to reach equilibrium. The driving force is the difference in concentrations of the solute on either side of the membrane. The transfer stops when equilibrium (equality of concentrations) is reached; to avoid this phenomenon, the concentration difference has to be kept significant, e.g. by transforming initially into another compound by a chemical reaction. This transfer is known as facilitated diffusion.

2.2.3.2.2 Carrier-Mediated Transport

The carrier mediated transport can be distinguished in two different mechanisms: mobile carrier-mediated transport and bonded carrier-mediated transport. In liquid membrane technique a mobile carrier is used. The carrier increases the velocity of the transport through the membrane by facilitating the solubilisation of the metal in the organic phase. For the facilitated transfer, equilibrium also has to be avoided to allow a good extraction until very low remaining concentrations.

2.2.3.2.3 Activated Transport

Activated transport is the transport of the metal that is related to the transfer of another component: co-transport or counter-transport in companion with the metal. In this case, enrichment against the concentration difference is possible.

[6)] In this form, the equation shows a diffusion through a membrane

2.2.3.2.4 Mass Transfer [8, p 85-117]

The mathematic modelling of the actual mass transfer through an emulsion is very complicated and is briefly considered here.

A lot of different models and approaches were developed for the mathematical description of the transport procedures in emulsion, but the description of a “three-phase-system” is complex, especially if surfactants have to be accounted for. Generally, the models for the mass transfer can be classified into two criteria:

(1) If the droplets are fixed or mobile:

A “real droplet” is mobile in the emulsion. This is described in the so called “general diffusion models”. The disadvantage of these models is that normally at least one or more parameters have to be determined experimentally. These models are complicated and mostly difficult to determine, thus commonly “border cases” are described.

One of these “border cases” is the “hollow-sphere-model”. Here all internal droplets are imagined as one big droplet, which is surrounded by an organic phase; are all mass-transport-resistance lies in the organic membrane phase.

In the second “border case”, the “advanced front model” or “shrinking core model” all stripping phase droplets are immobile in the organic phase and irreversible reactions at the receiving phase are possible. The metal is enriched in the outer stripping phase droplets, until the whole stripping agent is exhausted. Afterwards the metal diffuses into inner layers of stripping phase droplets, until they are also charged and followed by diffusion of the metal to the next inner layer.

(2) If a mobile carrier is used or not. Generally in the most models, mobile carriers are not accounted for, but in the emulsion liquid membrane processes normally mobile carriers are used.

2.2.3.2.5 Osmosis

A grievous problem during the mass transfer is the co-transport of water molecules (i.e. osmosis). This causes a dilution of the internal phase, which means a dilution of the extracted metal and an enlargement of the emulsion drops up to breakage. The amount of osmosis depends on the conditions of the system, i.e. surfactant and extractant concentration, ionic strength, and so on.

2.2.3.3 Splitting of the Emulsion [11, p 2-3]

An economic method to split the emulsion is an important factor for the feasibility of the whole ELM process. There are a lot of different methods for splitting an emulsion, but most of them are efficient and economic only at the lab scale.

2.2.3.3.1 Chemical Treatment

Flocculation allows the breaking the emulsion by adding electrolytes, salts, acids, alcohols, or a demulsifier. The disadvantage of this treatment is the intensive use of chemical substances and thus usually an after-treatment is necessary. Some of the compounds are soluble in organic phase. The recycling of the organic solubles is only possible after a separation of the additional compound, e.g. by distillation, which is expensive.

2.2.3.3.2 Thermal Treatment

Thermal treatment means the thermal disposal or combustion of the organic phase with an evaporation of the aqueous phase. If there is a high fraction of the aqueous phase, the combustion needs a lot of energy.

2.2.3.3.3 Physical Treatment

Physical treatments include adsorption, freezing separation, separation by heating and splitting in an electrical field (Electro-coalescence)

Splitting in an Electrical Field [8, p 59-81]

The drop coalescence is typically performed in three steps: (1) approaching of two droplets, (2) drain off of the film situated between the droplets, because of deformation during collision and finally (3) a destruction of the film, after it reaches a critical thickness and coalescence of the drops. The electric field polarises the droplets, thus augments the flexibility and so elevates the speed of coalescence.

The coalescence velocity can not be theoretically determined, because of the multiplicity of parameters for example field intensity, frequency, viscosity, concentration of the surfactant, drop diameter distribution etc [8, p 67].
The frequency (normally between 5 – 20 kHz) and the shape of the field are very important factors for the operation efficiency [8, p 79-80]. Insulated electrodes are preferred because of the lower energy consumption to avoid electrolysis and short circuits. [6, p 322-323] The problem is that insulation is in many cases rather expensive.

2.2.3.3.4 Mechanic Treatment

Mechanic treatments are ultra filtration, flotation, flocculation and centrifugation. Though if the emulsion is very stable, most of these methods cannot be used.

2.2.3.4 Components

2.2.3.4.1 Surfactant

The surfactant is an important component that affects not only the stability of the emulsion but also a lot of other phenomena for example osmosis, water solubility and mass transfer resistance [6, p 321]. This should be considered by the choice of the surfactant. By adding a higher concentration of surfactant, the emulsion droplets become smaller, which increases the stability of the emulsion and also increases the endeavours for splitting the emulsion [7, p 39]. For the W/O-emulsion a surface-active agent with a low HLB[7] number is required [20, p 318], to achieve a low solubility in the aqueous phases. The surfactant should be as less hydratable as possible to avoid osmosis [8, p 44].

2.2.3.4.2 Extracting Agent

The extracting agent acts as a carrier for the metal between the two interfaces and accelerates the mass transfer across the membrane.
Organic thio- and dithiophosphoric– and –phosphonic acids are very strong extracting agent for most heavy metals, acting as cationic exchangers. Cationic ion exchangers normally extract by exchanging a metallic cation in an aqueous phase for several protons (**Equation (2)**).

$$Me^{n+} + n\overline{HX} \Leftrightarrow \overline{MeX_n} + nH^+ \tag{2}$$

The efficiency of the extraction depends on the pH.

Another kind of ion exchangers are anion exchangers: amines or quaternary ammonium salts, exchanging a metallic anion for one or several other anions. For example for a tertianary amine in hydrochloric acid (**Equation (3)** and **(4)**):

$$\overline{R_3N} + HCl \Leftrightarrow \overline{R_3NH^+Cl^-} \tag{3}$$

$$MeCl_n^{p-} + p\overline{R_3NH^+Cl^-} \Leftrightarrow (R_3NH^+)_p MeCl_n + pCl^- \tag{4}$$

Mixture of extractants can give synergetic extractions.

---

[7] HLB stands for « Hydrophile-Lipophile Balance »and describes the balance between the oil soluble and water-soluble moieties in a surface-active molecule. A lower HLB means a more oil-soluble emulsifier and the reverse a more water-soluble emulsifier. http://www.surfactant.co.kr/surfactants/hlb.html

2.2.3.4.3 Solvents

Solvents with an aliphatic nature, a low viscosity and a high flash point [7, p 37-40] should be preferred, for the LMP

2.2.4 Advantages and Disadvantages [5, p 17-18]; [6, p 324]; [8, p 24-28]

The **advantages** of the LMP are:

- Very high enrichment factors can be obtained in one single stage, i.e. concentration of the metal in the stripping phase in recyclable concentration levels.
- A lower amount of extracting agent is sufficient compared with solvent extraction, because of the regeneration of the extractant during the process.
- Fast stripping reactions occur due to a high area of the internal interface
- Since the results of the simultaneous stripping free extracting molecules are available, there is no limitation due to equilibrium saturation of the surfactant.
- The lower solubility of the organic compounds in the aqueous feed makes LMP more attractive for the wastewater purification.
- In most cases a low selectivity for the extraction is observed, which can be an advantage in the wastewater treatment.
- Lower investment costs for the plant, due to smaller size of the devices and generally lower operating costs.

The **disadvantages** of the LMP are:

- Osmosis, which leads to the breakage of the emulsion.
- The emulsion breakdown causes an organic pollution of the aqueous feed and a back transfer of the metal in the feed.
- The composition of the emulsion is partially awkward, because of the multiple parameters, which have to be considered.
- A scrubbing stage, as in solvent extraction, is not possible, but often also not necessary.
- The non–ideal behaviour of the emulsion leads to a complex mathematic modelling.

Some of these parameters will be specified later in this work.

2.2.5 Osmosis [3, p 253-265]; [8, p 28-30]

Osmosis is an important factor for the efficiency of the process. Even though the effect of osmosis has no direct influence on the efficiency of extraction, it leads to a dilution of the stripping phase. This counts the major aim of the process, enrichment of the metal in the internal phase, for recycling reasons.

The reason for the transport of water across the membrane lies in the high acidity or basicity of the internal phase. An increase of the volume of internal phase in a range up to 50% even to 100% is possible, which results not only in the already mentioned dilution of the internal phase, but can also cause a breakdown of the emulsion. For industrial applications this effect can cause problems for flowing of the emulsion in the pipes and pumps because of the change of emulsion rheological properties [6, p 322].

The amount of osmosis depends on a multiple number of different parameters, for example:

- The residence time: between residence time and osmosis exists a positive linear relationship.
- Another influence factor is temperature. An increase of temperature causes a decrease of the viscosity, and a higher mass transfer rate, also increases the transport of water by osmosis.
- A greater interfacial area, by means of a smaller size of the emulsion droplets, also causes a facilitated mass transfer and consequently an enhanced osmosis
- A higher difference in the ionic strength between the phases also increases osmosis

A determination of osmosis is difficult, because of the change in the difference in ionic strength of both aqueous phases during extraction. Additionally, the knowledge of a lot of parameters is necessary to ascertain the effect of osmosis, as for example the actual interfacial area and changes in the ionic strength.

If there is no difference in the ionic strength between the aqueous phases, osmosis does not occur.

Industrial effluents have always a certain amount of salts, so that the difference in the ionic strength between feed and stripping phase is often rather low, reducing then osmosis [8, p 30].

2.2.6 Stability of the Emulsion [8, p 40-46]

Emulsions are thermodynamically unstable [8, p 40], but especially for wastewater treatment a long stability is important. The stability of an emulsion depends on many parameters, such as concentration of the surfactant, composition of the aqueous feed and the stripping phase [34, p 2]. There are several methods to increase the stability of the emulsion [8, p 41-46].

2.2.6.1 Increasing the Amount of Surfactant

An increase of the surfactant concentration arises stability, but results in problems during splitting. A compromise has to be found, i.e. a sufficient stability and easy splitting [6, p 322].

2.2.6.2 Increasing of the Viscosity

Increasing the viscosity is normally difficult, as the viscosity is usually fixed with the composition of the phases; Moreover, an increase of the viscosity leads to a decrease of the transfer rate.

2.2.6.3 Agglomeration of Solid Particles

An agglomeration of solid particles around an emulsion drop stabilises the emulsion, but for LMP this gives difficulties during the splitting of the emulsion.

2.2.6.4 Flocculation

Flocculation is the approach of two or more drops, which form a loose aggregate. This seems to stabilise the emulsion, but when shear stresses are applied, the aggregates break easily up again.

2.2.6.5 Decreasing of the Interfacial Tension

Interfacial tension is decreased, by using surfactants.

The estimation of the breakage is possible by using a tracer, in which is a compound that is present in the internal phase and insoluble with the organic one. Its presence in the external phase ascertains the breakage.

3 Description of the Experiments

3.1 Performance of the Experiments

The performed experiments can be distinguished in three parts:
(1) The determining of the stoechiometric complex during solvent extraction of mercury by TOA, (2) the optimising of the emulsion for the extraction of mercury in discontinuous experiments and finally (3) continuous experiments: testing of the optimised emulsion in a mixer-settler system.

3.1.1 Determining of the Stoechiometric Complex8)

The object of these experiments was the identification of the optimal extracting agent concentration and the determining of the stoechiometric complex.
The organic extraction phase consisted of (1) tri-octyl-amine, as extracting agent in a concentration range between 0.001 M and 0.02 M, (2) 5 % octanol as a modifier, to avoid a third phase formation and (3) dodecane as solvent. The stripping phase was composed of 1 M sodium hydroxide (NaOH) and 0.03 M Ethylen-di-amin-tetra-acetate (EDTA). The aqueous feed for the experiments was a synthetic solution, composed of 1000 ppm mercury and 0.025 M HCl (mother solution).

The experiments in this part were executed as follows:
Before the extraction, TOA was salified two times with 1 M HCl to form TOAHCl, with equal of both phases. The contact time was 15 minutes, followed by a settling of 10 minutes. The extraction of mercury was performed by contacting the mother solution with the salified organic phase. The solutions were stirred at approximately 900 rpm. The contact time was 15 minutes and the settling time 20 min.
This was followed by a stripping of the mercury from the loaded organic phase and was carried out with the stripping solution as described above. The other conditions (i.e. stirring speed, contact time and settling time) were the same as for the extraction.
To verify the results of the first stripping, a second stripping of the organic phase was realised under the same conditions as for the first stripping.
For the extraction as well as for the stripping, the volumes of the aqueous and organic phase were the same. Finally the samples were analysed by atomic absorption spectrometry.

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8) For a list of the used substances see **Appendix A** (**page III**)

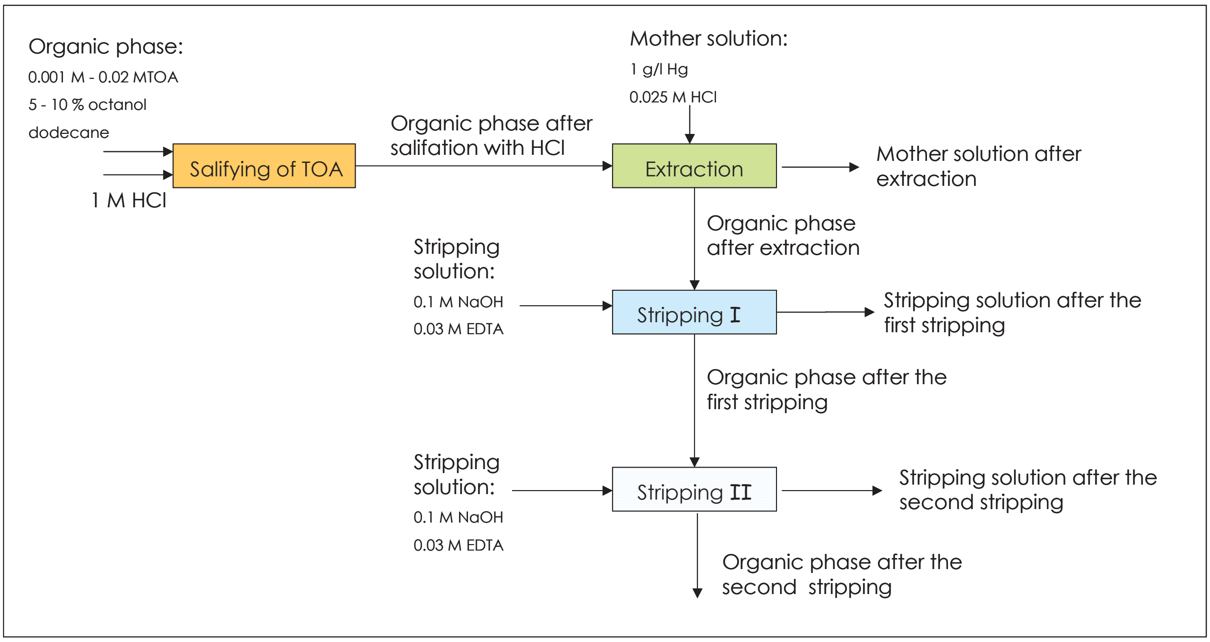

Figure 4: Schema of the solvent extraction experiments

3.1.1.1 Formation of a Third Phase

The third phase formation is a process in which the organic phase splits in two immiscible solutions: One organic phase containing the free extracting agent and the solvent and the other one the complexed extracting agent. This effect often occurs in the presence of amines. To avoid this effect modifiers, such as long chain alcohols, are used. For these experiments octanol was chosen as the modifier.

3.1.2 Optimising of the Emulsion

The aim of these experiments was to optimise the emulsion for the mercury extraction.
Here the organic phase consisted of (1) 0.001 to 0.05 M TOA, as extracting agent, (2) 5 % octanol as modifier, (3) 0.1 to 5 % Abil EM90 as surfactant, and (4) dodecane as solvent.
Abil EM90 (Goldschmidt (Degussa), Germany) [12, p 1-6] is a modified polyether-polysiloxane, which is also found under the name dimethicone copolyol, cetyl PEG/PPG-10/1 dimethicone or CL 530, usually used for the formulation of W/O creams and lotions. It has an HLB-value of approximately 5, is non-ionic and at 25 °C a colourless, odourless viscous liquid, with a specific gravity of 0.941 and a water solubility of 8 mg/L.

The internal aqueous phase was composed of 0.1 to 0.5 M NaOH and 0.04 to 0.16 M EDTA. The external aqueous phase was an acidic solution (0.1 M HCl) with 1000 ppm mercury.

3.1.2.1 Producing the Emulsion

The emulsion was produced by emulsifying the internal aqueous phase in the organic phase with Ultraturrax T25, a dynamic homogeniser.
First, the aqueous phase was dispersed in the organic phase with weak shear stress for approximately three minutes. Afterwards this mixture was emulsified with Ultraturrax at a speed of 8000 to 20500 rpm. The emulsion was then dispersed in the external aqueous phase, and thus the extraction of the metal was realised.

3.1.2.2 Splitting of the Emulsion

To obtain the internal phase the emulsion has to be split. The different methods of splitting are explained in **Chapter 2** (**page 19**). For these experiments, the splitting of the emulsion was executed by adding a chemical reagent as well as by an electric field. The chemical splitting was carried out with octanol as reagent. Emulsion and reagent were stirred for 2 to 3 hours and afterwards the two phases settled for 1 hour. For 20 ml of emulsion approximately 60 ml octanol was necessary.

External and internal aqueous phase were analysed with atomic absorption spectrometry and potentiometric titration.

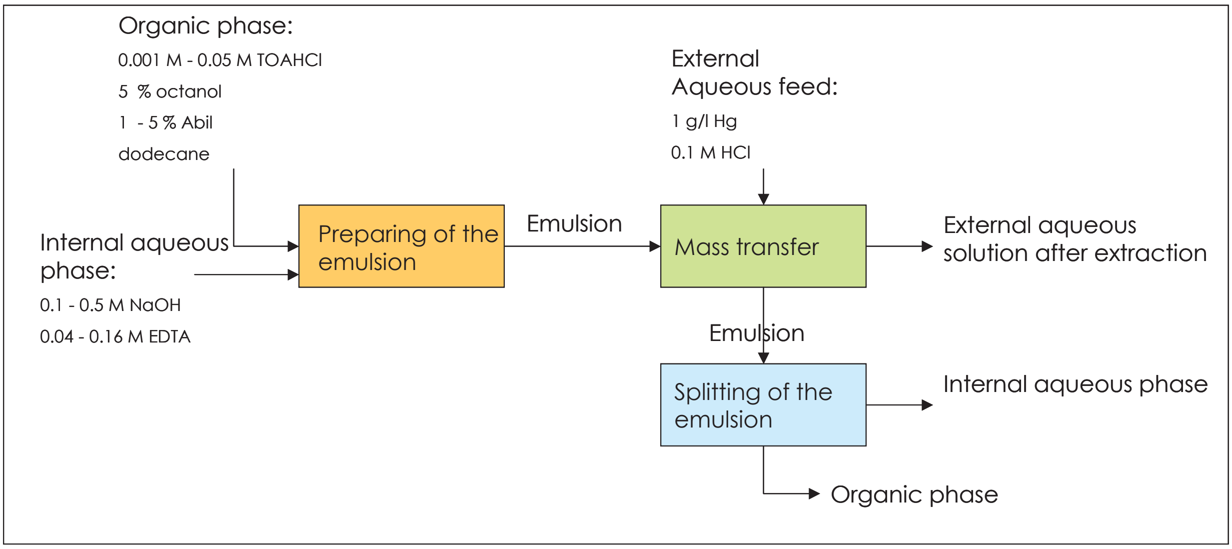

Figure 5: Schema of the emulsion liquid membrane process as executed in the experiments

3.1.3 Continuous Experiments in a Mixer-Settler System

The optimised emulsion was finally tested in continuous experiments in a mixer-settler system. For these experiments the organic phase was composed of:

- 0.01 M TOAHCl,
- 5 % octanol,
- 1 respectively 3 % Abil and
- solved in dodecane

And the aqueous phase consisted of:

- 0.5 M NAOH and
- 0.05 M EDTA

The aqueous feed was a solution of 1000 ppm Hg and 0.1 M HCl. For a detailed description and schematic of these experiments see **Chapter 6** (**page 53**).

3.2 Analysis

3.2.1 Analysis of Mercury

3.2.1.1 Atomic Absorption Spectrometer (AAS)

The atom absorption spectroscopy is a technique for the quantitative analysis of metals and semi-metals. The principle is the analysis of the absorption of light by atoms in a gas phase. The sample is vaporised in a flame. At high temperatures most compounds decompose into atoms in the gas phase. The quantity of the gaseous element in the flame is measured by absorption using ultraviolet or visible radiation.

This technique permits the analysis of mercury in a range of 2 to 400 ppm (at a wavelength of 253.7 nm) [31]. Notice that the analysis is already very unstable between 2 and 5 ppm. Furthermore sodium hydroxide, which is used as stripping agent, disturbs the analysis, because of its very bright orange flame. For these reasons other methods of analysing should be also considered, such as potentiometric titration. For the analysis in this work a Varian SpectrAA-220 was used.

3.2.1.2 Potentiometric Titration [4, p 431-436]; [22]

Titration is also a technique for quantitative analysis. Here the concentration of an unknown reagent is determined by observing the reaction with another reagent (titrant) with a known concentration.

In a potentiometric titration, the concentration of the reagent is found by studying the electrical potential difference between an indicator electrode and a reference electrode, measured as a function of the amount of added titrant.

For the experiments mercury was analysed with a solution of 0.025 M thio-acetamide

(C_2H_5NS)(titrant), diluted in: 0.1 M potassium-bi-phthalate ($KHC_8H_4O_4$)
0.05 M sodium-phosphate (Na_3PO_4) and
0.75 g thymol (to stabilise the solution)
} Solution pH 5

For the analysis, 10 ml of the sample, 20 ml of 0.1 M EDTA, 20 ml 2 M NaOH and 10 ml gelatine (w = 1.2 %) were mixed.

After producing this solution the titration has to be started immediately.

The problem, which normally occurs during the titration of mercury, is the formation of insoluble salts from halides with the mercury. Thus this problem does not occur when mercury is titrated with sulphide ions (except mercury sulphide).
In alkaline solutions thioacetamide is producing sulphide ions. Thus when thioacetamide is added to the solution a precipitation of mercury sulphide occurs very rapidly and a great change in the potential appears. The change in the potential is measured with a silver indicator electrode (Ag/AgCl). To avoid a too fast complexion and thus change in potential, EDTA is added to the solution to complex mercury. This would be not necessary in this case, as the mercury was already complexed with EDTA during the stripping.

The addition of gelatine avoids an agglomeration of the precipitates.

The concentration of Hg is finally determined using the following **Equation (6)**:

$$[Hg] = \frac{V_{C_2H_5NS} * [C_2H_5NS]}{V_{sample}} \tag{6}$$

[Hg]	*Concentration of mercury [ppm]*
S_{ample}	*Volume of the sample*
V_{C2H5NS}	*Volume of added titrant [ml]*
[C_2H_5NS]	*Concentration of the added titrant [ppm]*

The titration was preformed with a “Metrohm 736 GP Titrino” titrameter.

3.2.2 Analysis of Drop Size Distribution

3.2.2.1 Drop Size Distribution (Granulometry) [25, p 9-14]

The drop size distribution of the emulsion was observed with laser diffraction. The principle of this technique is the measuring of the scattered light intensity caused by a drop. The light intensity is measured with semicircular photo diodes. The measured light intensity is converted into a drop size distribution by a curve-fitting program.
An analyser typically consists of a transmitter, a receiver (with the diodes) and a device for the analysis (computer). The analysis range of diameters is normally between 1 to 3000 μm. The main problem of this technique is the appearance of multiple scattering due to high drop

density in the sample; it is often necessary to dilute the emulsion. In this case, for the analysis of the drop size distribution, a Malvern Mastersizer X was used.

The analysis data are normally collected in the form of drop numbers per class size and afterwards arranged into a mathematical representation referred to as the drop size distribution. The Malvern analyser uses the Rosin-Rammler [20]9) distribution (**Equation (7)**):

$$F(D) = 1 - e^{\left[-\left(\frac{D}{N}\right)^{X}\right]} \tag{7}$$

D	*Drop Diameter*
N	*fragment diameter corresponding to the 36,78 percentile of the cumulative probability function*
X	*Rosin-Rammler exponent*

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9) Schick, 1997 [20] according to
Atomisation and Spray drying.
W.R. Marshal, Department of Chemical Engineering. University of Wisconsin Madison,
PP 50-56, 1954,

4 Determining of the Stoechiometric Complex

The object of these experiments was to determine the stoechiometric coefficient in the extracted complex and the optimal concentration of the extracting agent

4.1 Results of Solvent Extraction Experiments

The execution of the experiments and the experimental conditions are described in **Chapter 3** (**page 25**). In this chapter the results are shown.

Solvent extraction of mercury was examined in a concentration range of 0.001 to 0.02 M TOA. The composition of the stripping solution was not varied during the experiments.

The mass balance for the extraction and stripping can be written as (**Equation (8)** and **(9)**):

$$[Hg]_0 * V_0 = [Hg]_{aq} * V_{aq} + [Hg]_{org} * V_{org} \tag{8}$$

$$V_0 = V_{Ext} = V_{org} \Rightarrow [Hg]_0 = [Hg]_{aq} + [Hg]_{org}. \tag{9}$$

$[Hg]_0$	*Concentration of mercury in the mother solution [mg/l]*
V_0	*Volume of the mother solution [ml]*
$[Hg]_{aq}$	*Concentration of mercury in the aqueous phase after extraction [mg/l]*
V_{aq}	*Volume of the aqueous phase after extraction [ml]*
$[Hg]_{org}$	*Concentration of mercury in the organic phase [mg/l]; was measured after stripping as seen before*
V_{org}	*Volume of the organic phase [ml]*

The efficiency of the extraction (**Equation 10**) is found as:

$$Efficiency[\%] = \frac{[Hg]_{org}}{[Hg]_0} * \frac{V_{org}}{V_0} * 100 \tag{10}$$

The distribution coefficient D (**Equation 11**) can be described as:

$$D = \frac{[Hg]_{org}}{[Hg]_{aq}} \tag{11}$$

The results of mercury solvent extraction can be seen in **Table 1** and **Figure 6** on the next page.

Table 1: Results of Solvent Extraction

[TOA]	[TOA]	$[Hg]_0$	$[Hg]_{aq}$	$[Hg]_{org}$	$[Hg]_{overall}$	D	Efficiency	Error
[mol/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[]	[%]	[%]
0,001	353,66	940	957	112	1069	0,12	11,90	13,71
0,002	707,32	940	727	209	936	0,29	22,23	0,43
0,004	1414,64	940	478	444	922	0,93	47,23	1,91
0,005	1768,30	940	454	558	1012	1,23	59,36	7,66
0,007	2475,62	940	256	636	892	2,48	67,66	5,11
0,008	2829,28	940	188	797	985	4,24	84,79	4,79
0,01	3536,60	940	93	764	857	8,21	81,24	8,86
0,012	4243,92	940	51	879	930	17,24	93,51	1,06
0,014	4951,24	940	26	982	1008	37,77	104,47	7,23
0,015	5304,90	940	19	944	963	49,68	100,43	2,45
0,016	5658,56	940	11	897	908	81,55	95,43	3,40
0,018	6365,88	940	11	947	958	86,09	100,74	1,91
0,02	7073,20	940	6	879	885	146,50	93,51	5,85

[TOA] *Concentration of TOA in [mol/l] respectively in [mg/l]*

$[Hg]_{overall}$ *is the sum of $[Hg]_{aq}$ and $[Hg]_{org}$*

The error (**Equation 12**) of the mass balance in [%] is defined by:

$$Error = Abs\left\{\left[\left(\frac{100}{[Hg]_0}\right) * [Hg]_{overall}\right] - 100\right\} \quad (12)$$

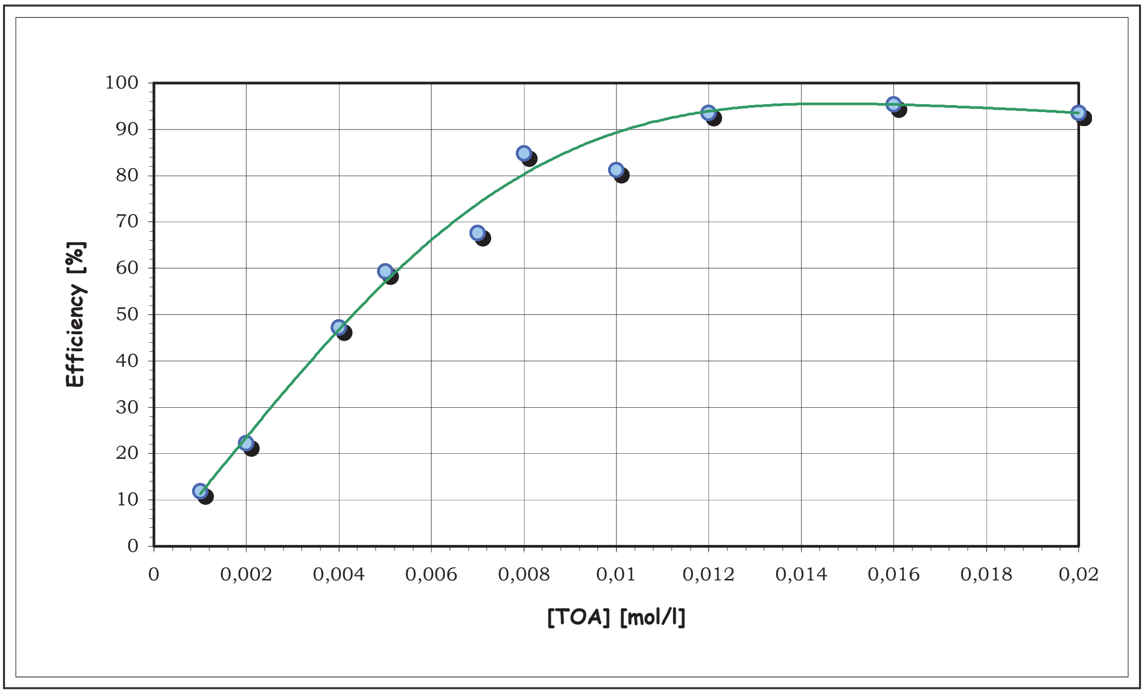

Figure 6: Efficiency of the extraction of mercury with different TOA concentrations

Observing the **Table 1** and **Figure 6** it can be said that the optimal concentration for the extraction is approximately 0.01 – 0.012 M TOA.

4.2 Reactions:

Before the extraction is realised, TOA is salified with 1 M HCl following the reaction (**Reaction (13)**):

$$\overline{TOA} + HCl \Leftrightarrow \overline{TOAHCl} \tag{13}$$

4.2.1 Extraction of Mercury

The extraction of mercury is proceeded by the reaction written beneath (**Reaction (14)**), depending on the stoechiometric coefficient n:

$$Hg^{2+} + 2Cl^{-} + n\overline{TOAHCl} \Leftrightarrow \overline{(TOAHCl)_n HgCl_2} \tag{14}$$

It is known that amines form with metals ion pairs in the organic phase, so it is more realistic to write (**Reaction (15a)** and **(15b)**):

If $n = 1$ $Hg^{2+} + 2Cl^{-} + \overline{TOAHCl} \Leftrightarrow \overline{(TOAH)HgCl_3}$ (15a)

If $n = 2$ $Hg^{2+} + 2Cl^{-} + 2\overline{TOAHCl} \Leftrightarrow \overline{(TOAH)_2 HgCl_4}$ (15b)

In addition in the aqueous phase, it is necessary to take into account the complexation of Hg^{2+} by Cl^- (**Reaction (16)**):

$$Hg^{2+} + xCl^{-} \Leftrightarrow HgCl_x^{(2-x)+} \tag{16}$$

Then in the aqueous solution (**Equation (17)**):

$$[Hg]_{aq} = [Hg^{2+}] + [HgCl^{+}] + [HgCl_2] + [HgCl_3{}^{-}] + [HgCl_4{}^{2-}] + ... \tag{17}$$

This can be also written as (**Equation (18)**):

$$[Hg]_{aq} = [Hg^{2+}] + \underbrace{(1 + \beta_1[Cl^{-}] + \beta_2[Cl^{-}]^2 + ...)}_{\alpha} \tag{18}$$

β_x is the constant of the reaction.

α depends only on Cl^- concentration.

4.2.2 Reactions of Stripping

During stripping NaOH reacts with the formed complex (**Reaction (19a)** and **(19b)**).

$$\overline{TOAHCl.HgCl_3} + OH^{-} \Leftrightarrow \overline{TOA} + Hg^{2+} + 3Cl^{-} + H_2O \tag{19a}$$

Or

$$\overline{(TOAH)_2HgCl_4} + 2OH^- \Leftrightarrow \overline{2TOA} + Hg^{2+} + 4Cl^- + 2H_2O \qquad (19b)$$

depending on the stoechiometry.

At the same time EDTA is forming a complex with mercury (**Reaction (20)**).

$$Hg^{2+} + EDTA^{4-} \Rightarrow Hg(EDTA)^{2-} \qquad (20)$$

The actually appearing stoechiometric complex is not known and has to be determined. Here the stoechiometric coefficient is ascertained with slope analysis. This can be seen in the next paragraph.

4.3 Slope Analysis Method

With the equilibrium constant for the extraction **Reaction (22)** and the distribution coefficient **Equation (11)** the stoechiometric coefficient (n) can be identified (**Equation (24)**).

$$K_{eq} = \frac{[Hg]_{org}}{[Hg^{2+}][Cl^-]\overline{[TOAHCl]}^n} \qquad (21)$$

$$K_{eq} = \frac{[Hg]_{org}\,\alpha}{[Hg]_{aq}[Cl^-]\overline{[TOAHCl]}^n} \qquad (22)$$

$$D = \frac{[Hg]_{org}}{[Hg]_{aq}} \qquad (11)$$

Then $\Rightarrow$ $$D = \frac{K_{eq}[Cl^-]^2\overline{[TOAHCl]}^n}{\alpha} \qquad (23)$$

$$\Rightarrow \log D = n\log\overline{[TOAHCl]} + etc.... \qquad (24)$$

In this equation $\overline{[TOAHCl]}$ is the concentration of free salified extractant, calculated as (**Equation (25)**):

$$\overline{[TOAHCl]}_{free} = \overline{[TOAHCl]}_{total} + n[Hg]_{org} \qquad (25)$$

It is then necessary to make a hypothesis on n before calculating $\overline{[TOAHCl]}_{free}$, and plotting $\log D$ against $\log\overline{[TOAHCl]}_{free}$. The assumption on n will be correct if the slope found for the variation of $\log D$ is the same.

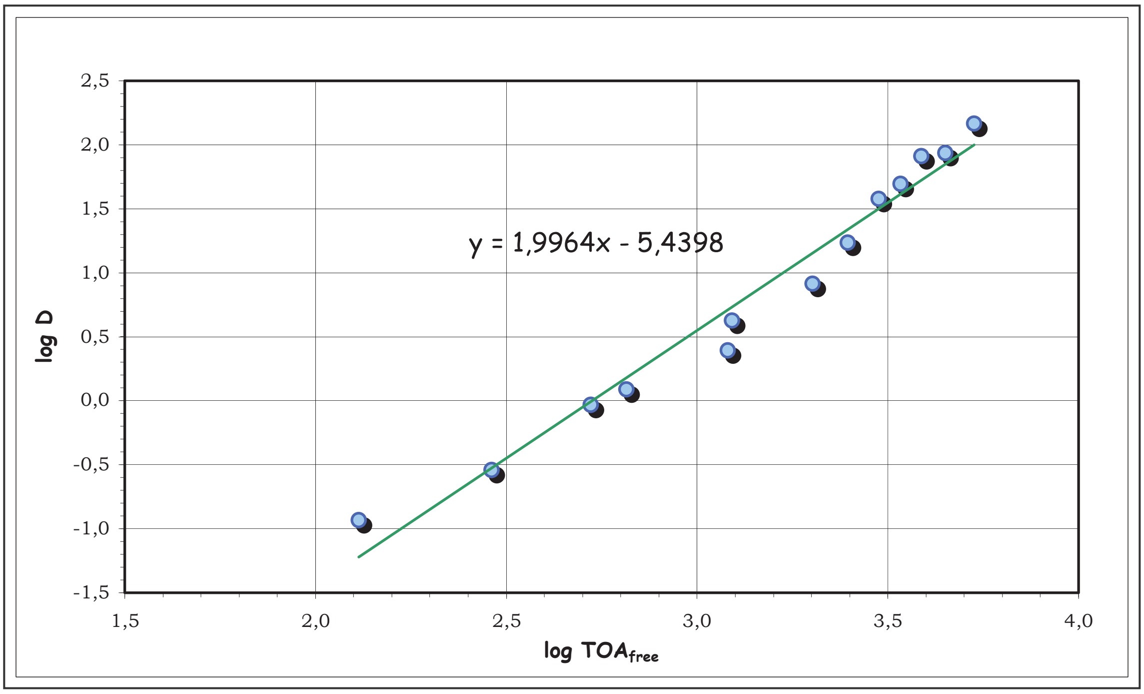

Figure 7: Determining of the stoechiometric coefficient with slope analysis

According to the **Figure 7** $n = 1.996 \cong 2$

Thus, the extraction follows the **Reaction (15b)**:

$$2Cl^- + 2\overline{TOAHCl} + Hg^{2+} \Leftrightarrow \overline{HgCl_4(TOAH)_2} \tag{15b}$$

And the stripping reaction, **Reaction (19b)**:

$$\overline{(TOAH)_2HgCl_4} + 2OH^- \Leftrightarrow \overline{TOA} + Hg^{2+} + 4Cl^- + 2H_2O \tag{19b}$$

5 Optimising of the Emulsion

The objective of these experiments is, as described in **Chapter 3** (**page 26**), the optimising of an emulsion for the extraction of mercury. Here, as in the solvent extraction experiments, an extraction in an acidic environment (HCl) was performed, with TOA as extractant, octanol as modifier and dodecane as solvent.
As octanol can break the emulsion a minimum amount of octanol has to be used. Diouf [5] found that for the described conditions the possible minimum of octanol is 5%.

For the internal phase, just as for solvent extraction, NaOH and EDTA were chosen as stripping agents. The actual production of the emulsion was described in **Chapter 3** (**page 26**)

5.1 Optimising of the Organic Phase

The organic phase of the emulsion was first optimised. As previously stated the organic phase consists of an extracting agent (TOA), a solvent (dodecane), a modifier (octanol) and a surfactant (Abil EM90). It is assumed that the amount of octanol is already optimised at 5 %.
For the beginning the following conditions were chosen: For the organic phase: 0.05 M TOAHCl, 5 % octanol, and 5 % Abil in dodecane. And for the internal phase: 0.5 M NaOH and 0.16 M EDTA

First the parameters for the emulsion production have to be chosen. Several emulsions were produced, whereby the speed (8000, 9500, 13500 and 20500 rpm) and time (between 5 and 45 min) for emulsifying were varied. The emulsion was produced with a ratio organic phase to internal phase of 1 to 1. Then these emulsions were examined by analysis of the drop size distribution measured by laser diffraction.

A speed of 8000 rpm is absolutely sufficient for an adequate even drop size distribution, with adequate small mean diameter. An agitation period of 20 minutes seems to be optimal; at this point the drop size distribution is the most uniform. For a shorter period of agitation the distribution is not even, which means greater drop diameter and thus less stability. If on the contrary a too long agitation time is chosen the emulsion can break up again. Therefore the emulsions are produced at a speed of 8000 rpm with agitation period of 20 minutes. During the emulsifying the emulsion was cooled with ice, due to heat build-up. After determining these parameters the amount of surfactant was optimised.

5.1.1 Surfactant

The surfactant has not only an effect on the stability of the emulsion, but also on the efficiency of the extraction and the amount of osmosis.

5.1.1.1 Long Time Stability

First long time stability (without an extraction) was tested. For this purpose several emulsions with the same conditions as mentioned above, were produced, whereby the amount of the surfactant was varied between 1 and 4%. The long time stability was examined again by analysing the drop size distribution. A relative small breakdown of the emulsions with only 1 and 2 % surfactant could already be noticed after only one day.

Because of the large interfacial area, the mass transfer during extraction with an emulsion is faster than during a solvent extraction; therefore extreme long time stability is not necessary. The emulsion has to be stable during the process thus 1 % surfactant was selected. As can be seen in **Figure 8** and **Figure 9** this amount is absolutely sufficient.

5.1.1.2 Efficiency of the Extraction

In the following the influence on the efficiency, of the extraction was tested. The extraction of mercury was accomplished in form of kinetics experiments. The surfactant was varied between 0.1 and 5 %, the extractant was either 0.05 M or 0.01 M TOA, and all the other parameters were the same as before. The aqueous feed (external phase) was a synthetic acidic solution (0.1 M HCl) with 1000 ppm Hg. The ratio between the aqueous phase and the emulsion during extraction was 2:1. This means a concentration of mercury of 4 times in the internal phase (with ratio organic phase to internal phase of 1 to 1). The results can be seen in **Figure 8**; **Figure 9** shows the change of pH during extraction.

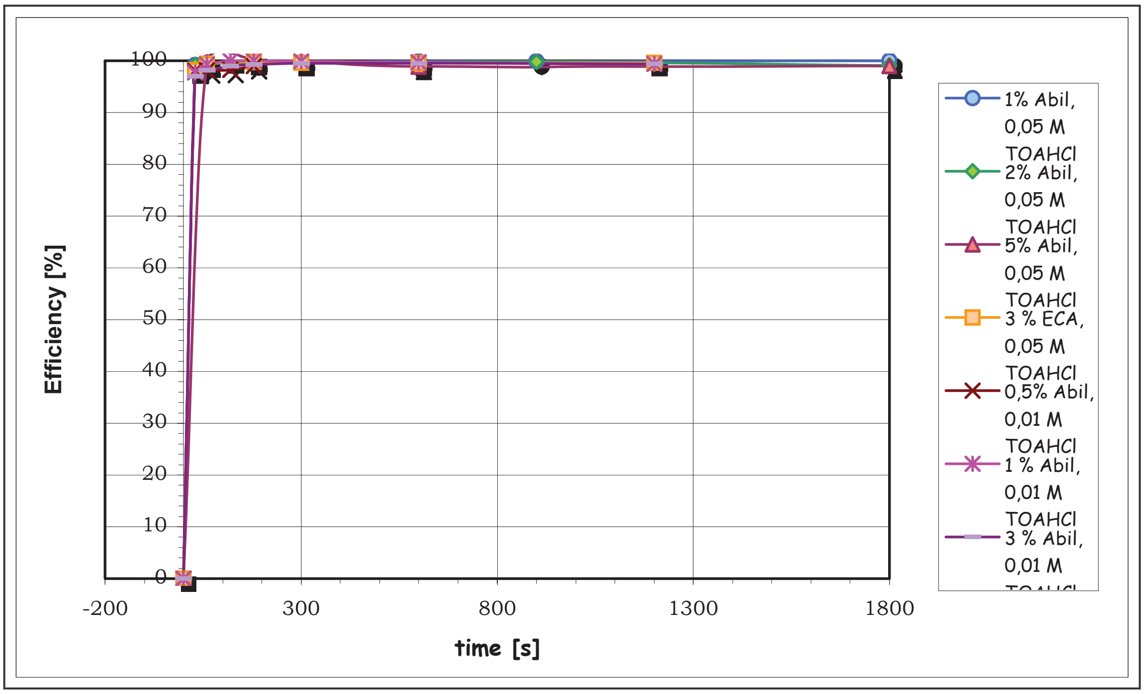

Figure 8: Comparison of the efficiency of the extraction of mercury with different amount of surfactant.

It can be seen that the extraction is already completed after approximately 2 min. (**Figure 8**). It was also observed that the amount of surfactant has practically no influence on the efficiency of the extraction.

For the results of these test series the following was noticed:

0.1 % Abil turned out to be an inadequate concentration and the emulsion was already broken during the kinetics experiments. (Due to this, there is not any data available). With 0.5 % surfactant, an extraction was possible; but the stability was not sufficient during the experiment. (After 30 min the breakdown was more than 30 %). For the experiments with 1 – 5 % surfactant, the results were more or less the same and the stability also by 1 % Abil was still sufficient, as can be seen by observing pH and what was later confirmed by measuring the tracer (Na) in the external phase. Therefore 1 % Abil was chosen as the optimal surfactant concentration.

5.1.1.3 Examination of the Change of the pH

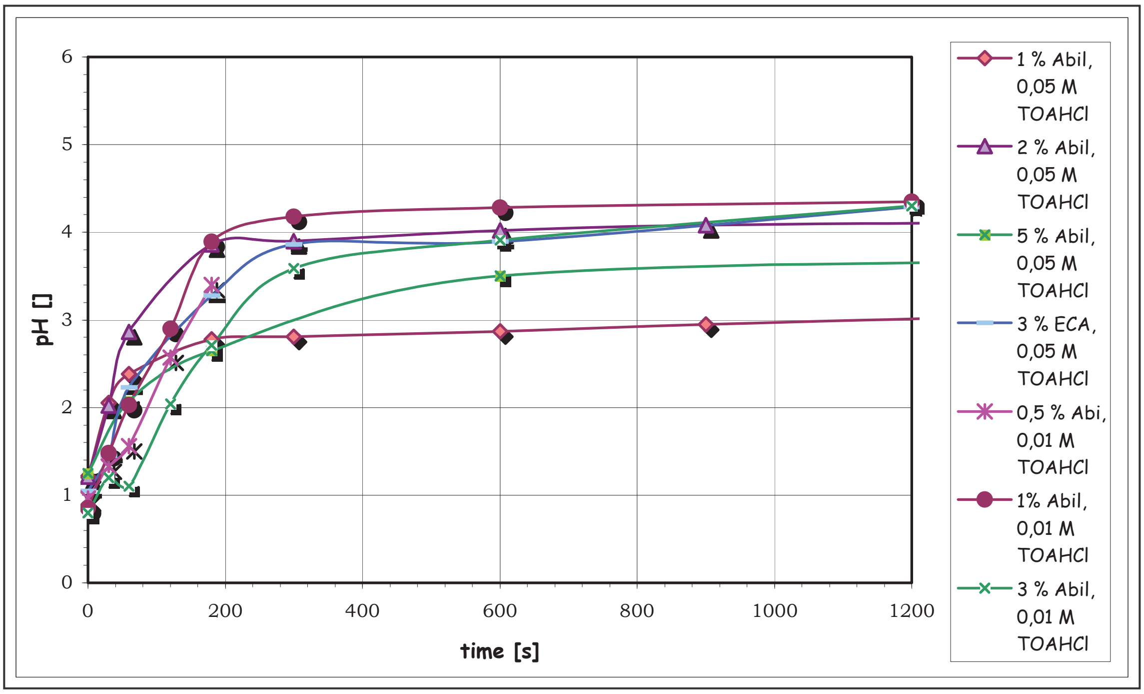

Figure 9: Comparison of the change of the pH during the extraction of mercury with different amounts of surfactant.

An increase of the external pH (in the same manner for all surfactant concentrations) during the extraction was noticed, as can be seen in **Figure 9**. It was questioned if this changing is a result of the exchange of mercury in the internal phase or if there are other reasons. As can be seen in **Appendix B** (**page II**) the pH increases in the same way even though no mercury is in the feed.

The reasons for the decrease in pH are:

- the co-extraction of protons with mercury (negligible),
- the concomitant extraction of HCl, and
- the breakdown of the emulsion.

While observing the pH of the internal phase it was noticed that it decreases with time; this is the result of the exhausting of OH^- due to the transport of H^+ to the internal phase. (For the reactions see **page 47**). It was also noticed that the efficiency decreases with pH.

5.1.1.4 Osmosis

The transport of water molecules into the internal phase is undesirable because of the resulting dilution of the internal phase. There are several evidences for osmosis during the kinetics experiments.

- An increase in the drop diameter, which was observed by analysing the drop size distribution by laser diffraction.

- A swelling of the emulsion, by means of an enlarging in the volume of the emulsion, respectively of the internal phase

The osmosis is an effect, which occurs because of the differences in the ionic strength between the external and internal phase.

Diouf 2001/2002 [5] tried to find a solution for this problem by adding certain salts (NaCl, NH_4Cl) to the external phase. He observed a decrease of osmosis, but at the same time a decrease of the efficiency of extraction.

The effect of osmosis increases with time but is rather slow. Since in this study the reaction is very fast and an optimum of extraction is already reached after 3 min, the problem of osmosis was neglected.

5.1.2 Extracting Agent

After the surfactant concentration was chosen, the amount of extracting agent (TOA) was optimised. For these experiments the same conditions as before were selected, only the amount of TOA in the organic phase was varied.
For the external aqueous phase:

- 1000 ppm Hg
- 0.1 M HCl

Organic phase:

- 0.001 – 0.05 M TOA
- 1 % Abil
- 5 % octanol
- in dodecane

Internal phase:

- 0.5 M NaOH
- 0.16 M EDTA

As previously these experiments were performed in form of kinetics experiments to examine the behaviour of the emulsion with time. The results can be seen on **page 43.**
Before the optimal extracting agent concentration could be chosen, some problems during the analysing had to be solved.

5.1.2.1 Problems during the Analysis of the Internal Phase

While optimising the organic phase, the efficiency of stripping was also examined, by measuring the mercury concentration in the internal phase. Thereby a concentration of mercury in the internal phase up to 8 times greater than the initial concentration was noticed (see **Figure 10**) against the expected value of a concentration of maximal 4 times, while there are no significant volume changes.

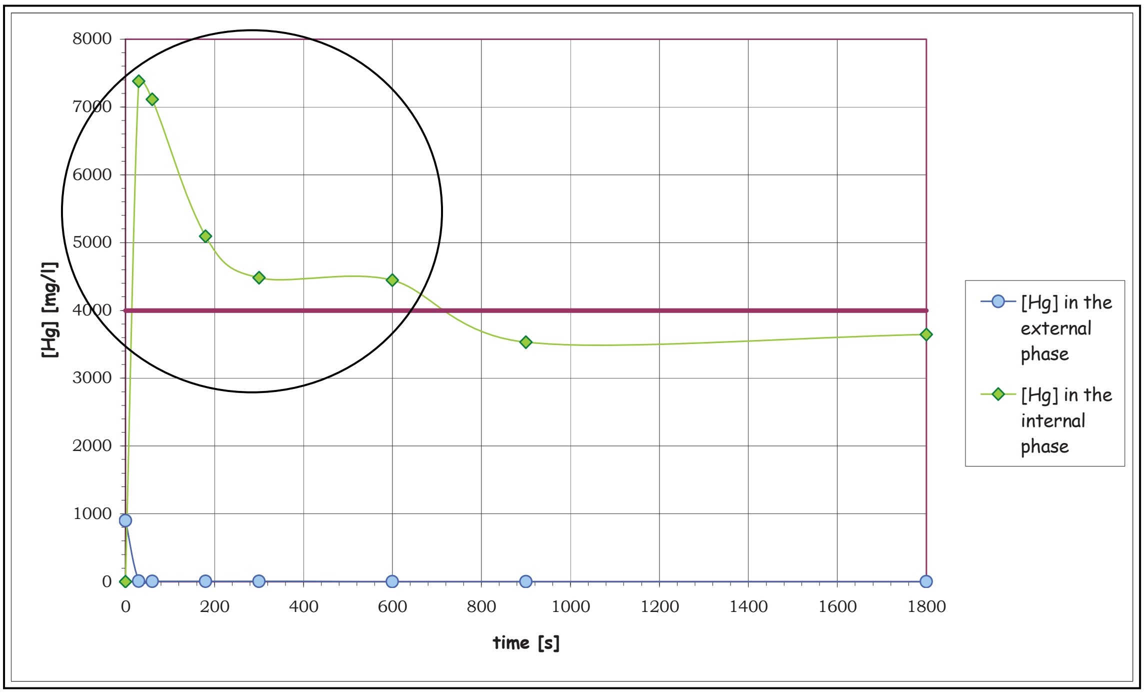

Figure 10: Problems during the analysing of the internal phase

Several possible sources of error for this concentration were identified.

- Volume of the samples: Only a small sample (2-5 mL) of the internal phase could be obtained. (A greater sample was technically difficult to withdraw). Because of that a partial evaporation, which occurs after a certain time, has greater influence on the concentration of the sample. To avoid this the sample has to be analysed immediately after splitting.
- Dilution: Even a small error in dilution, gives a great difference in the analysed concentration, due to the high concentration factor (1:100). Thus for the analysis, as a control, more than one dilution of each sample was produced.

Also after eliminating these possible sources of error, the aforementioned problem still occurred. So other sources of error were searched.

5.1.2.2 Measuring of the Concentration with Potentiometric Titration

The analysis method was identified as another possible source of error. As mentioned, the samples were analysed by atomic absorption spectrometry. For eliminating this possible problem several samples were both analysed with the atomic absorption spectrometry and also potentiometric titration.

Mercury was titrated with thioacetamide (C_2H_5NS).

For the titration, the samples of the internal phase of emulsion E32 an E33 with the composition:

Organic phase:

- 0.05 M TOAHCl (E32) respectively 0.01 M TOAHCl for E33
- 5 % octanol
- 1 % Abil
- in dodecane

Internal phase:

- 0.5 M NaOH
- 0.16 M EDTA was analysed

After performing a kinetics experiment, as described before, the emulsions were split and the internal phases both by atomic absorption spectrometry and potentiometric titration were analysed. The results of potentiometric titration and the atomic absorption spectrometry see **Table 2** and **3**: (For the titration curves see **Appendix C** (**page III**))

Table 2: Potentiometric Titration of the internal phase (E33)

time	$[Hg]_{int}$	$[Hg]_{Titration1}$	$[Hg]_{Titration2}$	$Aberration_{Titration1}$	$Aberretion_{Titration2}$
[s]	[mg/l]	[mg/l]	[mg/l]	[%]	[%]
120	5150,50	4038,07	3496,28	21,60	32,12
300	4895,56	4847,66	5070,30	0,98	3,57
600	4998,89	5002,55	-	0,07	-

Table 3: Potentiometric Titration of the internal phase (E32)

time	$[Hg]_{int}$	$[Hg]_{Titration1}$	$Aberration_{Titration1}$
[s]	[mg/l]	[mg/l]	[%]
180	5001,98	4951,18	1,02
600	4199,92	3980,05	5,24
1200	2759,67	2824,00	2,33

As can be seen in the **Tables 2** and **3,** the differences between the results of the two methods are acceptable. The analysis with atomic absorption spectrometry thus can be eliminated as a possible source of error. Due to the complexity of titration, the analysis with atomic absorption spectroscopy was preferred, for the following experiments.

5.1.2.3 Splitting of the Emulsion

A satisfactory explanation for the high concentration values of mercury in the internal phase was not yet found. Finally the splitting method of the emulsion was detected as another possible source of error. Until now the emulsion splitting was carried out with a chemical splitting reagent (octanol). An awkward disadvantage, as mentioned in **Chapter 3** (**page 27**), is that a great amount of octanol (for 20 mL emulsion approximately 60 mL octanol) is necessary for effective splitting and besides that this method is very time consuming (2 to 3 hours of stirring and 1 to 2 hour of settling).
It was observed that because of the great difference between the volume of the organic and aqueous phase, a reduction of the volume of the aqueous phase occurs, due to solubilisation of water in octanol. (This effect is even higher, if the aqueous solution is basic.) Then even though a swelling of the emulsion was noticed, the volume of the obtained sample was less than the theoretically assumed quantity.

Thus another method was used for splitting the emulsion – electro-coalescence was chosen to be the method of choice. With this technique, splitting was not only carried out faster (already very good splitting results after 15 minutes), the analysed concentration of the internal phase was also in the expected limit. Thus, for the following experiments the emulsion was split by an electric field.

5.1.2.4 Calculation of the Amount of Breakage of the Emulsion

The stability of the emulsion is an important factor for the efficiency of the process. A large breakdown of the emulsion during the extraction means not only a back-transfer of mercury in the aqueous feed, but also an additional contamination of the waste water stream with constituent parts of the emulsion.

As mentioned in **Chapter 2** (**page 24**), there one possibility to determine breakdown is by using a tracer. This is analysing the concentration of a compound in the external phase, which is normally found in the internal phase. In the experiments that were carried out, sodium was used as tracer. By measuring the concentration of sodium in the external phase by atomic absorption spectrometry, the breakage was determined by using **Equation (26)**.

$$B[\%] = \frac{[Na]_{ext}[ppm] * V_{ext} * 100}{[Na]_{int}[ppm] * V_{\text{int}}} \qquad (26)$$

B[%]	*Breakdown of the emulsion [%]*
$[Na]_{ext}$	*Measured concentration of sodium in the extern phase [ppm]*
V_{ext}	*Volume of the extern phase [ml]*
$[Na]_{int}$	*Concentration of sodium in the internal phase [ppm]*
V_{int}	*The initial Volume of the intern phase [ml]*

Although the analysis of sodium with AAS causes some problems, a good approximation for the breakdown can be achieved. (See for example **Figure 12** or **Figure 20**)

5.1.2.5 Optimisation of the Extracting Agent

As explained on **page 36,** the efficiency of extraction was examined while varying concentrations of TOA between 0.001 M and 0.05 M.
The results can be seen in **Figure 11**:

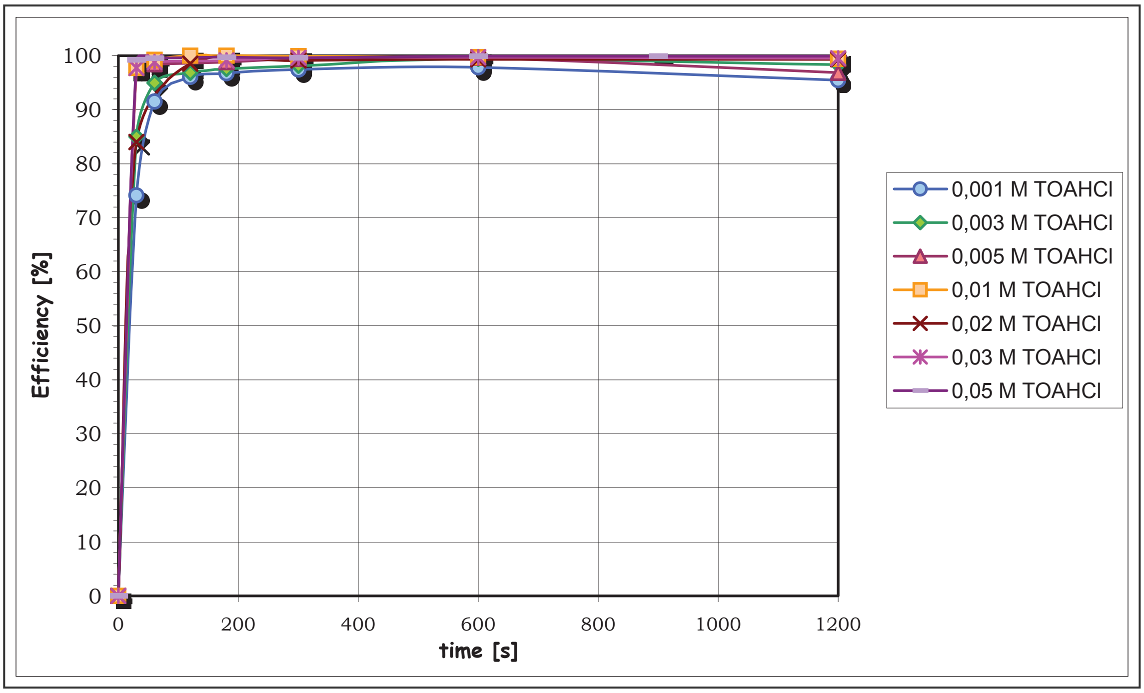

Figure 11: Comparison of the efficiency of the extraction of mercury with different concentrations of TOA

Observing the diagram above it can be seen that the efficiency of extraction between 0.05 M TOA and 0.01 M TOA is more or less the same. After decreasing the concentration of TOA to 0.005 M and smaller values the kinetic of extraction slows down and the efficiency is decreasing. Therefore 0.01 M TOA was chosen to be the optimal concentration for the emulsion.

Recapitulating the chosen optimal parameters for the organic phase are the following:
Organic phase:

- 0.01 M TOAHCl
- 5 % octanol
- 1 % Abil EM90
- in dodecane

The composition of the internal phase is still:

- 0.5 M NaOH
- 0.16 M EDTA

The results of a kinetics experiments with this composition can be seen in **Figure 12**:

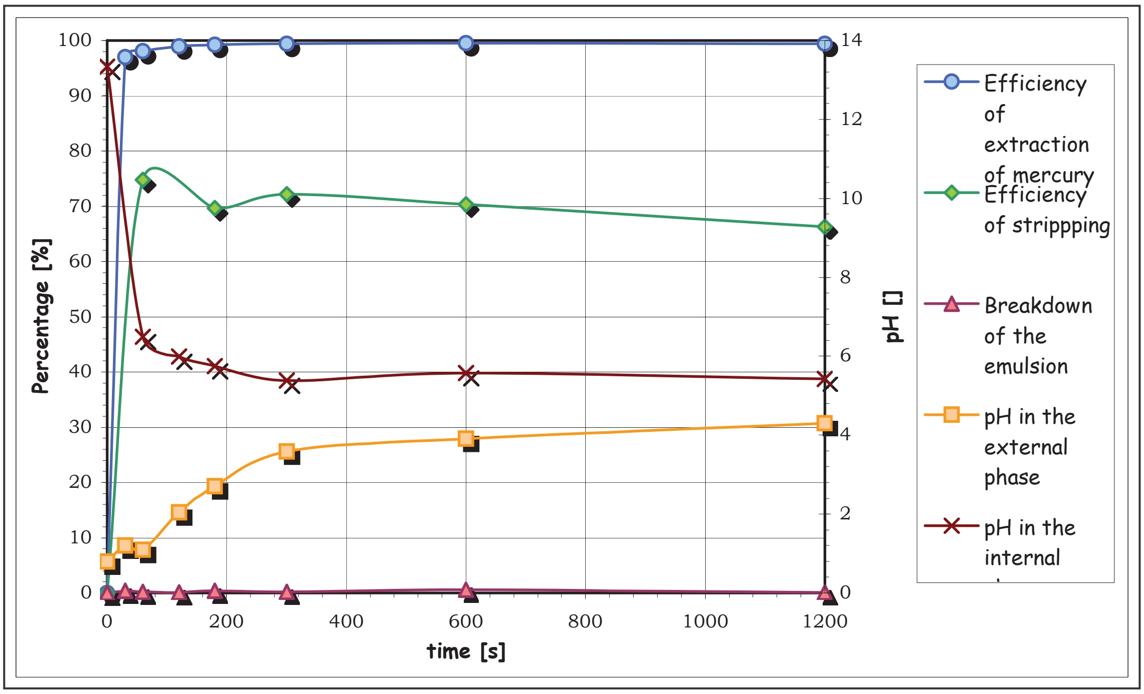

Figure 12: Kinetics with an emulsion with 0.01 M TOAHCl as extracting agent

The efficiency of the stripping is determined by calculating the ratio of the quantity of mercury in the internal phase to the initial quantity. This efficiency takes into account both extraction and stripping. Also, a volume ratio of 4 between the external and the internal phase was assumed, without taking in account a change of the volume due to breakdown or osmosis. As can be seen in **Figure 12** the efficiency of extraction is nearly 100 %; the efficiency of stripping is only about 75 %. It is necessary to understand the cause of this apparent lack of stripping.

5.1.2.6 Analysing of the Amount of Mercury in the Organic Phase

It is possible that a certain amount of mercury has not reached the internal phase, but is still in the organic phase, because the extraction is very fast. To confirm this assumption the organic phase was analysed. After performing an extraction and splitting of the emulsion, the organic phase was stripped. A solution with 1 M NaOH and 0.03 M EDTA was used as stripping phase. Under the conditions:

- Volume$_{aqueous}$ = Volume$_{organic}$
- Contact : 15 min
- Settling : 20 min

This stripping was performed two times, whereby the second time no mercury could be analysed in the stripping phase. The result of the first stripping can be seen in **Figure 13**

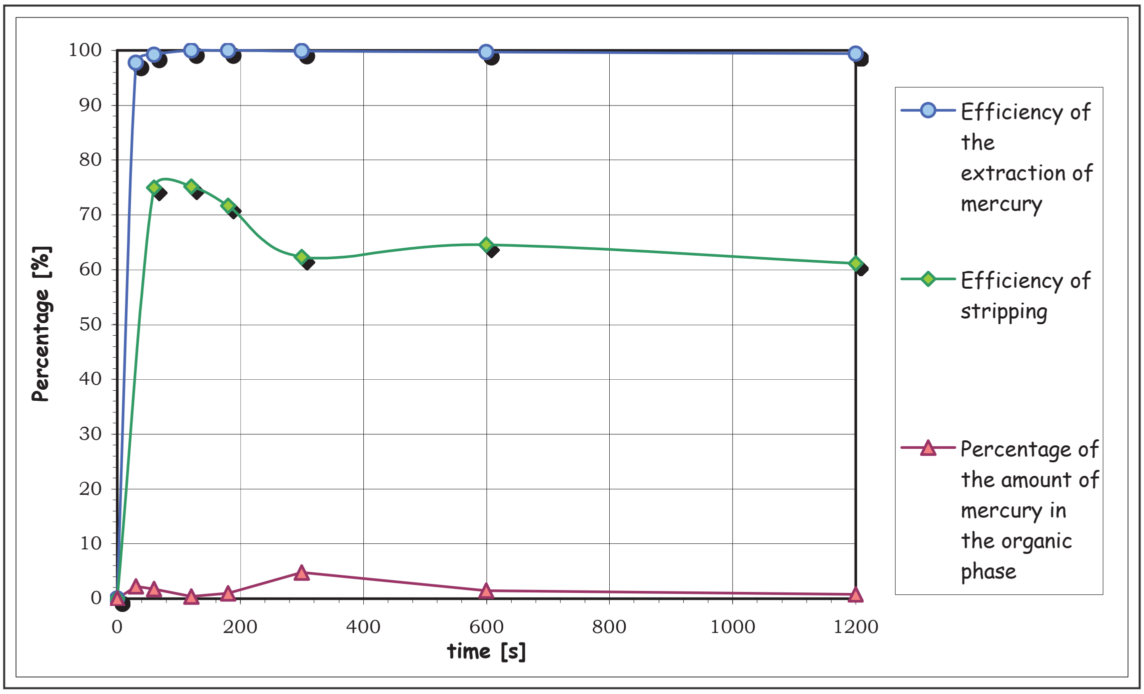

Figure 13: Analysing of the concentration of mercury in the organic phase

As can be seen in the diagram the amount of mercury in the organic phase is negligible.

5.2 Optimising of the Internal Phase

After optimising the organic phase the composition of the internal phase was examined. The composition of the organic phase was fixed with:

- 0.01 M TOAHCl
- 5 % octanol
- 1 % Abil
- in dodecane

First the effect on the efficiency of extraction and stripping, while varying the concentration of EDTA in the stripping phase, was tested. The results can be seen in **Figure 14**:

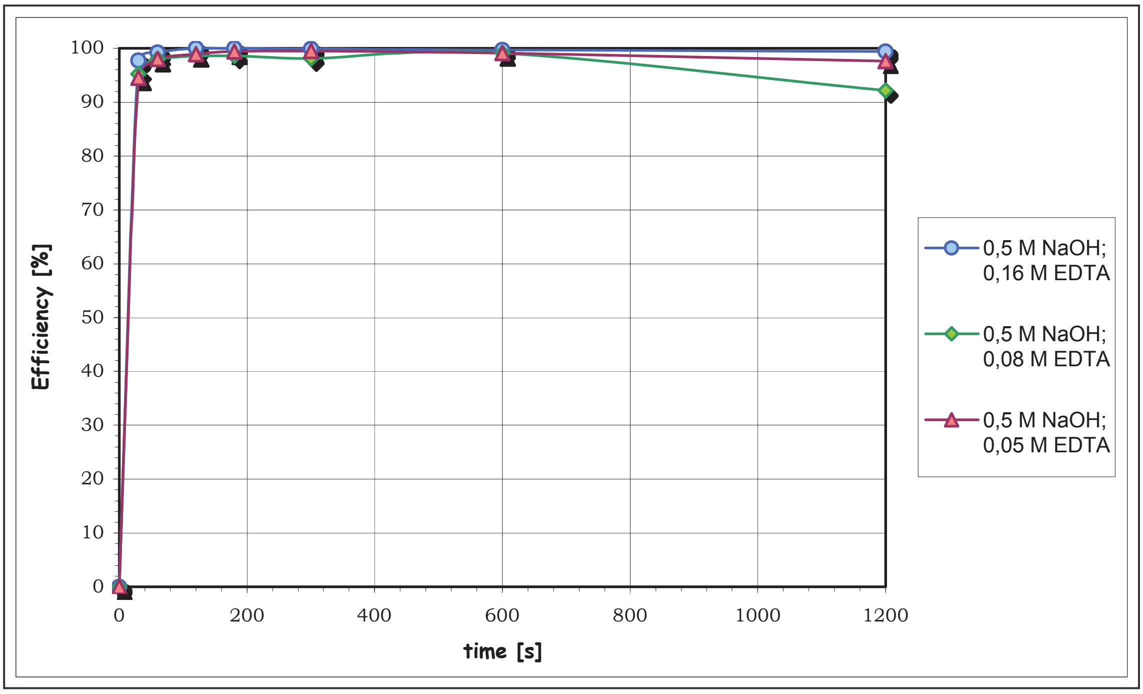

Figure 14: Efficiency of the extraction while varying the concentration of EDTA

It was observed that the extraction is most efficient with the composition of the internal phase 0.5 M NaOH, 0.16 M EDTA as was already used in the previous experiments. The efficiency of the extraction with the other compositions is lower.

The efficiency of stripping is calculated as the ratio of mercury concentrations in the internal and the aqueous phase. The theoretical ratio is 4. Normally a smaller ratio can occur, because the main reason of volume changes of the emulsion is swelling. A ratio smaller than 4 indicates a lack of stripping efficiency and/or swelling of the emulsion. A higher ratio than 4 would be also possible, due to breakage of emulsion.

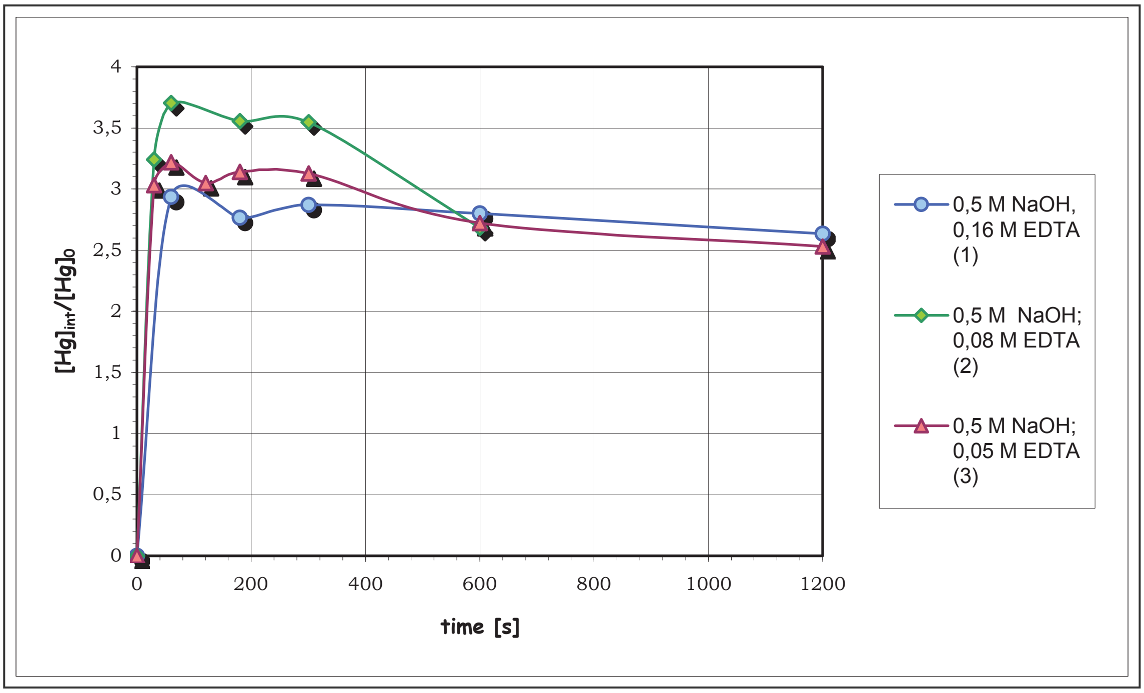

Figure 15: Efficiency of the stripping while varying the concentration of EDTA

Swelling does not occur in the first moments of the contact, so it can be assumed that for the first hundred seconds the measured values correspond with the real stripping efficiency. The further decrease is due to emulsion swelling.

The emulsion with 0.08 M EDTA shows the best stripping efficiency, whereas the emulsion with 0.16 M EDTA is the less efficient. These results are explained by the initial composition of the internal phase. EDTA is added to sodium hydroxide as its disodium salt Na_2H_2A, containing two protons, so the actual initial concentration of hydroxide is lower: (See **Table 4**)

Table 4: Concentration of OH- in the internal phase by varying EDTA concentrations[10)]

	1	2	3
$NaOH_{initial}$ [mol/l]	0,5	0,5	0,5
EDTA [mol/l]	0,16	0,08	0,05
$OH^{-}_{residual}$ [mol/l]	0,18	0,34	0,4

The rather deceiving results observed with 0.16 M EDTA can be explained by the low residual hydroxide concentration. In both other cases the OH^- concentration is sufficient but the stripping is more effective with the higher EDTA concentration, thanks to a better complexation.

All these conclusions are confirmed by the **Reaction (27)**, **(28)** and **(29)**:

$$\overline{(TOAH)_2HgCl_4} + 2\quad OH^- \leftrightarrow \overline{2TOA} + H_2O + Hg^{2+} + 4\quad Cl^- \qquad (27)$$

$$Hg^{2+} + A^{4-} \leftrightarrow HgA^{2-} \qquad (28)$$

$$\overline{TOAHCl} + OH^- \leftrightarrow \overline{TOA} + H_2O + Cl^- \qquad (29)$$

The complexation of mercury by EDTA does not occur at pH under 6, because of the protonation of A.
This can be confirmed by examining the complexing constant (stability constant) for the $HgEDTA^{2-}$ complex (**Equation (30)**):

$$K_{comp} = \frac{[HgEDTA^{2-}]}{[Hg^{2+}]*[EDTA^{4-}]} = 10^{-21,8} \qquad (30)$$

Together with the four acid constants and the EDTA and Hg concentrations, the amount of complexed Hg can be determined (**Equation (31)** to **(36)**):

$$K_{a1} = \frac{[H_3EDTA^-]*[H^+]}{[H_4EDTA]} = 10^{-2} \qquad (31)$$

$$K_{a2} = \frac{[H_2EDTA^{2-}]*[H^+]}{[H_3EDTA^-]} = 10^{-2,67} \qquad (32)$$

[10)] Numbers in the table correspond with the numbers in the **Figure 15**

$$K_{a3} = \frac{[HEDTA^{3-}]*[H^+]}{[H_2EDTA^{2-}]} = 10^{-6,16} \tag{33}$$

$$K_{a4} = \frac{[EDTA^{4-}]*[H^+]}{[HEDTA^{3-}]} = 10^{-10,26} \tag{34}$$

$$[EDTA]_{overall} = [H_4EDTA] + [H_3EDTA^-] + [H_2EDTA^{2-}] + [HEDTA^{3-}] + [EDTA^{4-}] \tag{35}$$

$$[Hg]_{overall} = [Hg]_{free} + [HgEDTA^{2-}] \tag{36}$$

Thus it can be determined that the amount of free mercury (with $[\mathrm{EDTA}]_{\mathrm{overall}} = 0.16\ \mathrm{M}$ and $\mathrm{pH} = 6$) is about $2*10^{27}$ times more the amount of complexed mercury.

Thus it can be assumed that if the residual concentration of OH$^-$ is too low, stripping is bad due to the lack of complexation (pH too low); to verify this hypothesis experiments were made with an excess of EDTA versus NaOH. The results however show that even with a lack of hydroxide in excess, there is a certain amount of stripping, due to an initial pH sufficient for complexation. This can be explained by another possibility of stripping as written below (**Reaction (37)**):

$$\overline{(TOAH)_2HgCl_4} + A \leftrightarrow \overline{2TOAHCl} + HgA + 2 \quad Cl^- \tag{37}$$

The trioctylamine base is not formed and **Reaction (27)** and **(28)** does not occur. The pH value seems to have smaller variations. Evidently **Reaction (37)** depends on the form of EDTA and its protonation also depends too on the pH. So an intermediate concentration is the best solution, as can be seen with the following results.

The trend of the pH for these experiments can be seen in **Appendix D** (**page VIII**).

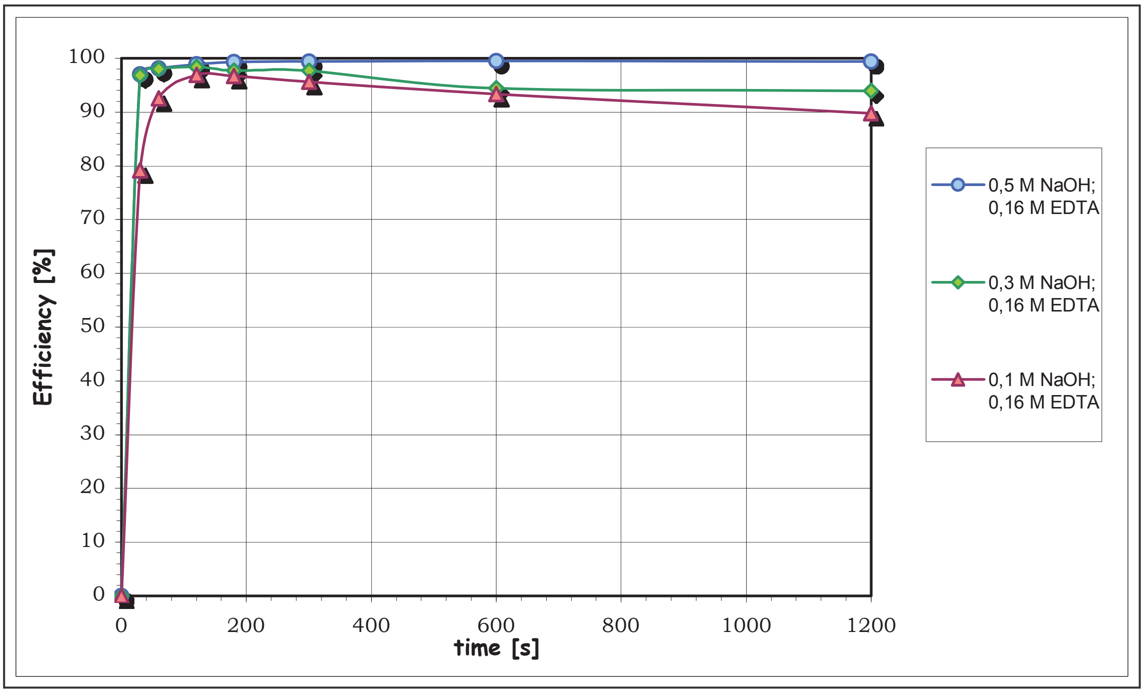

Figure 16: Examination of the efficiency of the extraction by variation of the concentration of NaOH

The efficiency of the extraction slightly depends on the concentration of NaOH. It can be observed that the emulsion with composition of the internal phase of 0.5 M NaOH, 0.16 M EDTA is the most efficient and also the most stable with time. For the other compositions the efficiency of extraction quickly decreases with time, which is explained by the breakdown and the swelling of the emulsion. The results of the stripping can be seen below (**Figure 17**):

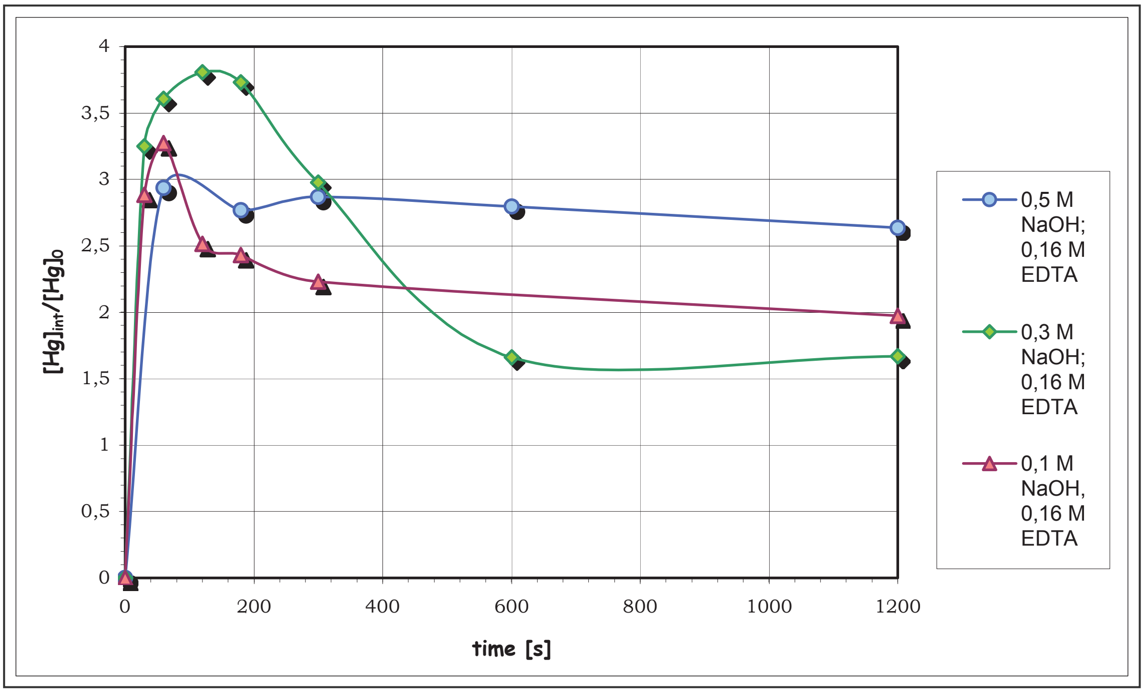

Figure 17: Efficiency of the stripping while varying the NaOH concentration

Even when there is no excess of OH^-, a good stripping is observed in the very first moments of contact, but the decrease that follows is rather important; it will then be preferred to operate with an excess of OH^-.

Finally an extraction by varying both parameters, both NaOH and EDTA concentration was tested. The results can be seen in **Figure 18** and **Figure 19**.

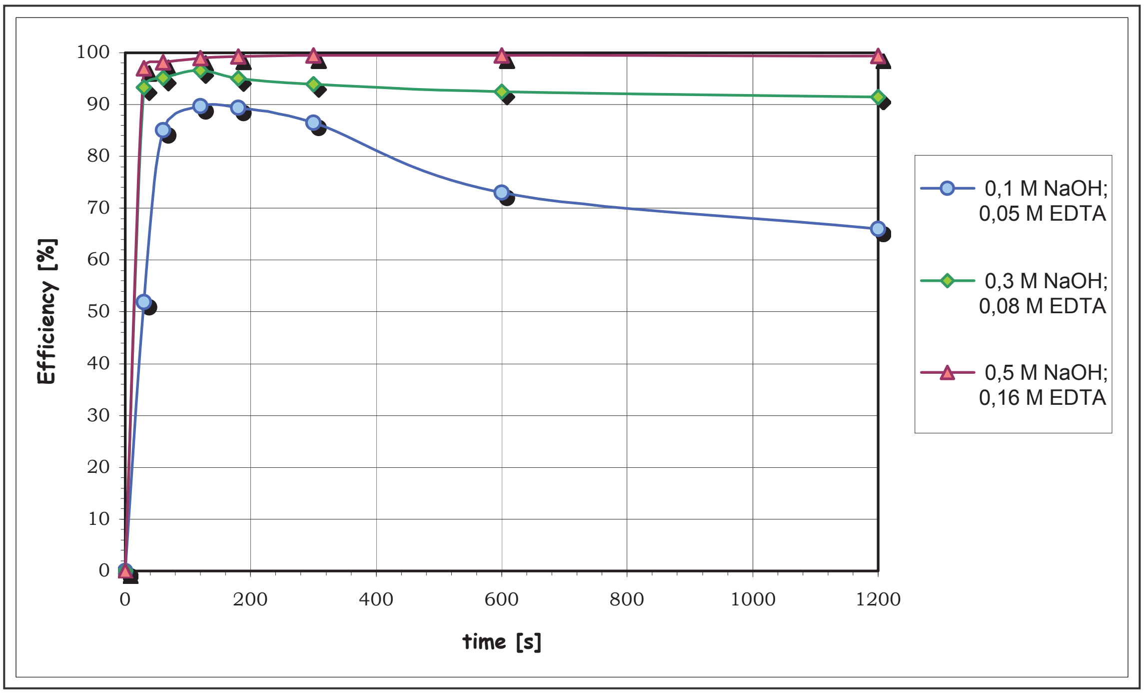

Figure 18: Efficiency of the extraction while varying both NaOH and EDTA concentration

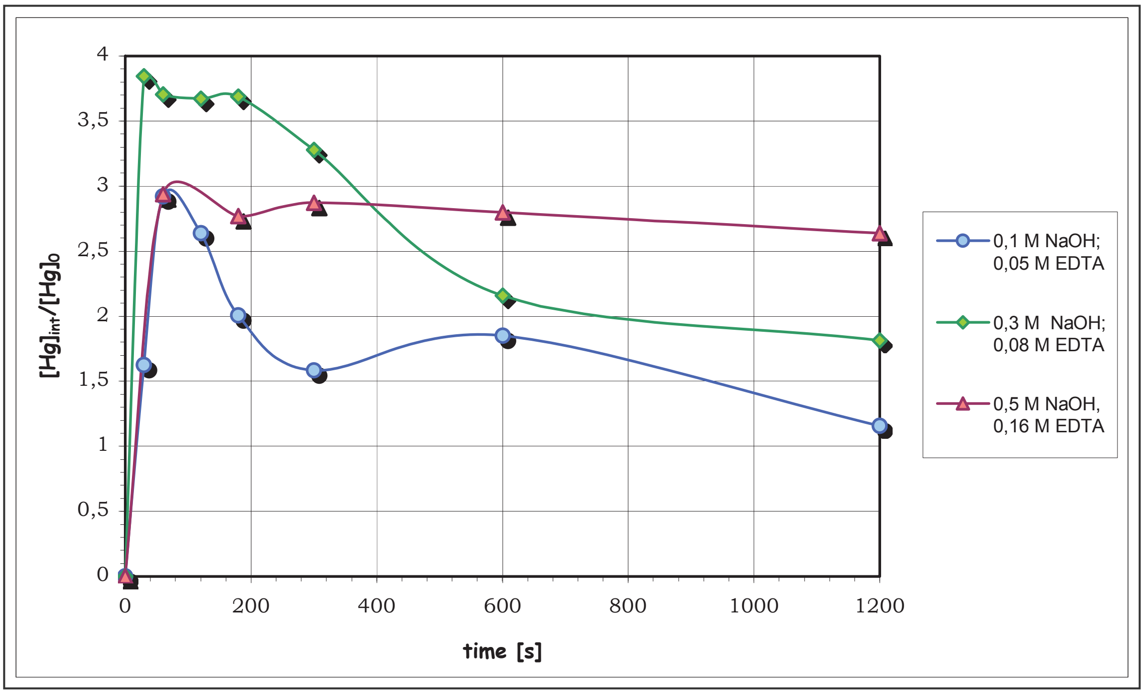

Figure 19: Efficiency of the stripping while varying both NaOH and EDTA concentration

As a conclusion it can be said too much EDTA is not very efficient, because of the fast pH drop; besides a too small concentration is not sufficient to give a good complexation of mercury, so a compromise has to be found.

In the end a composition of 0.5 M NaOH and 0.05 M EDTA in the stripping phase was chosen due to the high efficiency of extraction and relatively high efficiency of stripping, and while the trends of extraction and stripping are very constant with time.

So the optimised emulsion (final emulsion, EF) is composed of:
Organic phase:

- 0.01 M TOAHCl
- 5 % octanol
- 1% Abil
- in dodecane

The internal phase is composed as written above.
Figure 20 shows the results of a discontinuous experiment with this formulation.

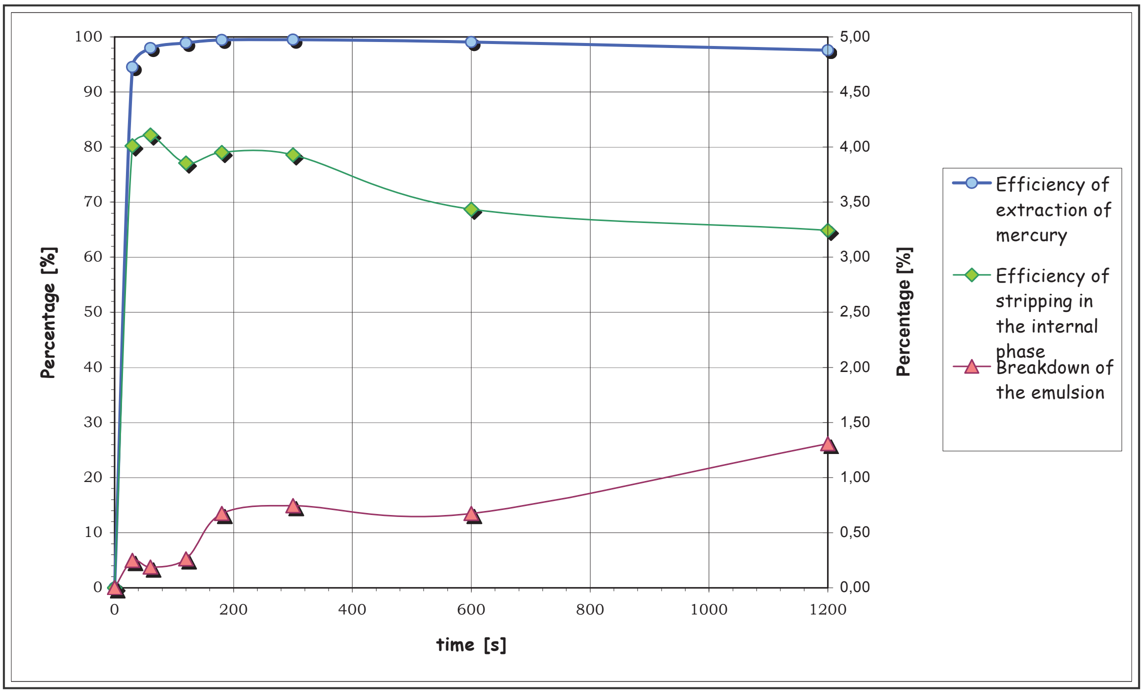

Figure 20: Results of the executing of an extraction with the final emulsion

It can be seen that the reaction is complete after approximately three minutes. The stripping of mercury has an efficiency of around 80 %. It can be also observed that the breakage of the emulsion is negligible in the first three minutes. The trend of the pH can be seen in **Appendix D** (**page VIII**)

5.3 Comparison of the Efficiency of the Extraction while varying the Concentration of Mercury in the External Aqueous Solution

Finally the efficiency of extraction by the optimised emulsion, while the concentration of mercury was varied between 10 to 500 ppm, was examined. The results can be seen in **Figure 21**.

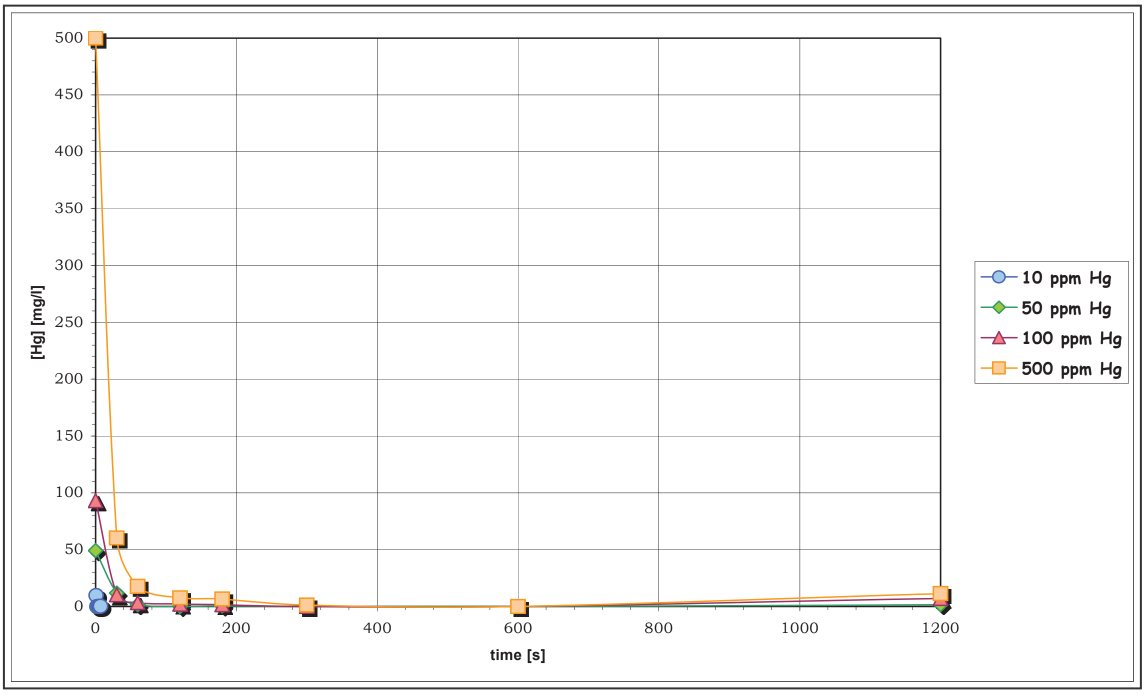

Figure 21: Efficiency of the extraction while varying the concentration of mercury in the extern phase

It was observed that after approximately three minutes extraction is complete for all concentrations. The chosen composition shows high efficiency also for smaller concentration levels. After 20 minutes the beginning breakdown of the emulsion causes a back-transfer of mercury in the external phase.

The optimised emulsion was then further examined in continuous experiments.

6 Results of the Continuous Experiments in a Mixer-Settler System

6.1 Description of the Experiments

The continuous experiments were performed in a mixer-settler system. The mixer with a volume of 0.1 L and the settler with a volume of 0.5 L were realised in Erlenmeyer flasks. The supply of the aqueous feed was supported by a membrane pump (ProMinent gamma G/4a, $\dot{V} = 0.5 - 3.5 \, {}^{L}\!/_{h}$) and the supply of the emulsion with a piston pump (Sonal, $\dot{V} = 0.1 - 2 \, {}^{L}\!/_{h}$).

The two phases (aqueous feed and emulsion) were stirred in the mixer with a Eurostar digital agitator (IKA-Labortechnik, 50 – 2000 rpm).

The transport of the mixture into the settler and the run off of the emulsion from the settler were performed via gravity.

The evacuation of the aqueous phase in the settler was realised either with a siphon or a flexible-tube (peristaltic) pump (Masterflex Pump Controller, Cole Parmer Instrument Co., $\dot{V} = 0.3 - 4 \, {}^{L}\!/_{h}$).

At the supply for the settler a metal helix was installed to avoid a too turbulent flow in the settler.

An illustration and the schema of the experiment can be seen beneath in **Figure 22**.

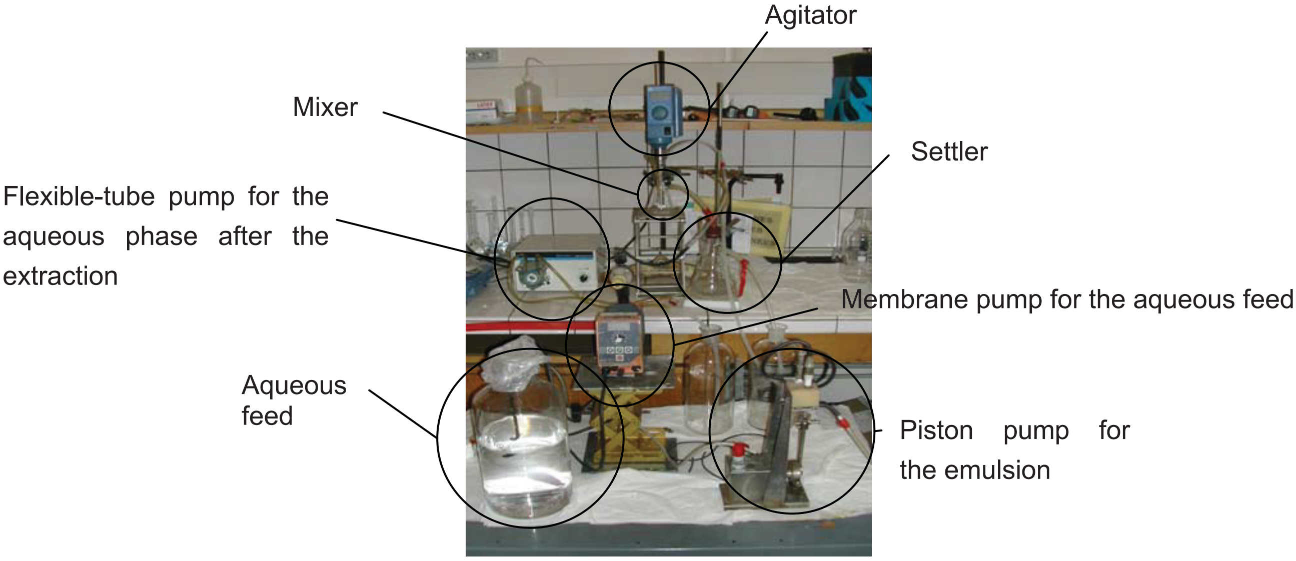

Figure 22: Illustration of the continuous experiment

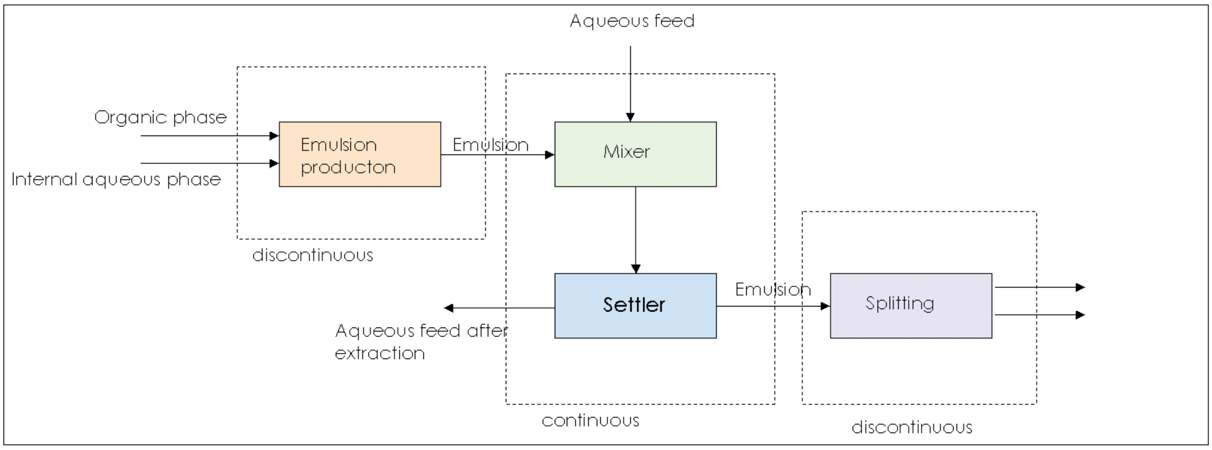

Figure 23: Schema of the continuous experiments

As can be seen in the schema above (**Figure 23**), the emulsion was not produced continuously. It was produced in amounts of 500 ml, with a ratio organic phase to internal phase of 1 to 1, at a speed of 13500 rpm with Ultraturrax and agitation time of 20 min.

For these experiments the optimised emulsion determined from the discontinuous experiments was used.

The organic phase was composed of: 0.01 M TOAHCl, 5 % octanol, and 1 % Abil in dodecane. And the internal phase consisted of: 0.5 M NaOH and 0.05 M EDTA

An analysis of the drop size distribution for an emulsion produced under these conditions and composition can be seen below in **Table 5** and in **Figure 24**.

Table 5: Drop size distribution (mean)

$d_{(0,5)}$ = 2.02 µm
$D_{[3,2]}$ = 1.84 µm
Specific Surface area = 3.267 m²/g

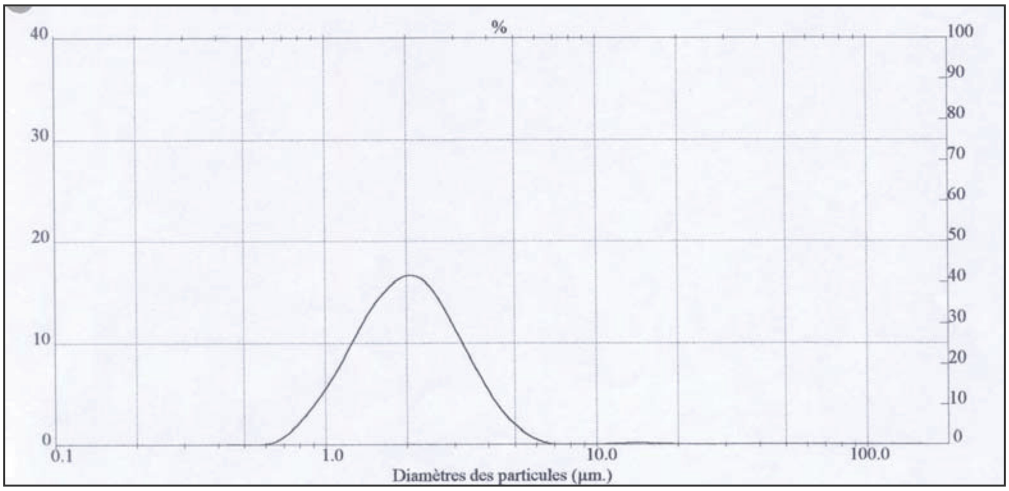

Figure 24: Drop size distribution of the emulsion for the continuous experiments

The splitting of the emulsion, likewise the production, was performed discontinuously by electric coalescence. Thus for the experiments only the taken samples were split. But for an actual economic continuous process, the organic phase has to be recycled.

The following schema (**Figure 25**) shows a continuous ELM process.

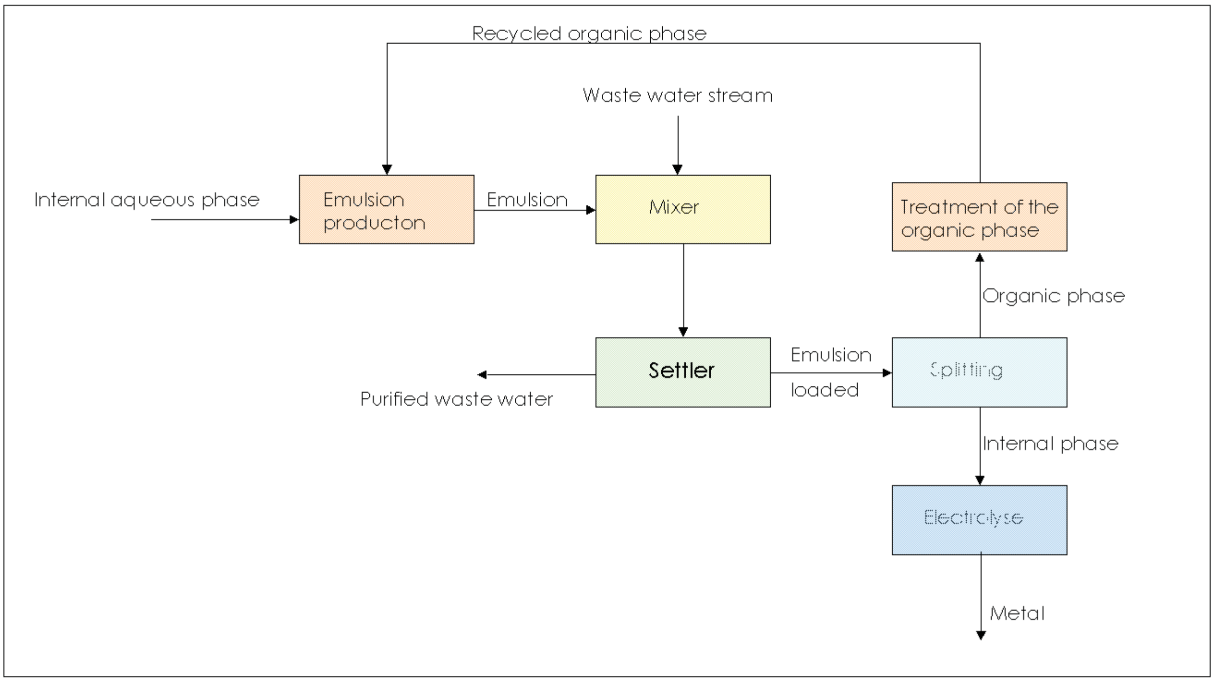

Figure 25: Schema of a continuous ELM process in a mixer-settler system

For the dimensioning for a continuous ELM process same effects and parameters have to be considered. Contrary to solvent extraction, too long residence is undesirable, because of the effect of osmosis and the breakdown of the emulsion. On the other side the residence time in the mixer must be sufficient to obtain a complete extraction [8, p 124].

It has also to be considered that in a mixer-settler system very often the effect of sedimentation appears. This means that drops of the stripping phase are settling slower than the rest of the emulsion. The result is the formation of two zones of emulsion: One with a high amount of stripping phase and one with more organic phase. Due to that the density of the emulsion can change and cause a settling of the emulsion to the bottom of the settler. This effect can be avoided by constantly renewing the interface between the emulsion and aqueous phase. This can be for example realised by constructing the supply of the settler at its bottom [8, p 121-130].

6.2 Continuous Experiment with the Optimised Emulsion (EF)

For the actual experiments, according to the results of the discontinuous experiments, a residence time of approximately 2 minutes in the mixer was chosen. For the first experiments

the ratio between the aqueous feed and the emulsion was 2 to 1.
The residence time was calculated according to **Equation (38)**:[11)]

$$\tau_{mean} = \frac{V_{Mixer}}{\dot{V}_{aqueousfeed} + \dot{V}_{Emulsion}} = \frac{0,1}{2+1} = 0.033h \mathrel{\hat{=}} 2\min \tag{38}$$

where $\dot{V}$ are the flow rates of both phases.

Before starting the experiments the pumps were standardized. The actual flow rate for each experiment, due to lack of a continuous flow-meter, was adjusted at the beginning of the test and controlled afterwards.
For the evacuation of the aqueous phase from the settler, a siphon was used. This caused problems because the flow rate of the siphon was difficult to control. Additionally on the interface between the aqueous phase and the emulsion, a formation of foam, due to turbulence at the supply, was observed. This foam sinks to the bottom of the settler and thus hinders a good separation of the aqueous phase and the emulsion.

Because of the form of the stirrer (another one was technically not possible), a speed of approximately 800 rpm has to be used to result in a homogeneous mixing. During the experiments, samples were taken every ten minutes; the time was counted after the settler was completely filled.
Figure 26 shows the results of this first continuous experiment.

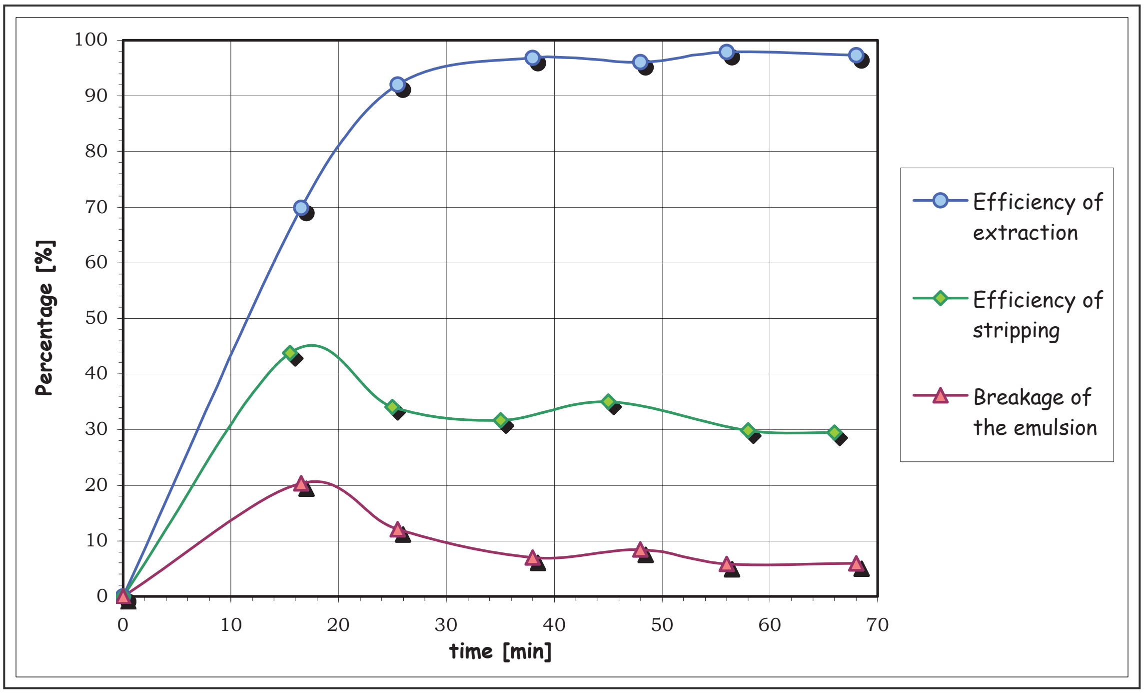

Figure 26: Results of the first continuous experiment

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11) This equation is only exact, if the hold-up is the same as the flow rates

As for the discontinuous experiments, the efficiency of the stripping is calculated by calculating the ratio of the quantity of mercury in the internal phase to the initial quantity. This efficiency takes into account both extraction and stripping.

The extraction of mercury was stationary after around half an hour. The efficiency of the extraction is high (~95 %), but due to the grievous breakage of the emulsion, the stripping (~30 %) was not very efficient. It can be concluded that a concentration of only 1 % surfactant is too low. The emulsion was already destroyed during the extraction. Thus for the following experiments, a higher amount of surfactant was chosen (3 %). The trend of pH during the experiments can be seen in **Appendix D** (**page VIII**).

6.3 Continuous Experiment N# 2

Before this continuous experiment has been started, a discontinuous kinetic experiment with this new composition, meaning higher amount of Abil EM90, has been performed. (All the other compounds and conditions were as before).
The results can be seen in **Figure 27** and **Figure 28**.

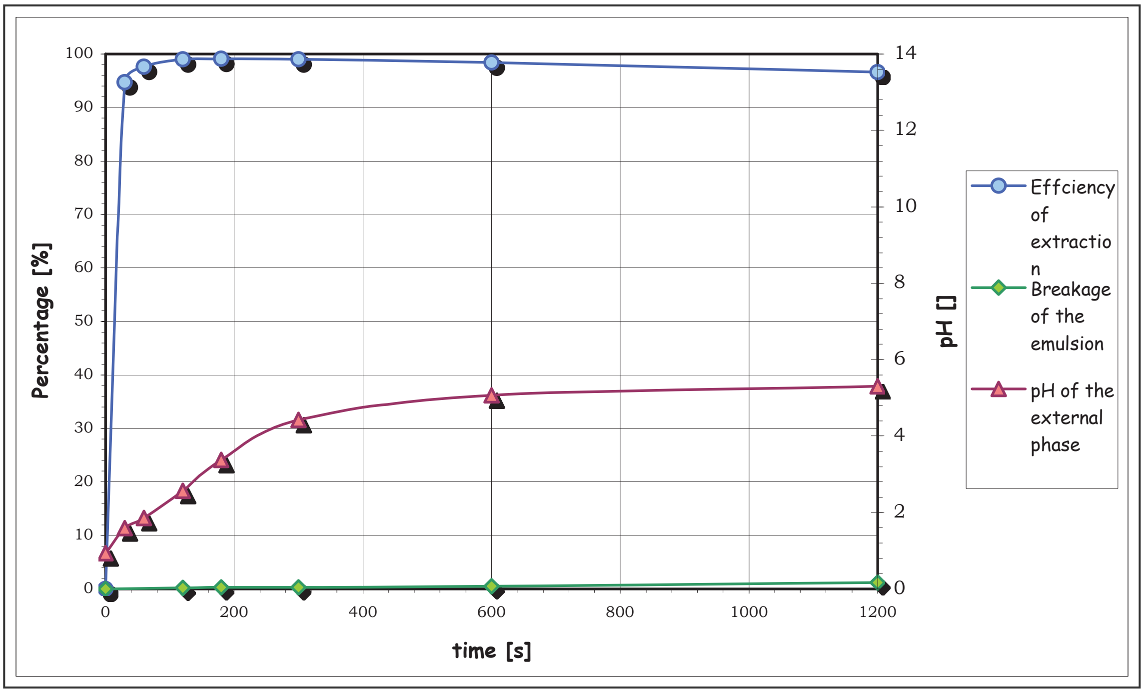

Figure 27: Kinetics of the optimised emulsion (EF) with 3 % Abil

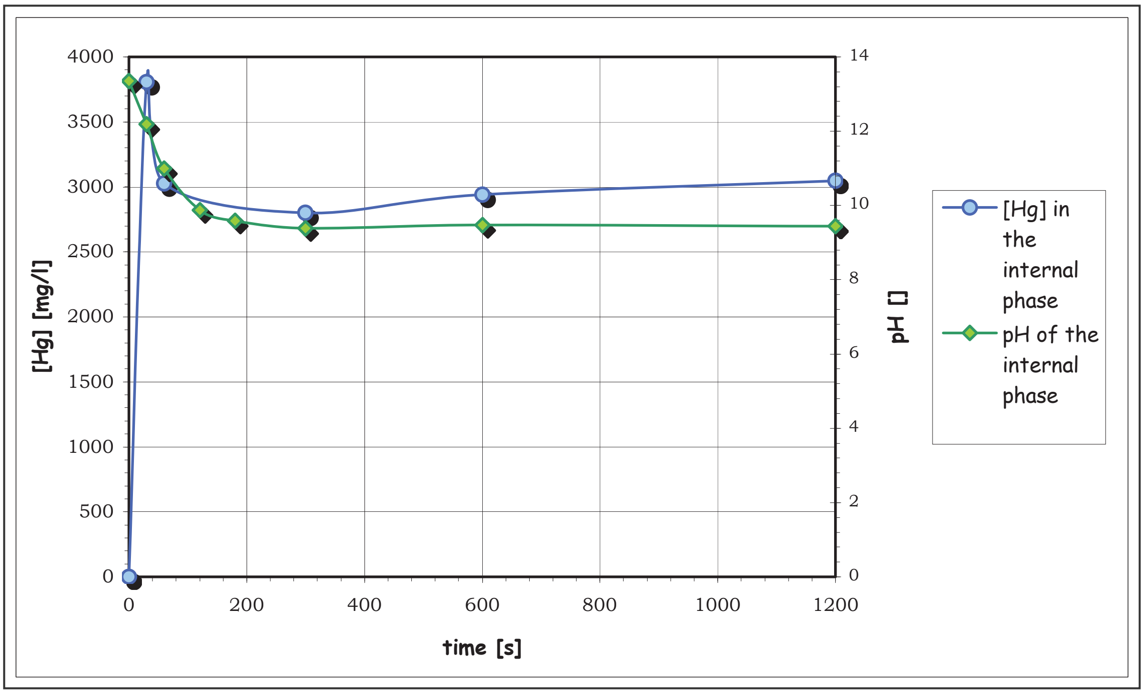

Figure 28: Kinetics of the optimised emulsion (EF) with 3 % Abil: Concentration in the internal phase

As expected, the results are more or less the same as for the discontinuous experiment with the optimised emulsion with 1 % Abil. It has been already observed during the discontinuous experiments that the surfactant has practically no influence on the efficiency of the emulsion.

With this emulsion, another continuous experiment was performed. The ratio between the aqueous feed and the emulsion was again 2 to 1. This ratio changed a bit because of the problem of keeping the same flow rate during the whole experiment with the membrane pump. This is a main disadvantage of membrane pumps: the precise adjusting of the flow rate is difficult and this latter is mostly unstable over a long time period.

A flexible-tube (peristaltic) pump was used, because of the problems for controlling the siphon, for evacuating the aqueous phase from the settler. The separation between the aqueous phase and the emulsion in the settler was better during this experiment, due to using a metal helix at the supply of the settler, to avoid turbulence. The flow rate of the aqueous phase was $\dot{V}_{aqueousfee\,d} = 1.9\, {}^{L}\!/_{h}$, whereas the flow rate of the emulsion was. $\dot{V}_{Emulsion} = 0.7\, {}^{L}\!/_{h}$. So the actual ratio between aqueous feed and emulsion was 2.7 to 1 and the mean residence time in the mixer was, according to the **Equation (38):** $\tau = 2.3\,\mathrm{min}$. The results of this experiment can be seen in the **Figure 29**:

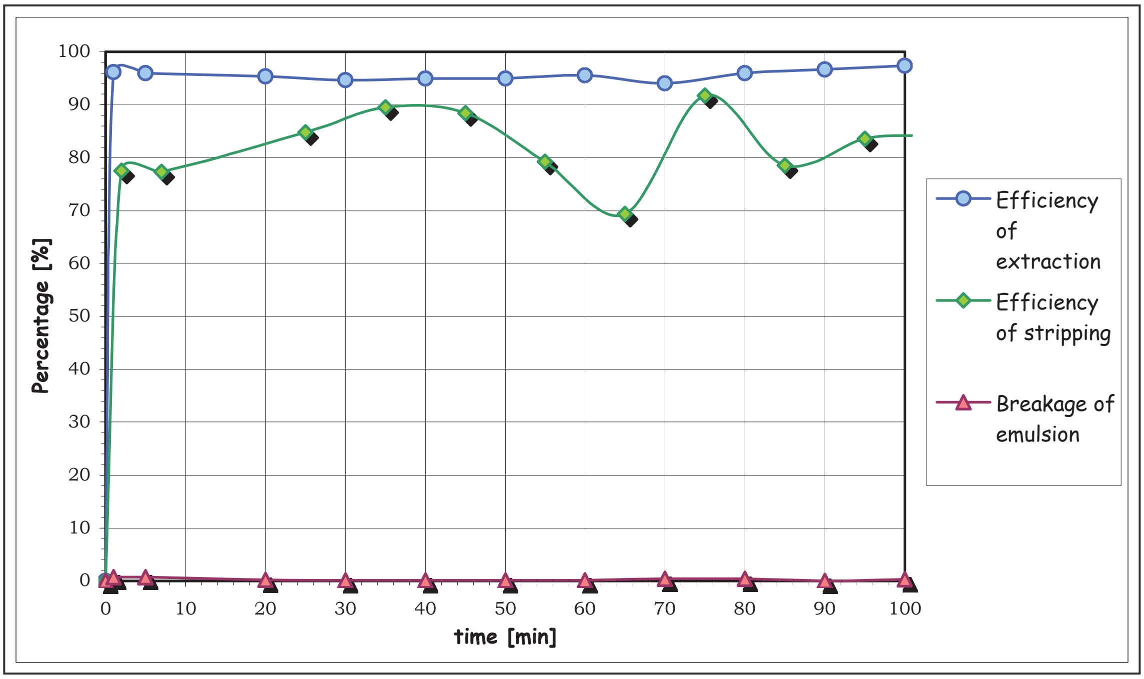

Figure 29: Results of the second continuous experiment

As for the first experiment, samples are taken every ten minutes; the time for the whole experiment is around two hours. The time for sampling is counted after the settler is filled. It can be seen that the stationary conditions have been reached after only approximately five minutes. The results are better than for the first experiment, an efficiency of around 95 % for the extraction and around 80 % for the stripping was achieved. The breakage of the emulsion during the experiment is negligible.

The trend of the pH can also be seen in the **Appendix D** (**page VIII**).

6.4 Changing the Ratio between the Aqueous Feed and the Emulsion

After the good results of the last continuous experiment, it was tried, for the next experiments to increase the ratio between the aqueous phase and emulsion; this was done to achieve a higher concentration factor of mercury in the internal phase.

Two experiments have been made with two different ratios between the aqueous feed and the emulsion. First an experiment with a ratio of 4 to 1 was performed, the second with a ratio of 6 to 1. All the other conditions and the performance of the experiment were the same as before. Due to problems with the tube of the peristaltic pump there are no samples between 10 and 40 minutes. The flow rate of the aqueous phase was $\dot{V}_{aqueousfeed} = 1.6\,{}^{L}\!/_{h}$, the flow rate of the emulsion was $\dot{V}_{Emulsion} = 0.4\,{}^{L}\!/_{h}$. The mean residence time in the mixer was $\tau_{mean} = 3\,\text{min}$.

The results can be seen in **Figure 30**.

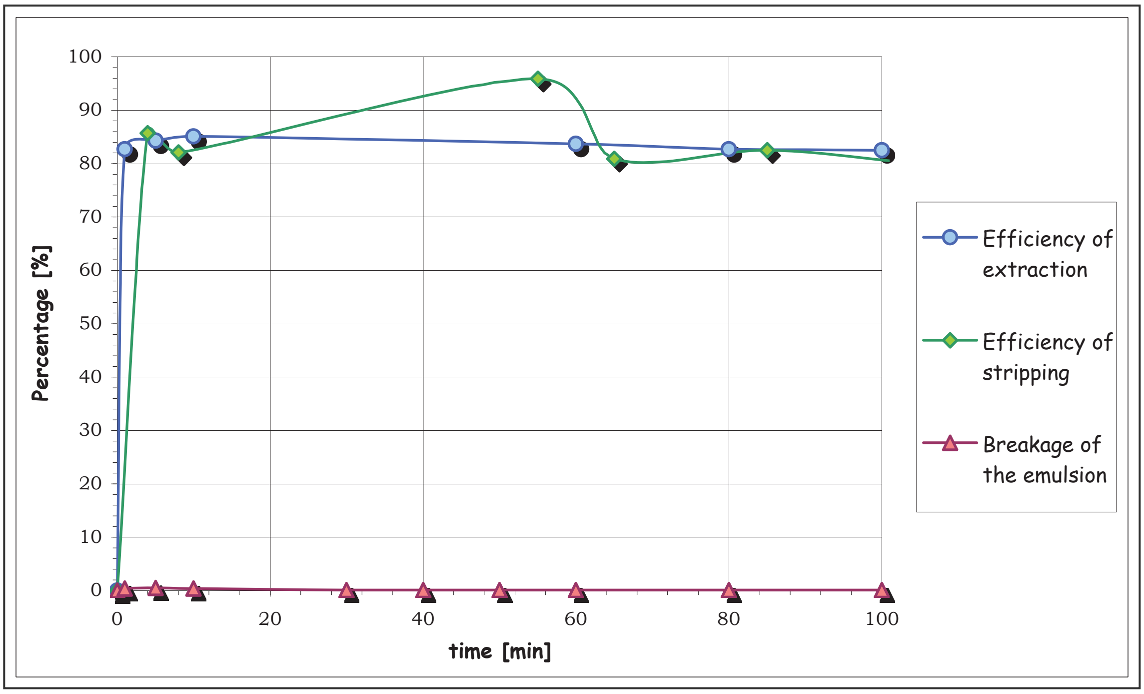

Figure 30: Continuous experiment with a ratio of 4 to 1 between the aqueous feed and the emulsion

The extraction is less efficient than with the smaller ratio: 80 % for extraction, 70 % for the stripping.

For the next experiment all the other conditions where the same as before. The ratio between aqueous phase and emulsion was 6 to 1. The flow rate of the aqueous phase was in this case $\dot{V}_{aqueousfeed} = 1.8\,{}^{L}\!/_{h}$ and for the emulsion $\dot{V}_{Emulsion} = 0.3\,{}^{L}\!/_{h}$. Thus the mean residence time in the mixer in this case was $\tau_{mean} \cong 3\,\text{min}$.

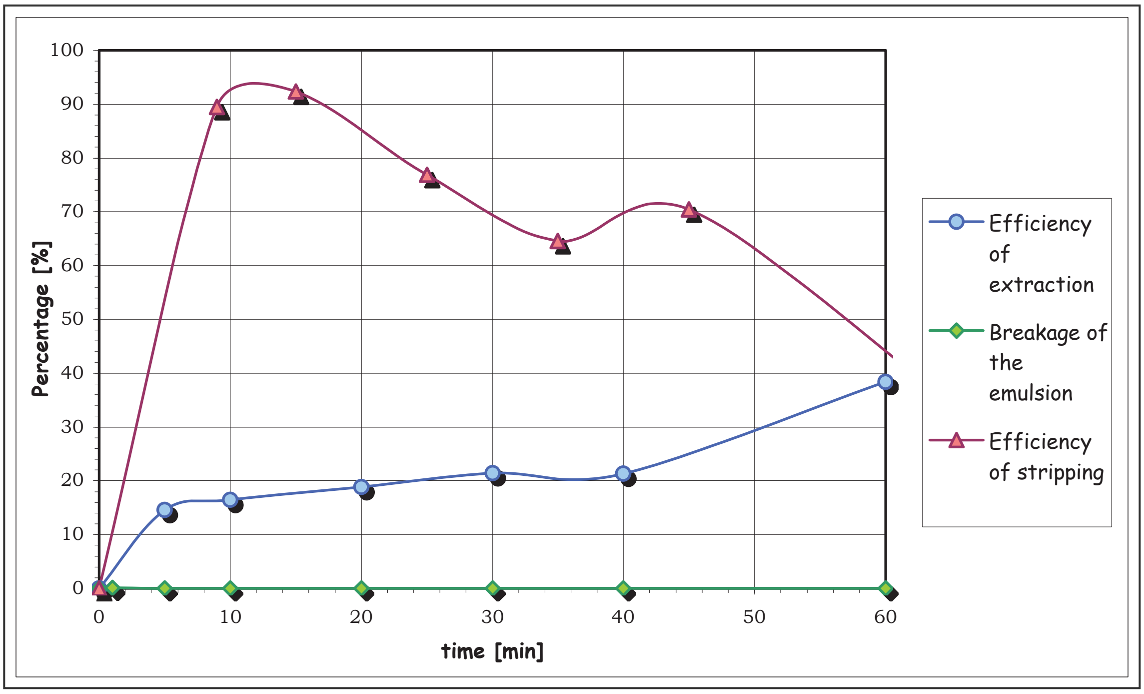

Figure 31: Results of the continuous experiment with the ratio of 6 to 1 between the aqueous phase and the emulsion.

It seems that, because of the high ratio between the aqueous phase and the emulsion, the extraction is not efficient (see **Figure 31**), only 15 % of the mercury can be eliminated from the aqueous feed. By increasing the residence time the efficiency could be augmented, but this would also increase the breakdown of the emulsion and the effect of osmosis.

There were also problems during the experiment to separate the emulsion and the external phase, a large amount of foam was formed. Also the splitting of the samples was difficult, a kind of powder in the emulsion was formed during splitting.

6.5 Changing the Ratio between Organic and Internal Phase

To achieve a higher concentration ratio of mercury in the internal phase, which was not possible by increasing the ratio between the external aqueous feed and the emulsion, the ratio between the organic and the internal phase was increased.

The same composition as before were used to produce the emulsion for this experiment, this means:

The organic phase consists

- 0.01 M TOAHCl,
- 5 % octanol, and
- 1 % Abil
- in dodecane

and the internal phase of

- 0.5 M NaOH and
- 0.05 M EDTA.

Here the ratio between the organic and the internal phase was 2 to 1, to reach a concentration of mercury in the internal phase of 8 times, by a ratio of 1 to 2 between the emulsion and the aqueous feed.

First this emulsion was tested in a discontinuous kinetic experiment and if the extraction is efficient this emulsion will be tested in a continuous experiment. The results can be seen in **Figure 32** and **Figure 33**. The results of this experiment are not very good. The extraction efficiency is only 60 to 70 percent, due to the decrease of the internal interfacial area.

Due to these results a continuous experiment was not performed.

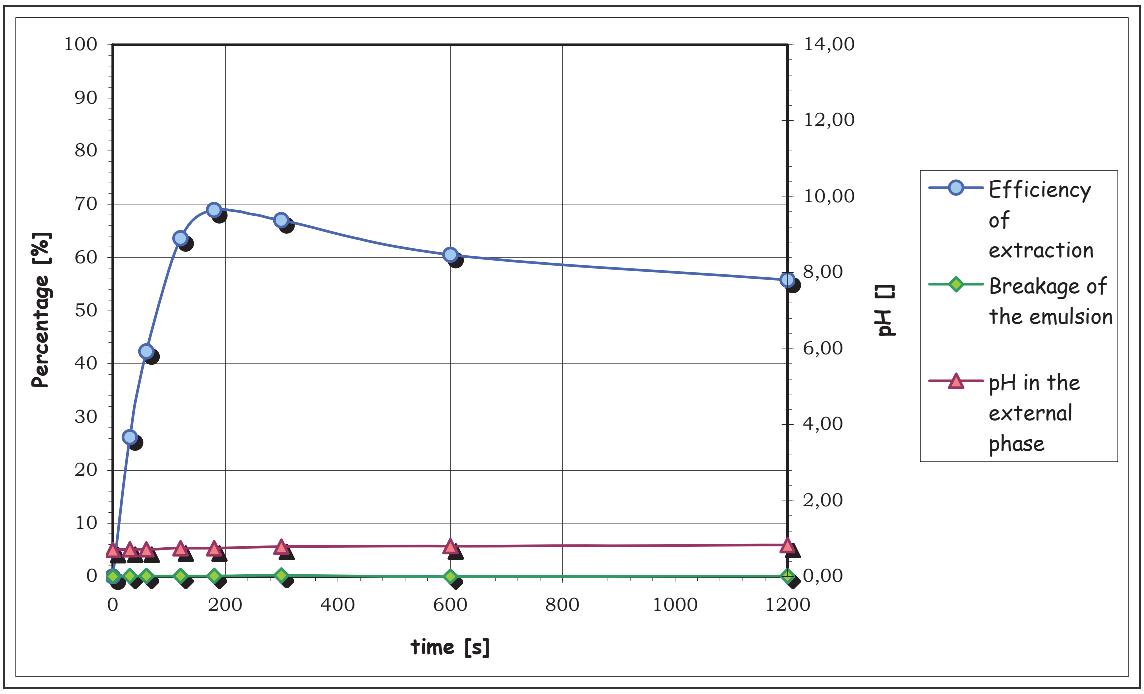

Figure 32: Kinetic of an extraction of mercury with the emulsion with a ratio between organic phase and internal phase of 2 to 1

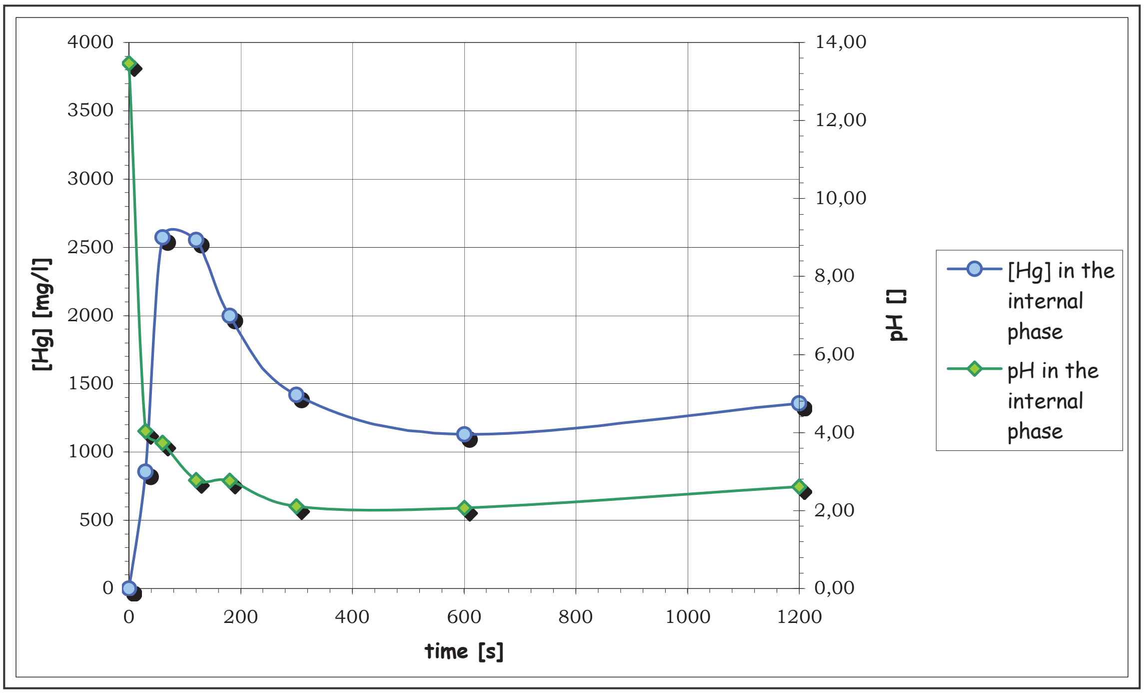

Figure 33: Kinetic of an extraction of mercury with the emulsion with a ratio between organic phase and internal phase of 2 to 1: Concentration of mercury in the internal phase

7 Conclusion

The objective of this study was the optimising of an emulsion for the extraction of mercury and testing this emulsion afterwards in a mixer-settler system.

During the discontinuous experiments the optimal emulsion for the extraction of mercury was chosen with a composition of: 0.01 M TOA (extracting agent), 5 % octanol (modifier), 1 % Abil EM90 (surfactant) in dodecane as solvent in the organic phase and 0.5 M NaOH and 0.05 M EDTA as stripping agents in the internal phase, with a ratio of 1 to 1 between organic phase and internal phase in the emulsion.
With this composition, a 99 % efficiency of the extraction after 3 minutes contact was achieved.

Two great problems were observed during the experiments; one was the breakdown of the emulsion, which is negligible by short contact times, and the effect of osmosis, which appears to have great influence on the concentration of the mercury in the internal phase due to the resulting dilution of this phase.

Testing the optimised emulsion from the discontinuous experiments in a mixer-settler system shows that the chosen surfactant concentration is not sufficient, thus the concentration of Abil was increased to 3 %.
With this new composition, an extraction efficiency of 95 % was achieved, at a ratio of 3 to 1 between aqueous feed and emulsion.

Further tests with a higher ratio between the aqueous feed and the emulsion (4 to 1 and 6 to 1) showed a worse efficiency. Thus to achieve a higher concentration of mercury in the internal phase an experiment with an emulsion with a ratio between organic phase and internal phase of 2 to 1 was performed, while the ratio aqueous feed to emulsion was also 2 to 1. But with this composition only 15 % of the mercury was eliminated from the aqueous feed.

To recapitulate, this work has established that at a laboratory scale, an ELM process can be used to separate mercury in a mixer-settler system from diluted solution. Though only a concentration factor of 4 times could be achieved; this could cause problems for the recycling of the mercury from the internal phase in very diluted solution.

To establish this tested emulsion for actual wastewater purification further tests and experiments in lab scale and pilot scale have to be made.

8 Indexes

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8.2 List of Abbreviations

AAS	Atomic absoption spectroscopy
ATSDR	Agency for Toxic Substances and Diseases Registry
bzw.	beziehungsweise
CERCLA	Comprehensive Environment Response, Compensation, and Liability Act
D	Distribution coefficient
d	diameter
$D_{3,2}$	Sauter diameter
etc.	and so on [e cetera]
e.g.	for example [exempli gratia]
EDTA	Ethylendiamintetraacetate
EF	Optimised emulsion
ELM	emulsion liquid membrane process
EPA	Environmental protection agency
EU	Europian Union
g	gramm
h	hour
HCl	Hydrochloric acid
Hg	Mercury
HLB	Hydrophile-Lipophile Balance
i.e.	that is [id est]
L	litre
LMP	liquid membrane technique
min	minute
n	stoechiometric coefficient
NAOH	Sodiumhydroxide
OECD	Organisation for Economic Cooperation and Development
p	page
ppm	parts per million
resp.	respectivley
rpm	route per minutes
s	second
TOA	trioctylamine
UNEP	United Nations Enviroment Programme
US	United States of America
W/O	water in oil
WHO	World health organisation

8.3 Tables

8.4 Figures

Appendix A: Used Chemicals

Name	Formula	Entreprise	Purifity	Utilisation
Abil EM 90	-	Goldschmidt		Surfactant
Dodecane	$C_{12}H_{26}$	Labosi	-	Solvent
EDTA salt disodic	$C_{10}H_{14}N_2O_8Na_2$, 2 H_2O	Labosi	> 99 %	Stripping agent
Mercury chlorid	$HgCl_2$	Prolabo	For analysis	Solute
Mercury AAS standard 1000 mg/l	-	Titrinorm	Tolerance ±0,5 ppm	Standard for AAS
Octanol-1	$C_8H_{17}OH$	ACROS	98 %	Modifier
Potassium chlorid	KCl	Labosi	For analysis	Standard for AAS
Sodium chlorid	NaCl	Labosi	For analysis	Standard for AAS
Sodium hydroxid 10 M	NaOH	Prolabo	-	Stripping agent
Tri-normal-octylamine	$C_{24}H_{51}N$	ACROS	98 %	Extracting agent

Appendix B: Examination of the Change of pH during Kinetic Experiments

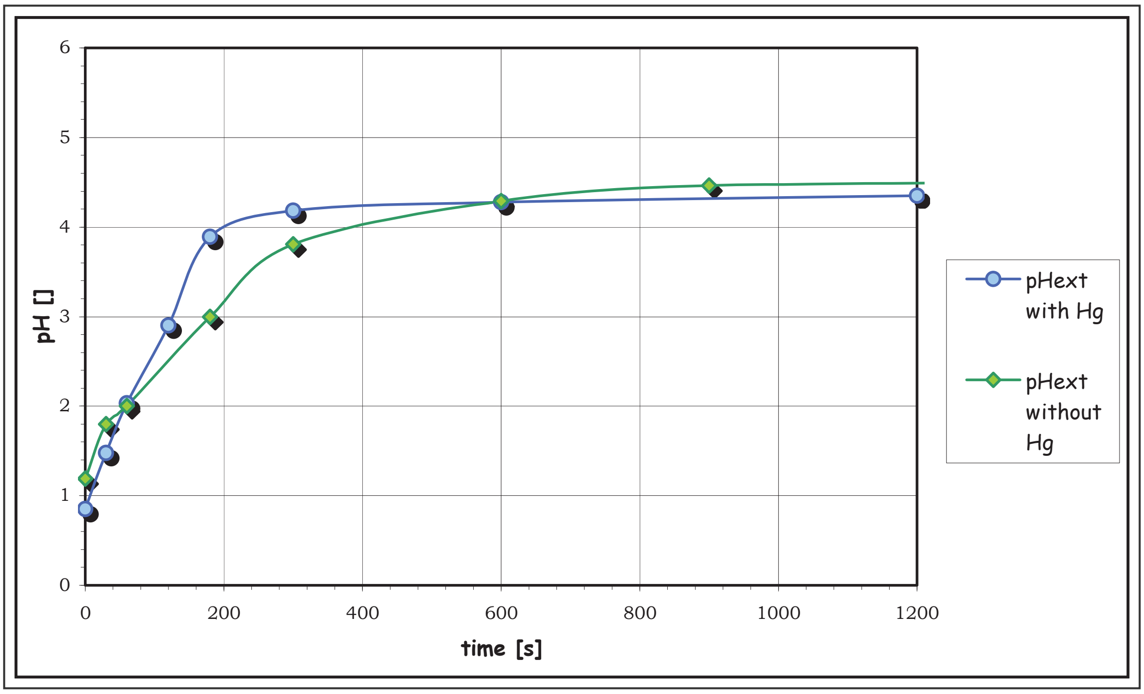

Figure B - 1: Comparison of the changing of pH during a extraction with and without Hg in the mother solution (5 % Abil) (to **page 38**)

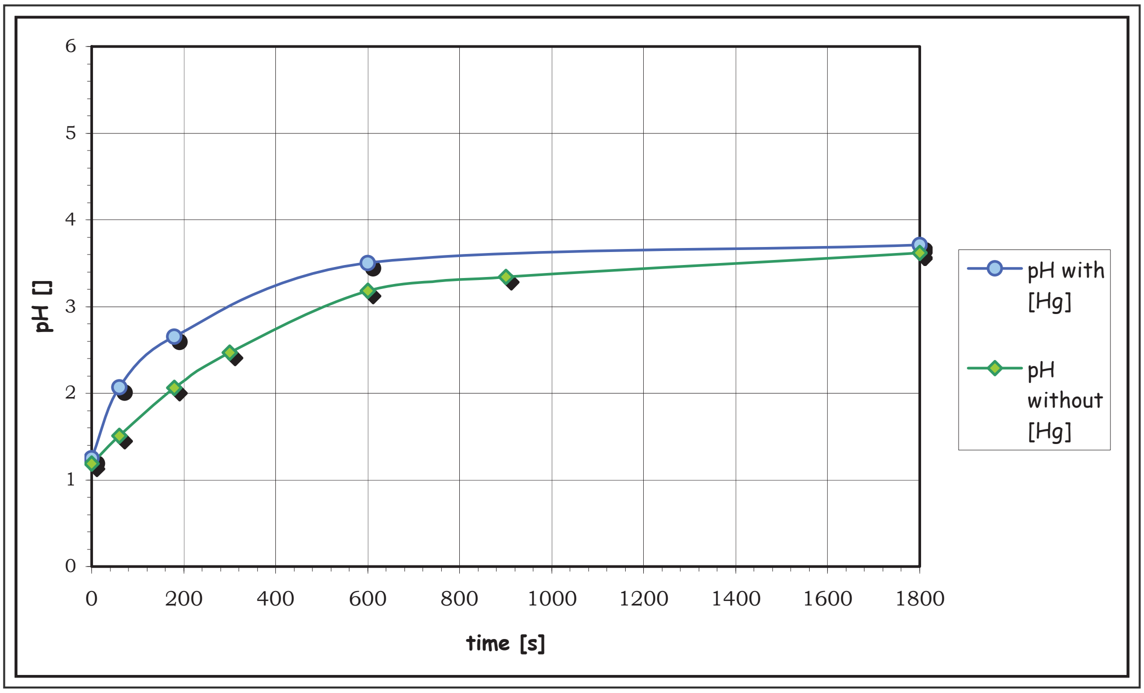

Figure B - 2: Comparison of the changing of the pH during the extraction with a mother solution with and without Hg (to **page 38**)

Appendix C: Results of the Potentiometric Titration

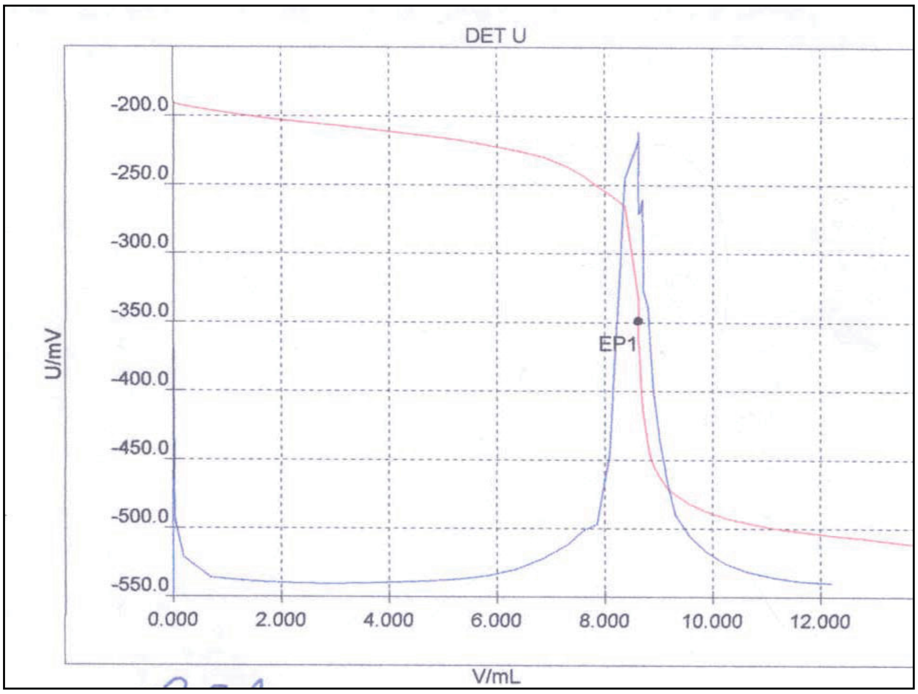

Figure C - 1: Titration curve of E32 – 3 min.

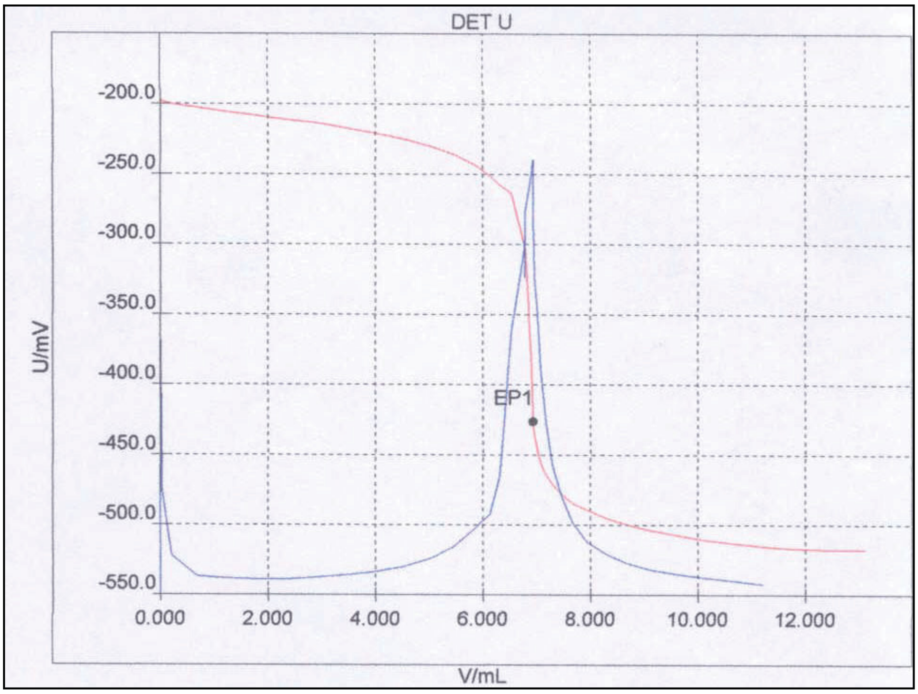

Figure C - 2: Titration curve E32 – 10 min.

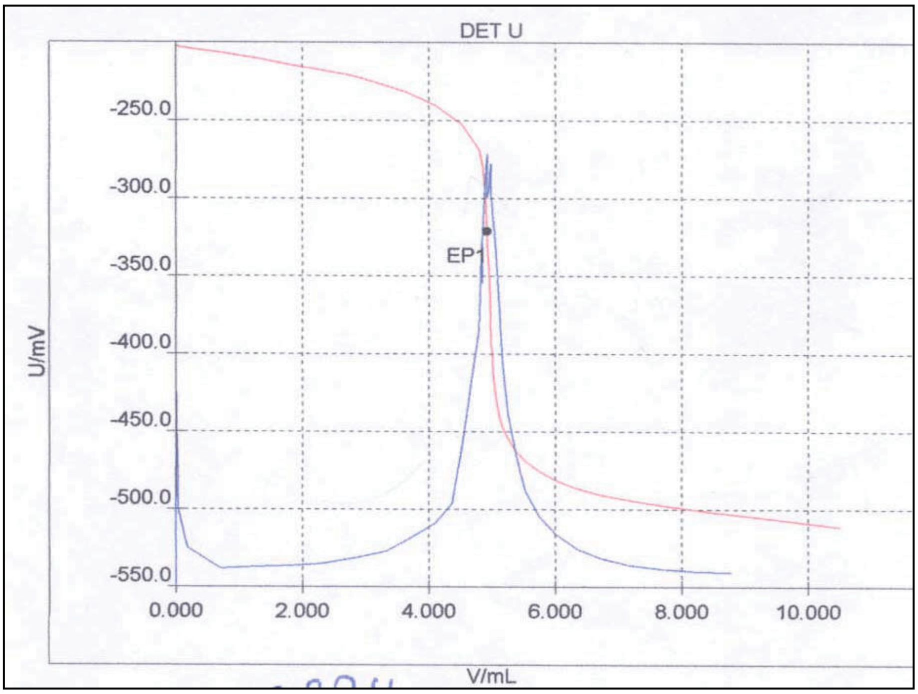

Figure C - 3: Titration curve E32 - 20 min

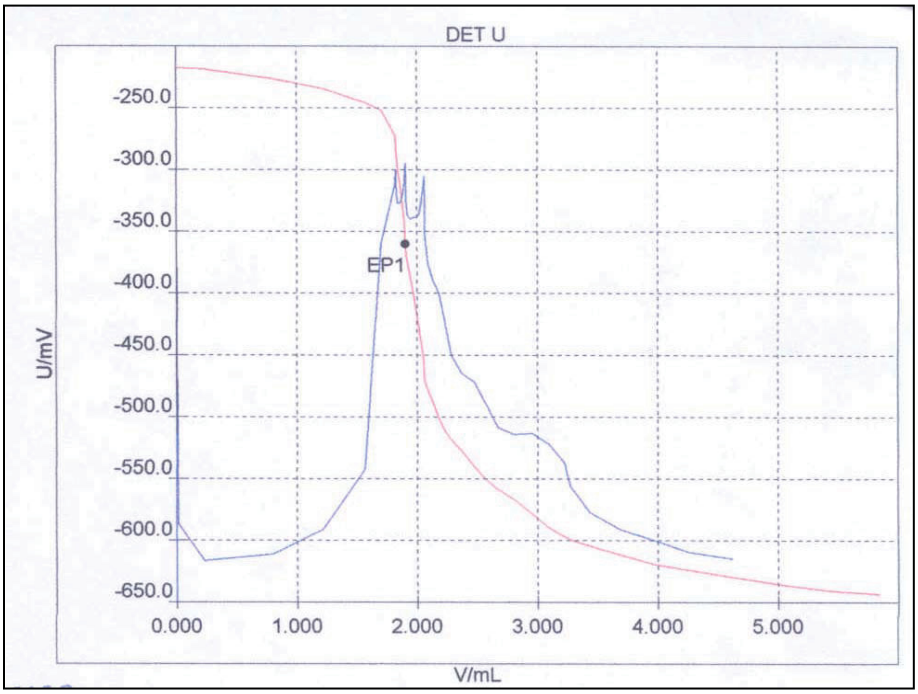

Figure C - 4: Titration curve E33 – 2 min (1)

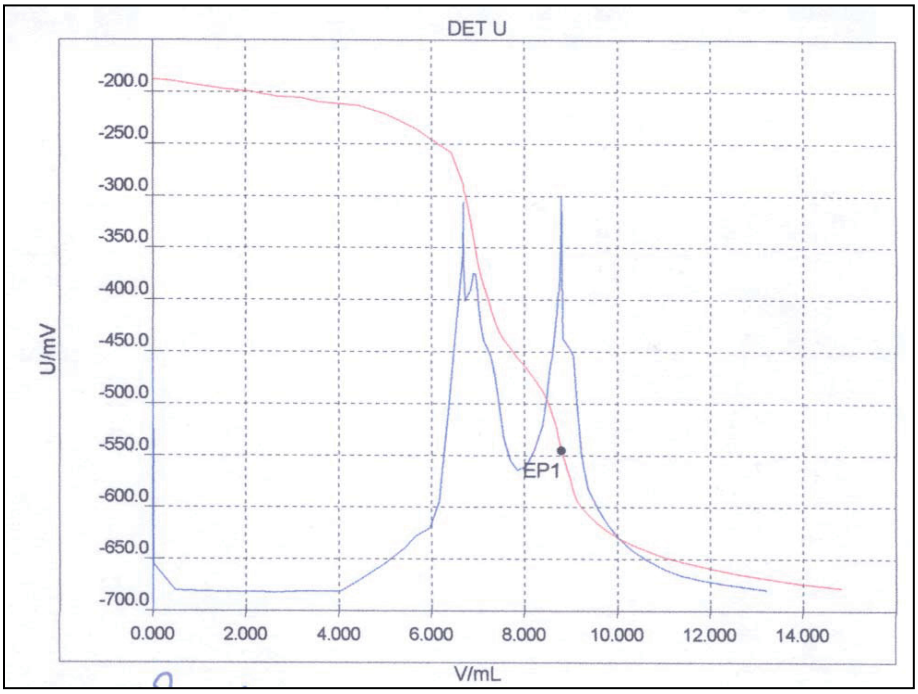

Figure C - 5: Titration curve E33 – 2 min (2)

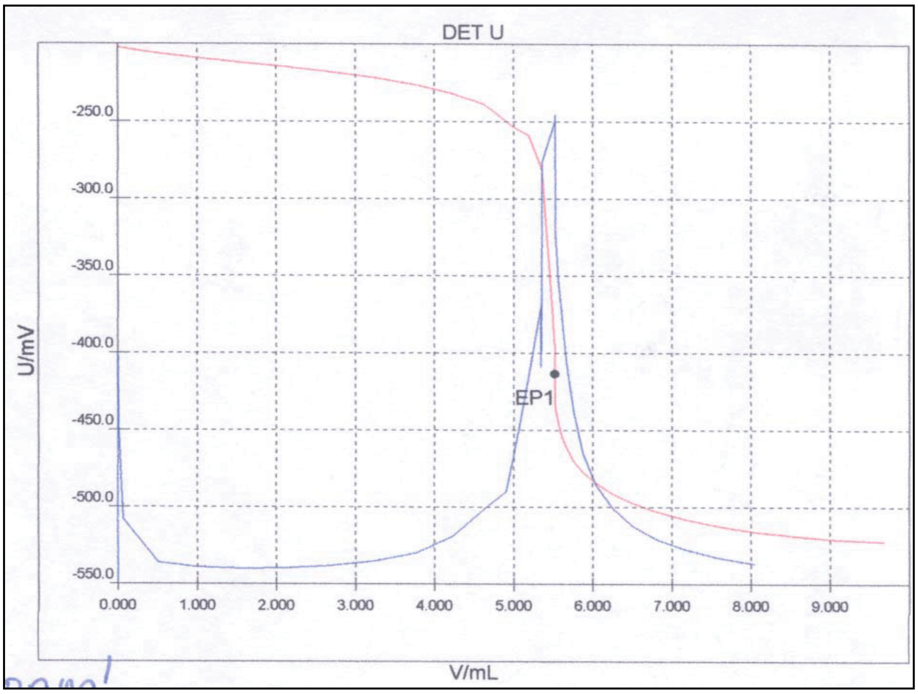

Figure C - 6: Titration curve E33 – 5 min (1)

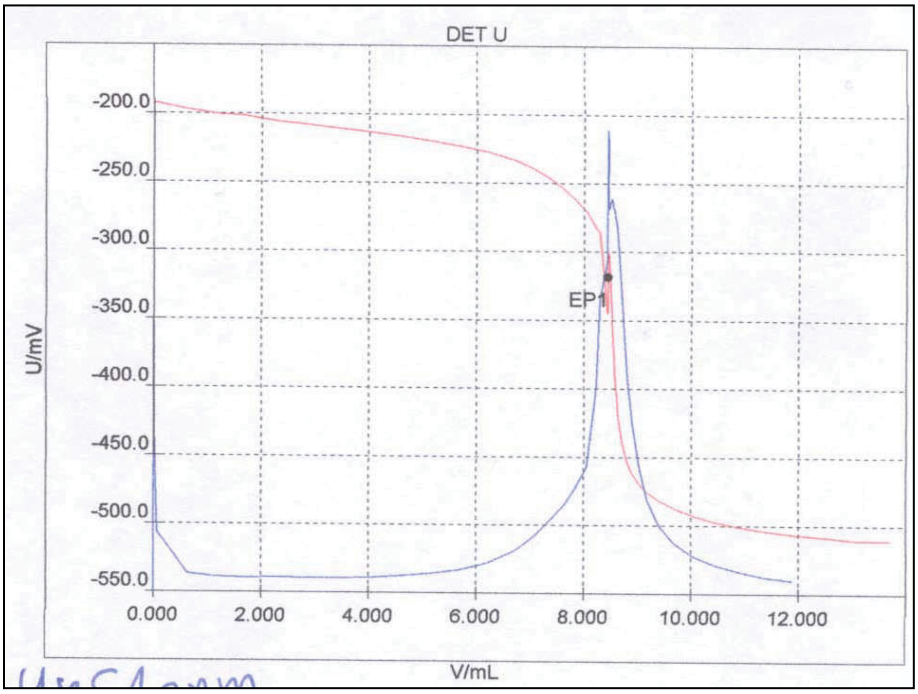

Figure C - 7: Titration curve E33 – 5 min (2)

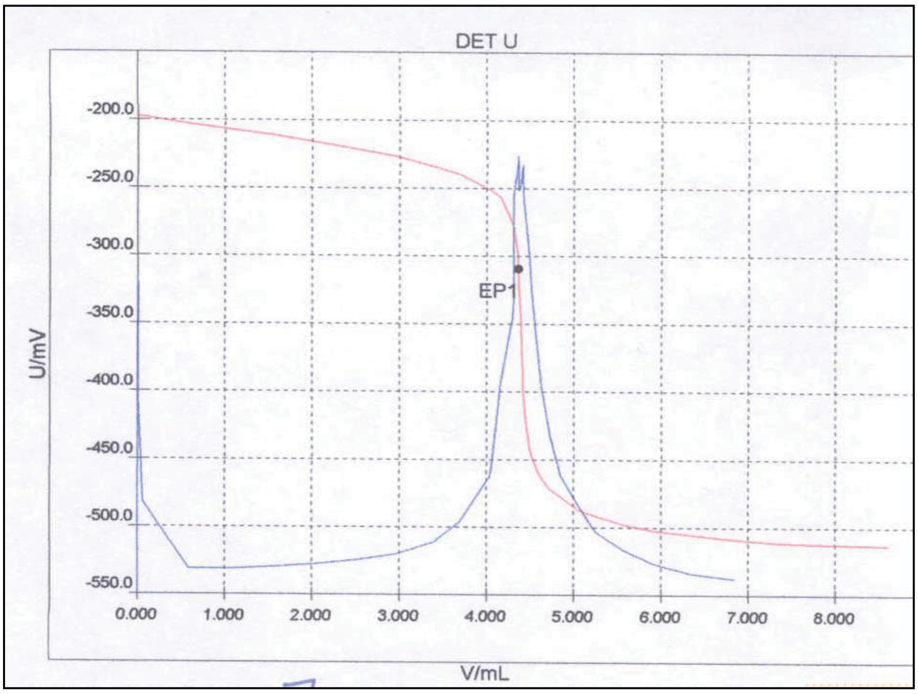

Figure C - 8: Titration curve E33 – 10 min

Appendix D: Observation of pH

To Chapter VI: Optimising of the Emulsion

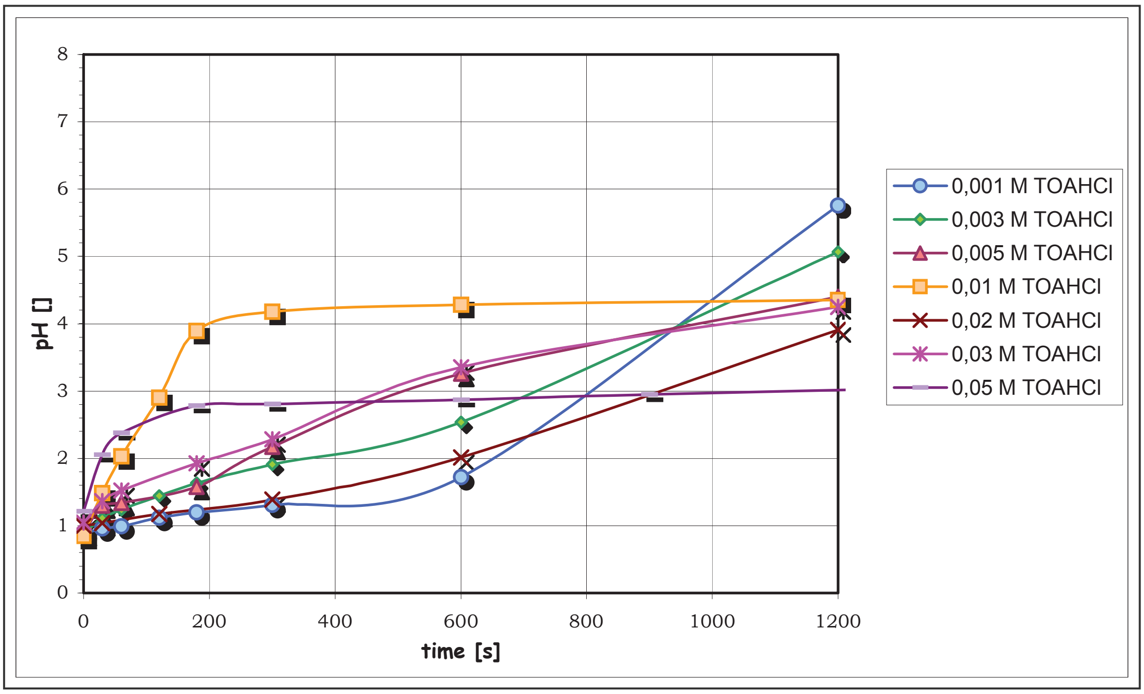

Figure D - 1: Examination of the changing of pH during the optimising of the TOA concentration (to **Figure 11**)

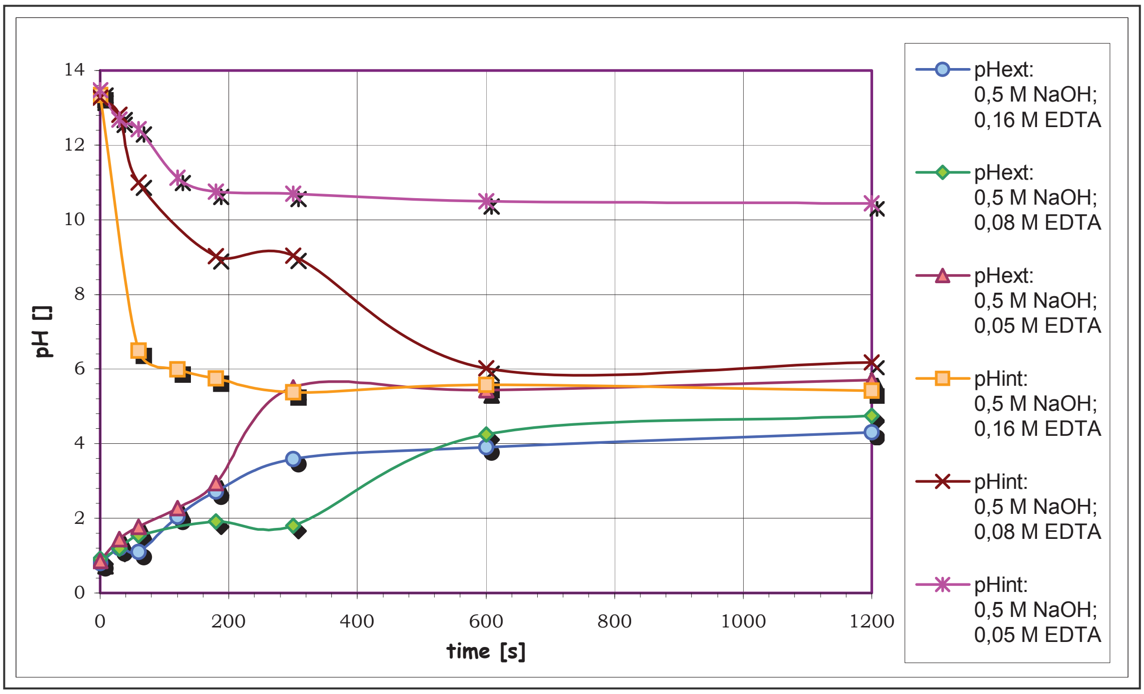

Figure D - 2: Observation of the changing of pH during the variation of the concentration of EDTA (to **Figure 14** and **Figure 15**)

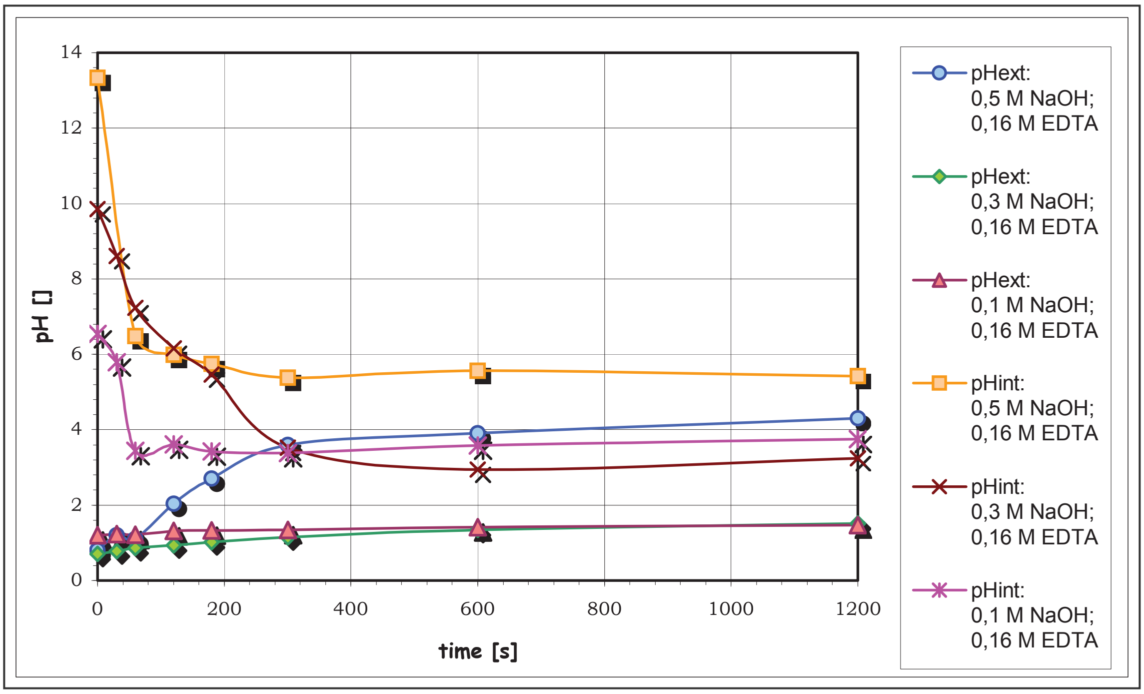

Figure D - 3: Observation of the changing of the pH during variation of the concentration of NaOH (to **Figure 16** and **Figure 17**)

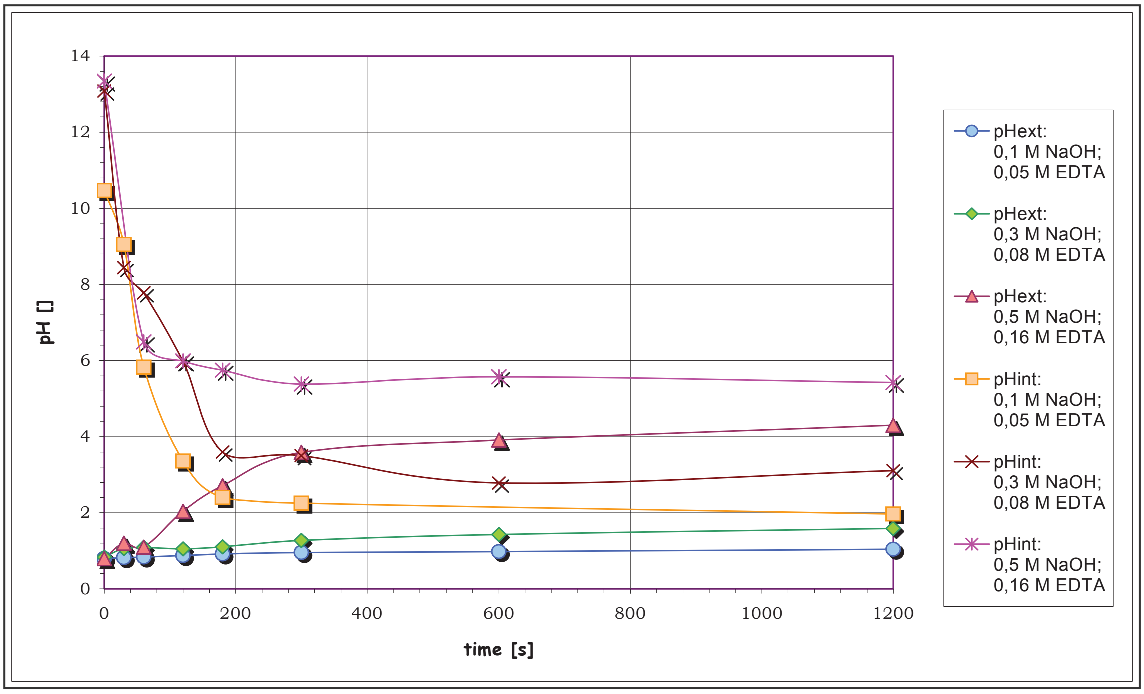

Figure D - 4: Examination of the changing of pH during the variation of the concentrations of NaOH and EDTA (to **Figure 18** and **Figure 19**)

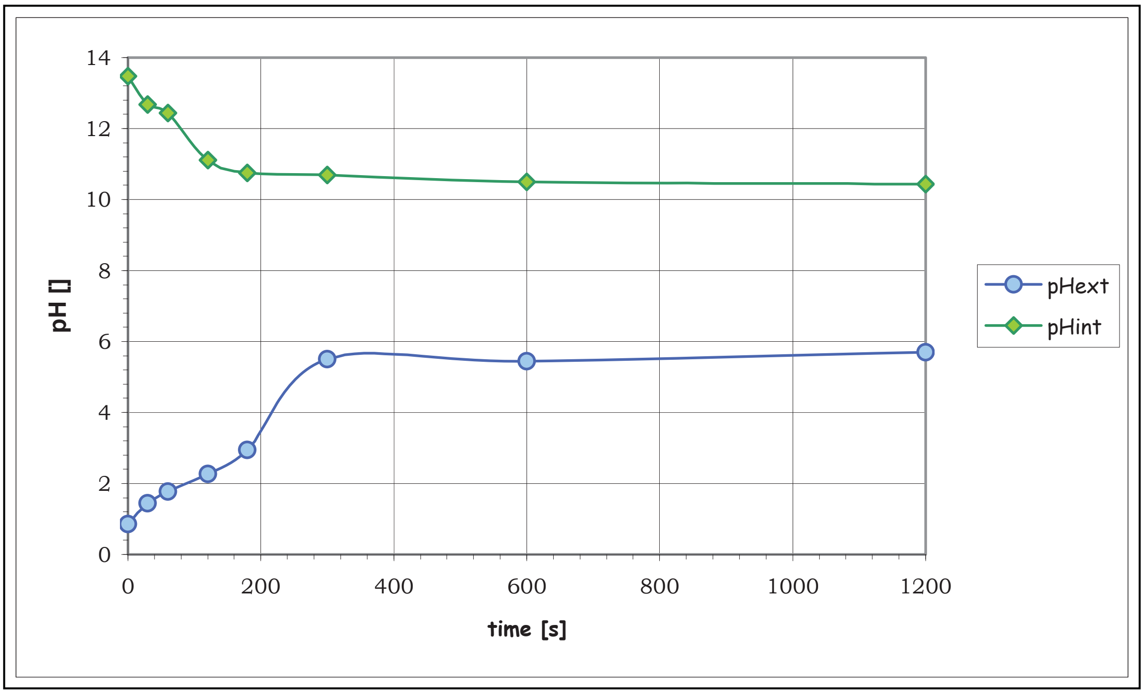

Figure D - 5: Trend of pH during a discontinuous experiment with the optimised emulsion (to **Figure 20**)

To Chapter VII: Continuous Experiments in a Mixer-Settler System

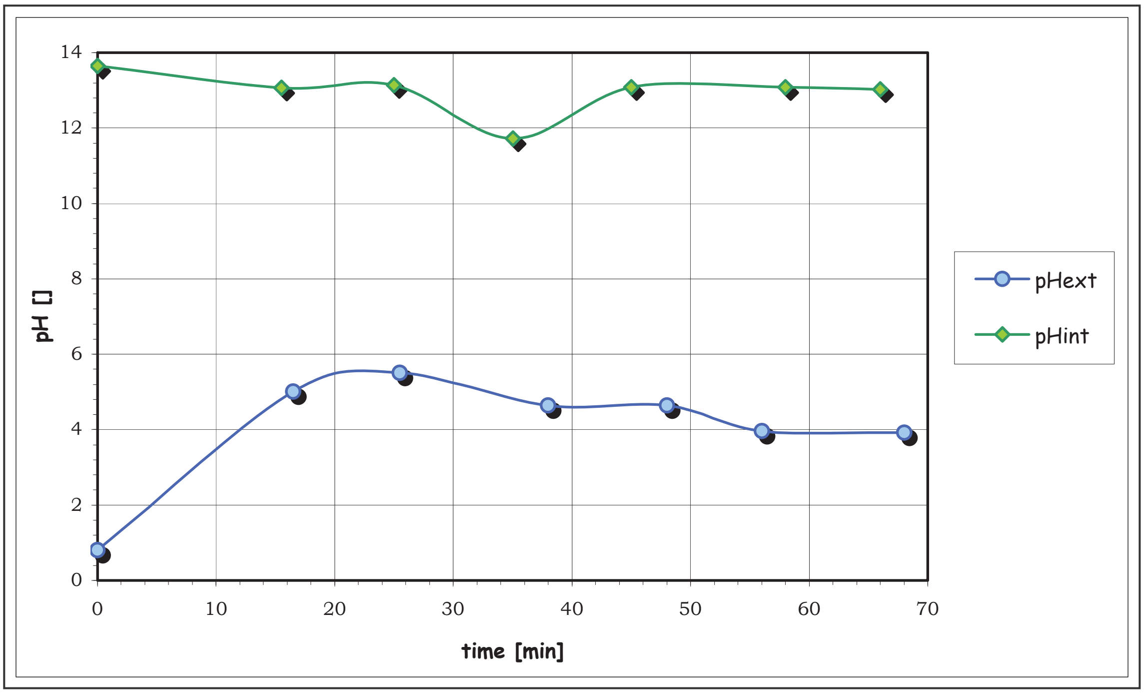

Figure D - 6: Changing of the pH during the first continuous experiment (to **Figure 26**)

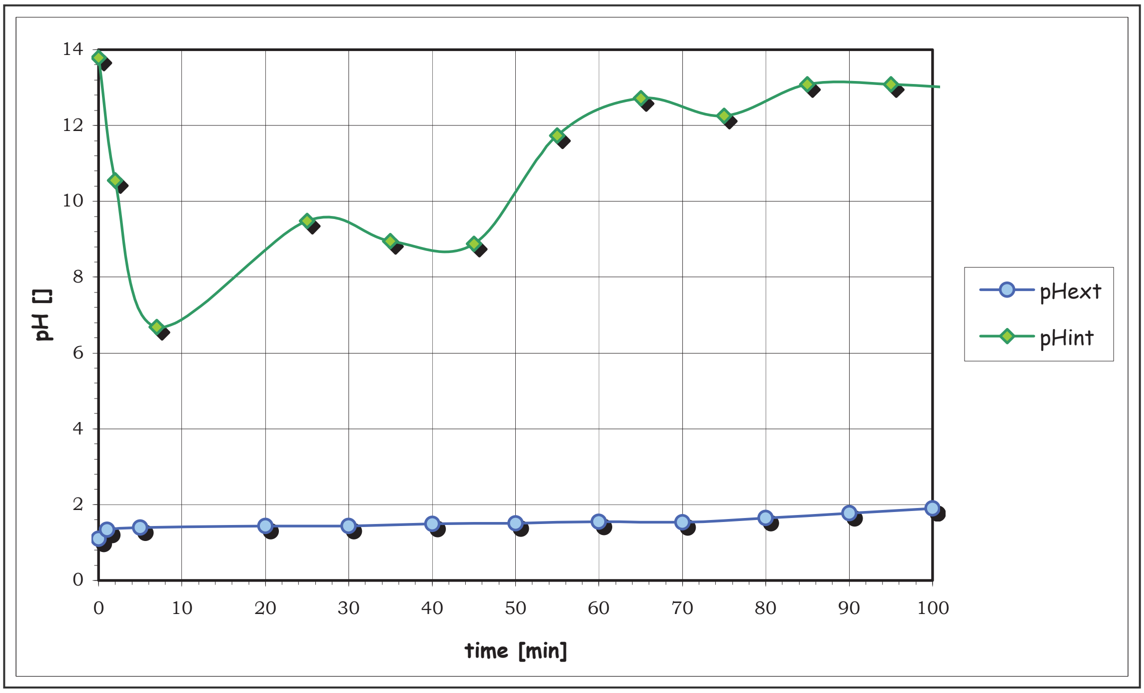

Figure D - 7: Changing of the pH during second experiment (to **Figure 29**)

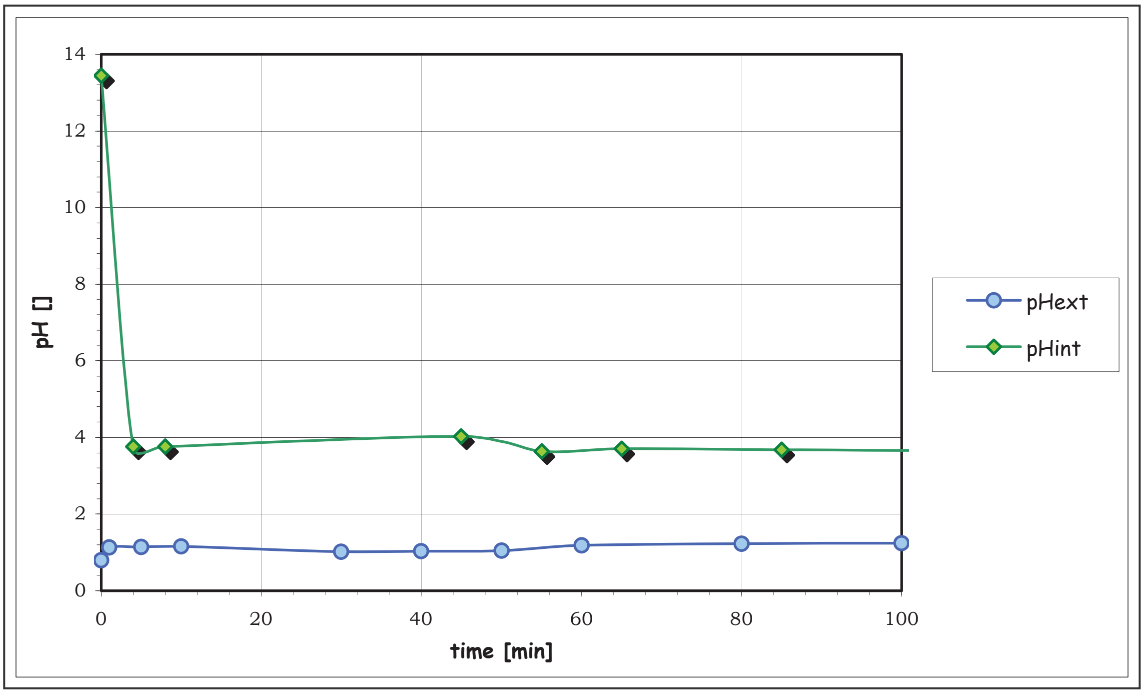

Figure D - 8: Changing of the pH during the third continuous experiment (to **Figure 30**)

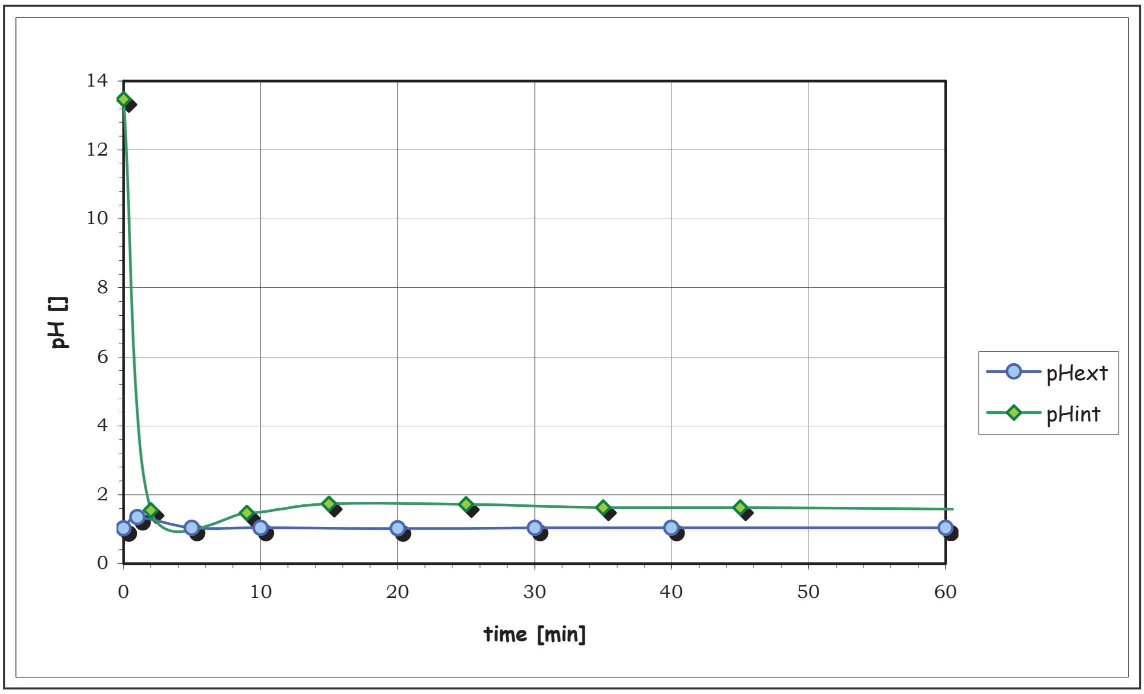

Figure D - 9: Changing of the pH during the fourth continuous experiment (to **Figure 31**)

Appendix E: Microscopic Photography of an Emulsion Drop

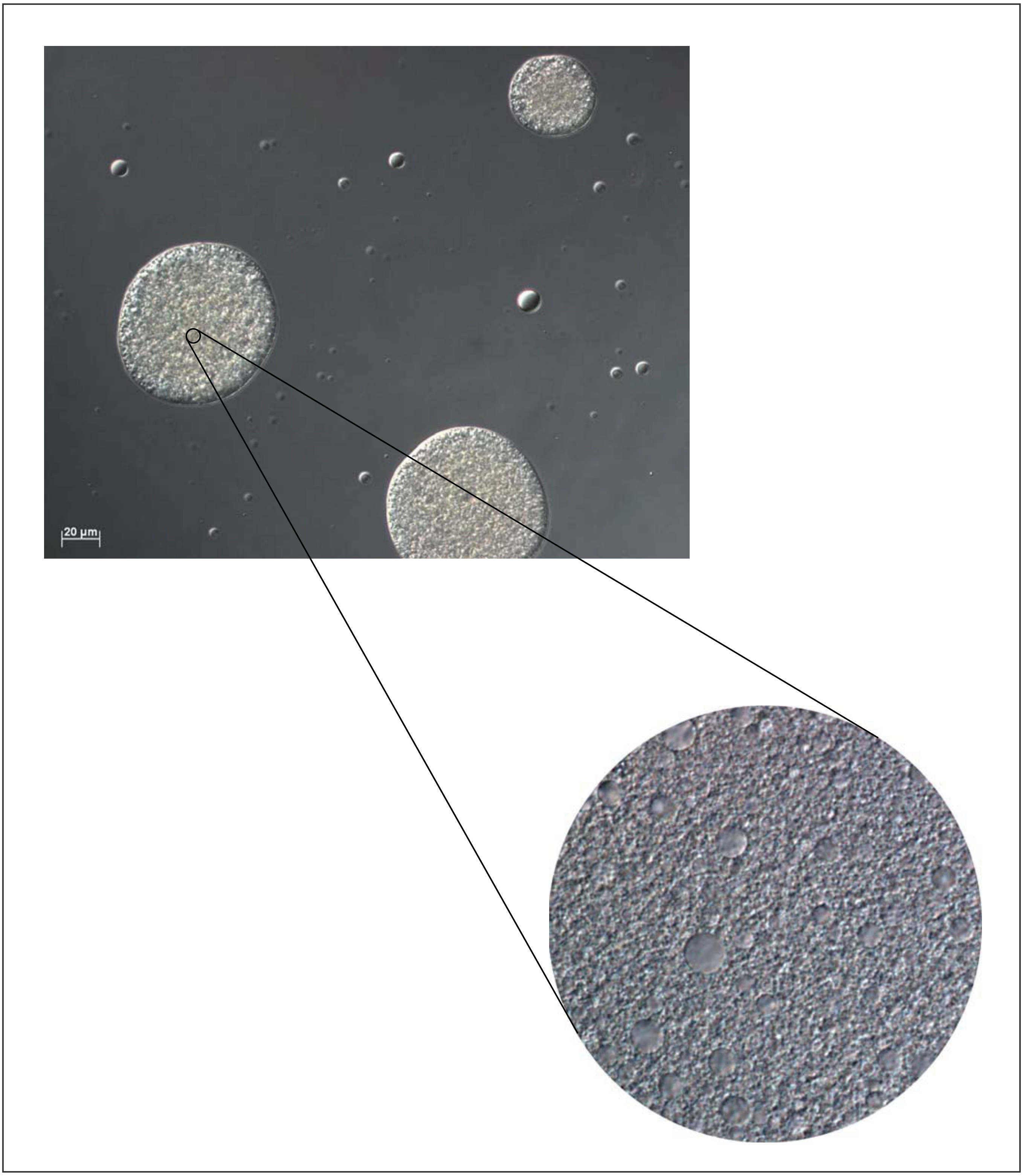

Figure E - 1: Emulsion droplet