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BARNES, DEON EUGENE

SUPPORTED LIQUID MEMBRANES IN FLOW SYSTEMS

DPhil UP 1993

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Supported liquid membranes in flow systems

by

DEON EUGENE BARNES

A dissertation submitted in partial fulfilment of the prerequisites for the degree Doctor in Philosophy in the faculty of Science, University of Pretoria, Pretoria.

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Supported liquid membranes in flow systems

by
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Degree : Doctor of Philosophy

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SYNOPSIS

The potential of supported liquid membranes (SLMs) is evaluated for automation of sample manipulation techniques in analytical chemistry. SLMs maximise the contact between immiscible phases by allowing the immobilisation of an organic phase on a hydrophobic solid which can be placed in an aqueous environment. An understanding of SLMs is developed from three perspectives. The use of SLMs is first viewed as an automated alternative to solvent extraction. Secondly, they can be used as a selective filtration technique. Thirdly, they can be used as a chromatographic technique. Each perspective allows a different insight on the subject of SLMs and their application in both the macro and micro scale. In doing so, existing systems are developed into new applications and modes of operation.

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OORSIG

Hierdie studie peil die potensiaal van ondersteunde vloeistofmembrane (OVM) vir geoutomatiseerde monster hantering in analitiese proseschemie. Organiese ekstraheermiddels, vasgevang in die porieë van hidrofobiese membrane, kan as OVM in waterige oplossings gebruik word om die kontak tussen onmengbare fases te verhoog. 'n Fundamentele begrip van OVM word vanuit drie gesigspunte ontwikkel. Eerstens word die gebruik van OVM beskou as 'n alternatiewe metode vir vloeistofekstraksie. Tweedens word dit gesien as 'n selektiewe membraanskeiding. Laastens word dit beskou as 'n chromatografiese tegniek. Verskillende aspekte word deur elk van die benaderings belig, beide vir gebruik op makro- en mikroskaal. Die benadering lei tot nuwe en gewysigde toepassings van bestaande kennis.

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CHAPTER 1
INTRODUCTION

The idea of using liquid membranes for selective extraction was patented in 1968 [1]. A thin layer of an organic liquid was used to extract a chosen solute from an aqueous solution. The idea was extended to include a thin solid support on which the liquid membrane could be immobilised as a supported liquid membrane or SLM [2-8].

The organic liquid usually contains one or more organic reagents that are traditionally used for solvent extraction. The support is a suitable porous and inert material often used for ultrafiltration. The SLM is placed between two aqueous solutions. On one side of the membrane the solute is extracted from the solution and on the other side it is back-extracted into a second solution. Extraction and a back-extraction are performed simultaneously. The extraction and back-extraction of a specific solute from one aqueous solution into the SLM are based on one of the many mechanisms recognised in solvent extraction, and can be achieved without the tedious phase-separating step used in traditional solvent extraction. At equilibrium, the effective concentration of solute in the SLM remains well below saturation point, since the solute is continuously removed from the SLM. This arrangement ensures the effective use of the extraction reagent which is often expensive or potentially toxic.

SLMs have been used for metallurgical extraction, as well as for the removal of contaminants from various process solutions [2-8] and have certain advantages over conventional solvent extraction. Because it is utilised so efficiently, only a small amount of organic phase needs to be used. The aqueous system surrounding the organic phase

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results in a minimum loss of expensive organic reagent as well as a reduction in the handling of the potentially hazardous organic phase. The use of SLMs eliminates the problems associated with homogeneous mixing and separation of the various phases. In addition, by restricting the volume of the aqueous phase efficient contact between the organic and aqueous phases both on the feed and the stripping side of the membrane is ensured. The intimate contact of the two phases is guaranteed by allowing the aqueous solution to flow in a confined space over the SLM. SLMs allow geometries suited to efficient permeation and high transport rates of the solute between two aqueous phases. The equipment is typically relatively simple and contains no moving parts; this simplicity implies ease of automation.

Although the multitude of papers on the application of SLMs illustrate the tremendous potential of this technique in the hydrometallurgical field, its full potential for the separation chemist in the analytical laboratory has not been realised. The success achieved in the use of SLMs in the hydrometallurgical environment, prompted investigation into the potential of SLMs in analytical science [9] to solve problems similar to those experienced by hydrometallurgical scientists regarding two immiscible phases. Since the use of SLMs originated in an process-related environment, it is appropriate to investigate their application in process analytical science.

1.1 PROCESS ANALYTICAL SCIENCE

Increasingly stringent demands are made on plant personnel in terms of productivity, quality and environmental awareness. These demands impact on the analytical scientist,

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and require superior solutions to achieve timeous analysis of an increasing workload. If the analysis is done in a laboratory distant from the process, the results are available hours - or even days - after a sample has been taken. This approach leads to a *post mortem* approach where the plant personnel have to learn from their errors in order to avoid similar situations. This approach to plant control and quality assurance is in direct contravention of present trends in quality management.

A new subdiscipline in analytical science, called process analytical science (PAS), has emerged and gained influence in the past decade. The approach adopted in PAS is quite different from the traditional philosophy of analytical science. The most obvious difference is the location of the measurement process. PAS has the objective of performing real-time analysis in or close to the process vessel, whereas traditionally analysis was confined to the pristine environs of a remote laboratory. The PAS approach is to strive to perform the analysis, preferably automatically, close to the process vessel, where the analyser becomes part of the process, and aims at producing results in real time. The results are then used to control the process in an automated fashion. The advantages of this approach to process monitoring and control are numerous: for example, improved quality assurance, a reduction in product wastage, improved effluent control and optimised productivity.

This approach has been developed and used successfully for almost 40 years [10]. The technology is constantly being developed, and a sound foundation of traditional analytical chemistry and techniques is a good starting point for the further development of this field.

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A host of dependable and established chemical methodologies provide a useful toolbox in PAS. In addition, well established and novel methods are combined to provide solutions. Few detectors are robust enough to deal with the raw sample. Apart from the matrix and concomitant interference, there is also the issue of sensitivity. Techniques are required that allow the separation and enrichment of a solute, and are simple and easy to automate. The current study is conducted against this background.

The demand for greater efficiency has also made its presence felt in the analytical laboratory. Owing to the escalating workload in the analytical laboratory, the demand for faster analyses is ever increasing. Shorter turnaround time of analysis, both in laboratory and process environments, makes automated sample manipulation increasingly important in analytical chemistry. Techniques developed for process analysis can also aid in the development of laboratory instrumentation, and assist in performing the tedious and often mundane routine analysis of a specific set of samples.

Although a typical sample from a process may be in solid, liquid, or gaseous state, this investigation focuses on sample manipulation for liquids. In the analysis of liquid samples, the most time-consuming part is usually the separation and enrichment of a specific solute. In this regard, solvent extraction and various filtration and chromatographic techniques have proved to be invaluable.

1.2 FLOW-BASED TECHNIQUES USED IN AUTOMATION

The separation of complex materials prior to measurement goes back to the invention of chromatography at the turn of the century. Since then, various separation techniques have

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been developed for use in analytical science. Some of these techniques include membrane separation, distillation, solvent extraction, and various forms of chromatography. Recently, the trend in separation techniques has shifted to favour the automation of the more classical labour-intensive wet chemical methods. Researchers integrate the ever-increasing power and speed of the microprocessor and developments in materials science to maximise the potential of separation techniques.

In the automation of wet chemical techniques, the mere mechanisation of the traditional analytical techniques is not sufficient. The traditional techniques were invented and evolved with the analyst in mind, and are often not the most effective way of achieving the required analysis. Techniques that have the best track record in achieving fast and reliable results are those based on flowing systems rather than batch-type mechanisation. These techniques include air-segmented flow analysis, continuous-flow analysis, high performance liquid chromatography, flow-injection analysis and sequential-injection analysis.

One of the first techniques to be used in process analysis was continuous-flow analysis [11]. In this technique the sample is mixed with the reagent by means of confluent streams. The sample and the reagent, in the simplest case a colouring reagent, flow continuously and are mixed with a T-junction. The intensity of the resultant colour, as measured by a flow-through spectrophotometer, determines the concentration of the sample.

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This technique was followed by air-segmented flow analysis [12]. Both flow techniques rely on a similar principle. In air-segmented flow analysis, however, air bubbles are introduced intermittently into each stream by a mixing T-piece. In this way a series of discrete mixing vessels is simulated.

Both these techniques are easily automated, but suffer some inherent complications. The main source of error stems from the fact that neither technique compensates for a changing baseline. The baseline signal from a flow-through detector changes due to various factors. One reason might be the coating of the detector cell. A slow build-up on the conduit walls, blockages or degrading pump tubing may result in a change in flowrate. This might also cause drift in the detector reading. In both continuous-flow, and segmented-flow analysis there is no way of keeping track of such a changing baseline. Another concern in these techniques is the excessive reagent consumption.

Flow-injection analysis (FIA) addresses many of the problems experienced by its precursors, and has gone a long way to successfully addressing the automation of analytical procedures. FIA is based on the reproducible introduction of a small but well-defined sample volume into a continuously flowing reagent stream, the carrier solution which carries it to a flow-through detector. *En route,* the sample disperses and reacts in an extremely reproducible manner to form a detectable species. The detector registers the passage of the sample bolus. The result is a flow-injection peak whose height indicates the concentration of the sample, and the baseline is continuously monitored and

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considered. The peak shape, peak width and area underneath the peak relate diagnostic data about the reaction and flow dynamics of the sample.

The concept of introducing an sample aliquot into a flowing stream has been utilised for years in gas chromatography. In the 1960s this principle was adapted for use in high-performance liquid chromatography (HPLC), and in 1970 the concept of injecting a sample without the use of a column was used by Naggy, Feher and Pungor [13]. They described the injection of a portion of a sample into a stream flowing through a stirred mixing chamber, where the chosen analyte was determined by potentiometry. This concept was defined, and the term flow-injection analysis (FIA) was coined in 1975 by Růžička and Hansen [14].

FIA has led to dramatic improvements in the speed and quality of analysis. In FIA the chemical environment of the sample can be adjusted by a careful choice of the carrier solution or by merging various reagent streams with the carrier stream. During transport, the sample disperses and reacts with the components of the carrier solution. Volumes and concentrations of the various streams can be controlled precisely in space and time by well-controlled shuttling, such as moving, stopping, restarting, oscillating, mixing, splitting and resampling the flowing stream or parts of it. Clever manifold design and controlled flowrates allow highly reproducible reaction times. The power of an FIA manifold can be enhanced even further by placing catalytic, reducing or oxidising surfaces, as well as photo-, bio-, or electro-active membranes in the manifold. Sensing surfaces can be placed individually or in arrays at selected positions. This added versatility in chemical

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manipulation also permits the detection of a specific stage in the transient formation of complexes, especially those that are too rapid for detection by normal batch operations.

FIA as an analytical technique has certainly distinguished itself as a fast, precise, accurate and extremely versatile analytical tool. Although FIA is predominantly reserved for liquids, it provides an easy and powerful way to simplify traditional batch analytical methods. A further advantage is its proven suitability in both the laboratory and the process environment. At first FIA was used for the quick determination of chemical solutes [14]. As the technique developed, various sample-handling procedures were added to the FIA tool kit [15-18]. FIA has been used to automate wet chemical techniques to improve analysis time, and quality and the reproducibility of the analysis. In addition, the miniaturisation achievable with FIA resulted in an inevitable reduction in space requirements and sample and reagent consumption. This has tremendous potential as far as the development of rugged micro-detection systems and micro-analysers are concerned. In addition to its versatility these characteristics of FIA have made conventional laboratory methods much more accessible to process analysts.

Separation and selective enrichment are currently challenging areas under investigation in FIA.

1.3 SEPARATION AND TRACE ENRICHMENT

Separation and selective enrichment are two of the most fundamental steps in analytical chemistry. With the increasing demand for fast and accurate analysis, it is not surprising

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that the automation of separation processes should play a major role. Several investigators have discussed techniques for both the separation and the preconcentration of chemical solutes.

Separation is performed frequently on soluble species in solution. Techniques that have proved themselves invaluable in this respect are filtration (in the broadest sense of the word), distillation, solvent extraction, and electrochemical and chromatographic separation.

1.3.1 Solvent extraction

Solvent extraction is often used as an analytical technique to achieve selective separation of both inorganic and organic compounds from solutions. It is also used to remove interferences, or to preconcentrate the analyte where selective separations are required.

Solvent extraction is a powerful analytical technique that has proved itself in batch-type operation for sample clean-up. It originated as a batch method, and involves the tedious and time-consuming manipulations of two immiscible phases. Large volumes of sample and potentially hazardous organic solvents are required. Various attempts have been made to automate this technique to capture its power in an automated and continuous-flow fashion [17]. These include mechanical shakers and continuous countercurrent extractors. In the hydrometallurgical field, large cross-flow mixing and settling tanks have been developed to obtain continuous or multiple extraction.

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The greatest success in the attempted automation of solvent extraction in analytical laboratories is achieved with the continuous-flow approach, the first of which is air-segmented flow that preceded FIA. Karlberg *et al.* [19] originally designed FIA-solvent extraction (FIA-SX) apparatus, and since then more than a hundred publications that describes the use of FIA-SX have appeared [20-31]. FIA has integrated solvent extraction with most instrumental analytical techniques such as atomic-absorption spectrophotometry (AAS) [27], inductive-coupled-plasma (ICP) spectrophotometery [28], HPLC [29] and gas chromatography (GC) [30]. Even with the simplicity of FIA, the intricate manipulation of two immiscible phases remains a difficult and cumbersome task, and in the routine analytical laboratory, batch methods are still favoured. Phase-contacting and phase separation remain challenging areas of research. In addition there is also the problem of emulsion formation between the phases.

A number of authors have described phase-contacting and phase-separating devices [20, 31].

- Recently Bäckström [27] reported on a segmenter for continuous extraction with an eight-stream manifold. Although this is an improvement on manual solvent-extraction processes the system is still complex and not really suited to unattended process analysers.
- Dasgupta [32] reported on a novel approach where a solvent is injected into an aqueous sample stream that contains a surfactant. The solute is extracted from the sample. By intelligent zone sampling, the enriched

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organic plug is removed from the sample stream and injected into a second organic stream flowing through the detector. The organic phase supported on the tube wall can be seen as an forerunner of the use of SLMs even though this association was not made before.

- Audunsson [9] used an SLM for an excellent theoretical study, but remarks that the slow kinetics of the extraction process might pose problems in the use of this technique.
- Another solvent-extraction approach that links closely with SLMs is the use of a stabilised emulsion, where the droplets of the emulsion represent the liquid membrane. The stripping solution is contained in tiny droplets in a water-in-oil emulsion. The emulsion is suspended in the feed solution to extract the solute of interest.
- Kumamura [33] used this principle (not in an FIA system) to pre-concentrate cobalt before introduction into an AAS detector.
- Toei [34] approached solvent extraction more from a chromatographic point of view when he remarked that phase separators must be able to remove all traces of the unwanted phase, and simultaneously isolate a large fraction of the phase of interest. He did this by using a hydrophobic gel in a glass column to absorb the aqueous phase. (The gel was in the form of distinct particles, not unlike the supports usually used in HPLC, over which the solution could flow). This approach can be likened to partition chromatography in a reversed form.

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1.3.2 Filtration and distillation

Filtration, in the broadest sense of the word, includes the whole spectrum of membrane separation techniques such as filtration, ultrafiltration, dialysis, and osmosis, as well as other more sophisticated membrane separation techniques that will be discussed in detail in Chapter 4. These techniques have found wide application in a variety of situations, and can be traced back to the earliest days of civilisation. Membrane separation techniques have been automated to various degrees for different applications. With the introduction of automated wet chemical analysis various novel filtration devices have become commercially available. A number of designs, including cross-flow filters of sintered metal and ceramics, have been patented [35, 36]. The current development of various designs illustrates the demand from industry for sophisticated filtration technology.

In the development of ultra-filtration technology, porous polymer membranes became commercially available. The membranes used are traditionally flat sheets and are used for batch treatment of samples. These porous hydrophobic membranes are robust and versatile, and are especially popular in the bio-sciences. Various materials, such as polytetrafluoroethylene (PTFE), polyethylene, polypropylene, and polycarbonate have been used for their fabrication. These materials give each membrane characteristic properties that can be exploited in various applications.

Membranes are traditionally associated with filtration techniques, and their use to separate chemical species is not immediately apparent. With the introduction of an assortment of

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polymeric materials, the use of membranes was extended to include dialysis, osmosis, and cation and anion exchange membranes. The development of these membranes made it possible to use membranes to effect more than just a separation on physical grounds. Some measure of chemical discrimination could now be engineered into the membrane.

Recently, with the emphasis on automation, geometries have been developed to include long narrow-bore tubes. These tubes have found a unique application in fermentation processes, where they are used as long collection tubes of the gaseous (or sometimes organic) phase from fermentation broths. This inspired their use for the separation of gases from liquid streams in FIA. The membranes have been used either as degassing devices for flow streams, or for the low-pressure distillation of volatile compounds such as cyanide, ammonia, hydrogen sulphide and the hydride-forming elements [37]. In these cases the solute of interest is liberated from the solution by, for example, changing the pH-value. The gas permeates selectively through the small pores of the tubing and is collected on the other side of the tube, either in a second liquid stream or in a gaseous carrier.

Another application of automated membrane separation in FIA is dialysis. Various papers have appeared on dialysis in flow systems, and as early as 1957 Skeggs described automated continuous flow dialysis [38]. Hansen exploited dialysis for dilution [39] and since then various authors have used dialysis for sample clean-up, physical separation of unwanted phases, and chemical discrimination based on size of the solute [15, 16, 19]. A dialysis membrane used prior to sample injection [40] illustrates the potential of

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membranes for sample manipulation. The use of the membrane in this role allowed sample clean-up, micro-filtration, changing the sample matrix and dilution.

1.3.3 Chromatography

Chromatography covers a wide field in separation science. Most chromatographic separations have been automated to various extents. GC and HPLC have achieved a high level of automation, not only in the laboratory but also in the processing plant. Chromatography was one of the first instrumental techniques to be used on-line and has an exceptional track record [41]. Various investigators have reported on the use of HPLC in an on-line monitoring of various components [42].

Chromatography is an extremely powerful separation tool that also lends itself to automation. A present concern is the rate of measurement (2 to 4 measurements per hour being typical). HPLC and FIA have certain equipment in common and also share the concept of introducing a small sample volume into the flow stream. In a recent publication Růžička and Christian [43] took a closer look at FIA and HPLC and asked the cryptic question: "twins or siblings ?" While some chromatographers may understand FIA as chromatography without a column, columns have recently been finding their way into the FIA manifold, thus clouding the distinction between the two techniques. In general FIA is much faster than HPLC.

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Columns have been successfully used in FIA, first as packed bed reactors or ion exchange columns for sample clean-up. More recently an FIA technique called sorbent-extraction or solute focusing has been introduced [44]. A soluble derivative of an organic complex is immobilised on a small amount of chromatographic support; the sample is then passed over the support, and the solute of interest is captured and concentrated on the modified support. After a suitable preconcentration time, the solute is washed from the support and carried to a flow-through detector by a suitable stripping solution.

1.4 AIM OF THE INVESTIGATION

In this work the application of SLMs in a flowing system will be investigated in an analytical environment. The aim is to obtain selective separation and enrichment of inorganic solutes in order to improve the quality of analysis, reduce manual sample manipulations and shorten analysis time, both in the laboratory and in the process environment.

The use of SLMs leads to an interdisciplinary technique that is based on principles associated with solvent extraction, membrane separation and chromatography. Because SLMs may be seen as a hybrid of techniques, the various areas will be briefly introduced without going into a comprehensive review of all the previous work on these separation sciences. This study concentrates rather on SLMs and provides a selected overview of work in the various related fields that are relevant. The basic theory of each technique will be discussed in the appropriate chapters on solvent extraction, membrane separations

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and chromatography. FIA, because of its excellent track record, is chosen almost exclusively as the basis for both development and (combined with various other detection techniques) for analysis.

By placing SLMs alongside related established separation techniques new insights into this powerful tool will emerge. The improved understanding of SLMs will subsequently be demonstrated by studying several practical aspects of SLMs and their implementation in measurement systems for both the laboratory and the process environment.

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CHAPTER 2
THEORY

The theory behind the transport of species through SLMs has been the subject of many papers, reviews and monographs [1-41]. Because SLMs have both a physical and a chemical character, theoretical considerations have been developed from different perspectives. Indeed, even in this investigation the application influenced the theoretical perpectives. Furthermore, the technology associated with SLMs has developed independently in different technological fields: notably the fields of membrane science and solvent extraction. The enhancement of the permeation rate of a specific solute makes the SLM an attractive option in membrane science. Several models that describe this permeation have been proposed by researchers [1-4]. In the hydrometallurgical field, investigators concentrated on the use of SLMs as an alternative technique to conventional solvent extraction [5-7]. Both approaches will be considered. The limitations of these approaches as a tool for the analyst in the study of SLMs in a flow system will be highlighted, and some suggestions to address these shortcomings will be made.

2.1 BACKGROUND

The idea of facilitated transport originated in the field of gas separation. Biologists as early as the 1800s studied the perm-selective permeation of oxygen from the lungs to the blood system, with the associated diffusion of carbon dioxide in the opposite direction. Although this classical example of selective membrane separation was studied quite intensively (mainly for gas separations) it did not find wide application outside of biology until recent times.

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Olander [8] (1960) used reaction equilibrium conditions on either side of a semi-permeable membrane to describe one-dimensional unfacilitated mass transfer through a flat membrane. He studied four reversible reaction schemes in his analysis. Ward [9-11] (1967-72) used the principles developed by Olander to pioneer the industrial application of facilitated transport for gas separations. A review of relevant mathematical models is described by Blumenthal and Katchalsky (1969) [12].

Li [13] (1969) suggested the first process application of liquid membranes using facilitated transport. The proposed process allow the selectively separation of chemical species in solution. His patent dealt with the separation of a binary aqueous mixtures consisting of aromatic and paraffinic hydrocarbons with a similar carbon chain length. A polar surfactant was used to encapsulate an aqueous phase in tiny droplets. The emulsion was then dispersed in the aqueous phase, which contained the aromatic and paraffinic hydrocarbons. The aromatic hydrocarbons were preferentially extracted into the emulsion by the surfactant. This patent marked the beginning of a spate of investigations into the application of liquid membranes.

The theory behind SLMs that was developed during this period in membrane science originated from theoretical models for the facilitated transport of gases. Goddard *et al* [14, 15] (1970) discussed diffusion through finite membrane systems at near-equilibrium conditions. They proposed a model which uses the concept of an equilibrium core in each phase, with boundary layers between the adjacent phases. This model still forms the basis of various investigations concerning mass transport through SLMs. At the same time, a

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notable development was the immobilisation of liquid membranes on solid supports, proposed by Cussler [1] (1971) for selective gas permeation. In Cussler's work [1, 16, 17] (1973), a rigorous but theoretical approach to facilitated transport was taken. His results are general, and contain parameters which are difficult to measure, and afford little insight into the physical parameters which control the mass transport. Cussler used membranes made of filter paper in laboratory studies. These membranes had limited stability, and could hardly be considered for industrial application [18].

During the period 1974-1979 various investigators used the idea of SLMs to develop either macro scale applications or mathematical models to describe certain aspects of the transport through SLMs. Early applications include a Russian patent that was registered in 1974 by Ivanovskii et al [19] for the extraction of copper. This patent marks the first reference to SLMs for solvent extraction. Baker *et al* [3] (1977) give an overview of the development of SLM theory, and illustrate the use of SLMs as an alternative to solvent extraction. Various other publications addressed the application of SLMs and most of these concentrated on hydrometallurgical processes. (Specific applications are summarized in *Table 3.1 - 3.3.)*

During this time a variety of models were developed by different authors [1-7, 17]. The theoretical models are specific and can be used for the accurate prediction of the influence of the various parameters on the behaviour of an SLM. They are useful for the design and scale-up of specific SLM processes. In contrast to the present investigation, these earlier studies concentrated mainly on batch processes with flat sheets separating stirred solutions.

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Essentially they have been confined to steady-state transport through SLMs in flat-plate geometries [20].

- Schultz *et al* [21, 22] (1974) reviewed theoretical progress in facilitated transport systems. Their evaluation included an overview of mathematical methods for solving transport models. They provided an extensive review of the entire field of facilitated transport, and covered the mechanistic aspects, experimental systems and mathematical analysis. An important conclusion was the relationship established between the permeation rate and the various equilibrium constants. They showed that when two solutes compete for the same reagent, conditions can be found where one of the solutes can be transported against its overall concentration gradient (uphill transport). The solute can also be accelerated in the usual direction of diffusion by changing specific parameters.
- Smith *et al* [23] summarized experimental and theoretical work in the field of facilitated transport up to 1974. They favoured the perturbation technique using the concept of film thickness. They showed that for thin films, the transport is reaction-limited, and for thick films the transport becomes diffusion-limited.
- Halwachs and Schügerl [24] (1980) presented a general discussion of liquid membranes, carried out some mathematical modelling, and described some possible industrial applications.
- Danesi *et al* [25-29] conducted a thorough investigation into the application SLMs and in an extensive series of publications (since 1982) they developed various models for the permeation of chemical species through SLMs. They suggested various modes of operation, of which the use of porous tubular membranes [5]

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(1984) and a composite membrane system (consisting of a combination of two different and complimentary SLM systems [27] (1984)) are among the more significant developments. They also developed a set of simplified mathematical expressions that describes the permeation of species through SLMs based on both membrane and solvent extraction principles. Their investigation was aimed at hydrometallurgical applications, and they addressed separation factors for various mixtures of metal ions [25].

The application of SLMs in analytical science has been limited. However, there have been a few innovative investigations with limited application.

- Bartsch *et al* [30] (1982) concentrated sodium preferentially to lithium.
- Similarly, Sakamoto *et al* [31] (1987) used crown ether SLMs to concentrate lithium preferentially to sodium.
- Danesi and Rickert [25] (1984) separated cobalt and nickel with an SLM containing Cyanex 272.
- Lindegard *et al* [32] (1986) preconcentrated amines on a flat sheet SLM unit before introduction into a gas chromatograph.
- Audunsson [33] (1986) gave an in-depth analysis of the unfacilitated transport of the amines through an SLM. His results showed that when the transport through the membrane is facilitated (using an alcohol instead of an aliphatic alkane), the permeation can be doubled.

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- Cox *et al* [34] (1990) studied the selective pre-concentration of zinc between two stirred solution using a di-alkylphosphoric acid SLM. The preconcentration was selective but took several hours.

2.2 THEORY

For the macroscale, several theories have been proposed by different investigators and applications are focused on hydrometallurgical processes. The application of these theories, to the somewhat unique environs of a flow-based analytical procedure, is difficult. Nevertheless, certain aspects are relevant, *viz.*

- the various components of the SLM system,
- the stages in the overall permeation, and
- the controlling parameters in the development of an SLM system.

2.2.1 Terminology

The diversity of disciplines reflected in the literature resulted in a proliferation of nomenclature. In an attempt to eliminate confusion a list of the definitions, used in this study is provided.

- *Solute* - The chemical species of interest that has to be separated from its matrix by the SLM.
- *Feed solution* - The aqueous phase from which the solute is extracted.

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- *Stripping solution* - A second aqueous phase, into which the solute is back-extracted from the SLM.
- *Co-ion or counter-ion* - A chemical species in one of the aqueous phases that aids the permeation process and is usually present in high concentrations. The concentration difference of this compound in the two aqueous solutions provides the driving force for the overall permeation. If its concentration in the feed solution is higher than in the stripping solution it is called a co-ion, and if its concentration in the stripping solution is higher than in the feed solution it is called a counter-ion.
- *Extractant* - The active reagent in the SLM which is responsible for the complexation of the solute and thus the extraction of the solute. (In some publications this is referred to as the *carrier*, but this term will be avoided in this study because of confusion that may arise with the use of the term in FIA.)
- *Diluent* - The organic solvent that is used to dilute the extractant. It is usually inert but can influence the performance of an SLM.
- *Modifier* - An auxiliary organic reagent that augments the performance of the SLM - usually by a synergistic extraction mechanism.
- *Organic phase* - The organic solution that forms the physical partition between the feed and the stripping solution. It is a mixture consisting of the reagent, the diluent and sometimes a modifier.
- *Support* - An inert, porous, hydrophobic, solid polymeric material.

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- *SLM* - When the organic phase is immobilised in the pores and on the surface of the support to form a thin organic liquid layer reinforced by the support, the combination is called a supported liquid membrane.

Various terms have been used for the permeation of the solute through the SLM, for example carrier-mediated transport [35, 36], facilitated transport [37-39] and coupled transport [3-5, 34]. The use of this terminology will become clear in Chapter 4 in a more detailed differentiation, based on the mechanism of transport through the membrane.

2.2.2 What are supported liquid membranes?

A typical SLM system involves an organic phase, a support and two aqueous solutions. The organic phase is an aqueous-immiscible phase. It contains the reagent, a diluent, and sometimes a modifier. The reagents are those typically used in solvent extraction. They can be present in trace amounts, or more often in significant amounts of up to 30 per cent. The bulk of the organic phase consists of the diluent. The diluent is usually an inert organic solvent, which acts as a solvent medium for the organic reagent. In some cases, however, the solvent plays a much more active role in enhancing either the extraction kinetics or the selectivity of an SLM. In addition the organic solution can also contain modifiers. The modifiers usually favour the extraction of a certain selected species in a synergistic fashion, thus improving the selectivity of the SLM.

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The support is typically an inert porous hydrophobic material, and can be one of many geometries. The supports are often membranes commonly used for ultra-filtration. Currently there is a large selection of such supports commercially available as either flat sheets or tubes.

The organic solution permeates into the pores and coats the surface of the support. The thin film of organic solution forms the SLM. When an SLM is interposed between two aqueous solutions, it acts as a selective semi-permeable membrane for the transport of a solute from one aqueous solution to another.

Selective permeation is achieved when the extractant in the organic phase selectively interacts with the solute in the feed solution. A selective complexing reaction usually increases the effective solubility of the solute in the SLM. The solute of interest is captured and concentrated in the organic phase, and the complex diffuses through the membrane. On the opposite side of the membrane, the reaction between the solute and the reagent is reversed due to different prevailing conditions. In a specific case the prevailing conditions favour the formation of a stronger complex between a counter-ion, present in the stripping solution, and the extractant. The complex dissociates and both the solute and the extractant are released; the solute passes into the stripping solution, and the extractant stays in the SLM to repeat the cycle.

The driving force of the mass transport through the SLM is the concentration difference of an unrelated compound, the co-ion or counter-ion. The concentration difference of this ion in the two aqueous phases determines to what extent the solute can be enriched. Because the

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permeation of the solute is independent of its own concentration in the stripping solution, the solute can be enriched against its concentration gradient. The rate of permeation between the two phases is controlled by various factors, including the composition of the SLM and the composition of the two aqueous phases.

2.2.3 Components of an SLM system

In the literature on SLMs three phases are usually identified [7, 27, 40, 41]. These are shown in *Figure 2.1*.

- Phase I - The first aqueous phase, the feed solution from which the solute is extracted.
- Phase II - The organic phase that forms the physical partition between phase I and phase III.
- Phase III - The second aqueous phase, or stripping solution into which the solute is back-extracted from phase II.

The specific physical and chemical parameters which determine the diffusion through the three phases are listed in *Table 2.1*.

The total mass transfer of the solute through SLMs can be ascribed to two processes. One is the diffusional process that is controlled more by the physical parameters of the system, and the other is a process based on the chemical reactions which allow the transport and the respective kinetic rates governing these reactions [28].

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Table 2.1
Parameters that influence permeation

Feed solution	**Organic phase**	**Stripping solution**	**Physical parameters**
Type of solute	Type of extraction reagent	Type of co-ion	Flowrate of the feed
Concentration of solute	Solvent /diluent	Concentration of co-ion	Flowrate of strip
pH value	Auxiliary reagent	pH value	Contact area of SLM
Type of buffer	Concentration of reagents	Type of buffer	Geometry of SLM
Concentration of the buffer	Support	Concentration of buffer	
Ionic strength		Ionic strength	

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The chemical reactions are associated mainly with the aqueous phases - phase I and phase III, and their boundaries with the organic phase. The diffusional process is determined largely by the composition of phase II. The constituents of phase I and phase III will be discussed in Chapter 3, from a solvent extraction point of view. The physical conditions will be considered in Chapter 4, where the SLM will be studied as a membrane.

2.2.4 Stages of the transport through SLMs

Danesi [38] and various other investigators developed a model based on the three phases identified in *Figure 2.1*. In the transport of the solute from the feed solution to the stripping solution, through the SLM, the following five stages were identified [6, 42].

- Stage 1. Diffusion of the solute through the semi-stagnant region between the feed solution (phase I) and the SLM (phase II) - also known as the Nernst layer 1.
- Stage 2. Complexing of the ion with the reagent in the SLM (phase II).
- Stage 3. Diffusion of the solute through the SLM (phase II) due to its concentration gradient.
- Stage 4. Decomplexing of the solute and the complexing reagent from the SLM, with the subsequent release of the solute into the Nernst layer 2.
- Stage 5. Diffusion of the solute out of the Nernst layer 2, on the stripping side, into the stripping solution (phase III).

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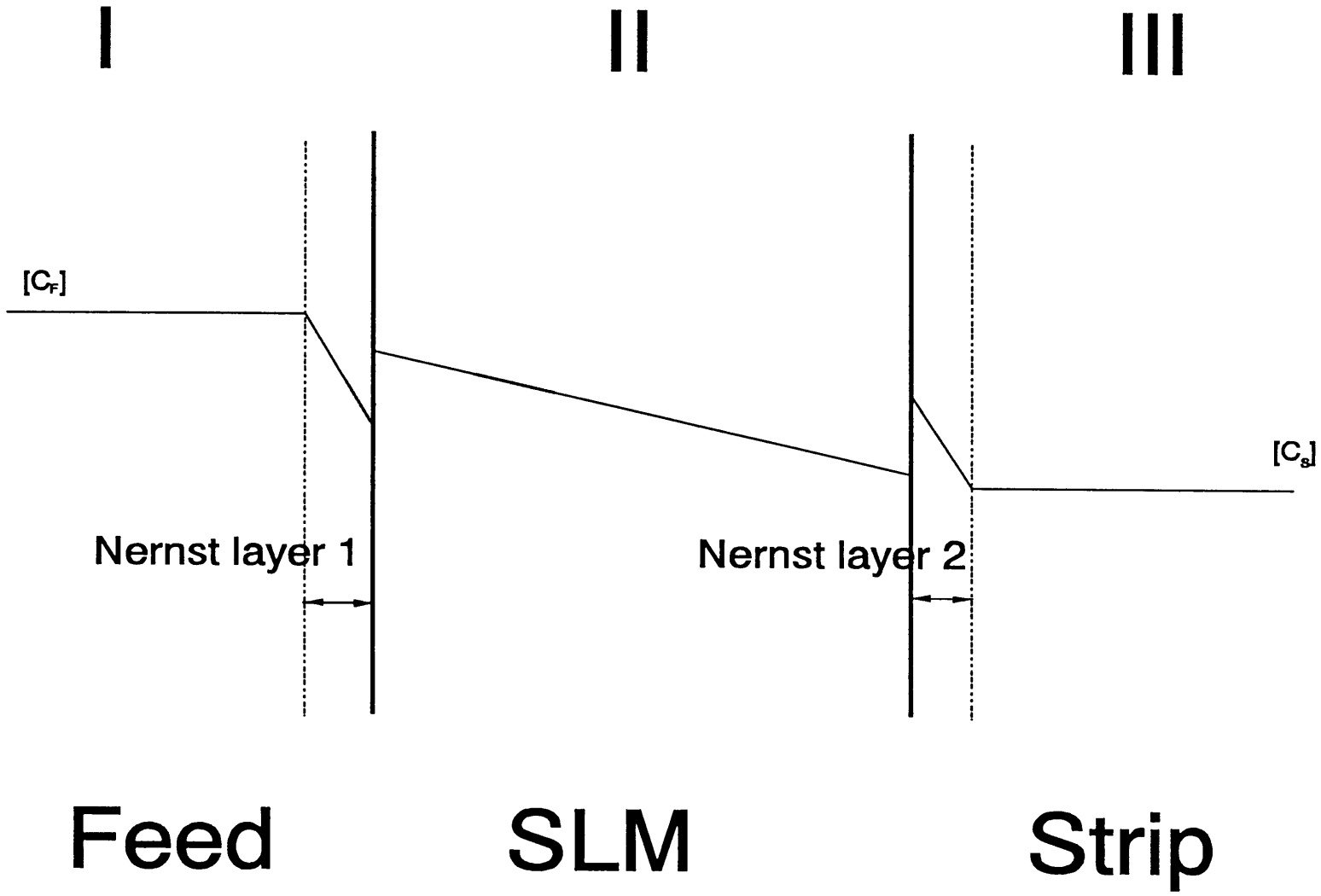

Figure 2.1 Schematic of an SLM, showing the typical concentration gradients of the solute in the various phases.

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The study of Kreevoy [6] illustrates the functionality of this approach for four SLM systems. He used these five stages of permeation to postulate a permeation model. The flux in each of the five stages J_n (where n identifies the respective stage) can be expressed as the product of a rate constant K_n with units $cm.s^{-1}$ and the concentration of the solute in the previous stage C_{n-1}.

$$J_n = K_n C_n \tag{2.1}$$

Kreevoy used an analogy between the rate constants (K_n values) and electrical conductances in series in an electrical circuit to determine the overall permeability. He postulated that the respective rate constants behaved like electrical conductances. Thus the inverse of each K_n value behaved as an electrical resistance. The inverse of the overall permeability, K_{tot}, is then the sum of the inverse of the K_n values.

$$\frac{1}{K_{tot}} = \sum_{n=1}^{5} \frac{1}{K_n} \tag{2.2}$$

The stage associated with the smallest K_n value will be the rate-determining step, and will have the greatest effect on the overall permeation. To optimise an SLM system one must identify and improve the conditions that would favour permeation through this particular stage. Kreevoy went further to suggest methods to identify the rate-determining stage and calculate the respective K_n values.

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Each stage involves both chemical reactions and physical diffusion processes. By changing the chemical conditions one can shift the equilibrium of the reaction to improve a particular K_n value. Physical conditions, such as the flowrates of the feed and/ or the stripping solution over the SLM, can also improve K_n values.

2.2.5 Controlling parameters for the evaluation of SLM systems

In the evaluation of SLMs, various parameters have been proposed. The parameters that most investigators used to base their selection for a particular SLM system are:

- the flux,
- selectivity,
- enrichment, and
- stability [7, 27].

Each parameter is discussed and the basis of its suitability as means of evaluating SLMs.

2.2.5.1 Flux

The rate of mass transport of the solute through an SLM is the most common criterion for evaluating a particular SLM. Most investigators use the laws of diffusion to formulate their mathematical models.

The basic laws of diffusion of chemical species through various membranes were formulated by the German physiologist, Adolf Eugen Fick (1829-1901). Fick's first law states that the

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rate of diffusion *(dn/dt)* of a solute across an area (A), known as the diffusive flux (J) is calculated as follows [43]:

$$J = (dn/dt) = -DA(dC/dx) \quad (2.3)$$

where *(dC/dx)* is the concentration gradient of the solute and *dn* is the amount of solute passing across the membrane in time *dt*. D is a diffusion coefficient that accounts for the environment of a specific membrane.

This law describes the diffusion in terms of the physical characteristics of the support. Current mathematical models that describe the mass transfer of solutes through SLMs are based predominantly on Ficks first law of diffusion.

In a study of SLMs it is convenient to use the parameter **Flux** to describe the complex process of the permeation of the solute through an SLM. Various investigators have described this process combining concepts such as diffusion through the aqueous stagnant layer, interfacial chemical reactions and membrane diffusion in terms of the flux. Several techniques have been reported for the measurement of flux. In measurable terms, it is best to express flux as the decrease in the initial concentration (C) of the solute in the feed solution with time (t) [25, 26, 28, 44].

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$$J = DV \times \frac{dC}{Cdt} \tag{2.4}$$

where V is the volume of the feed solution and D is the diffusional coefficient. The diffusional coefficient is a composite constant which incorporates the respective distribution coefficients as defined in solvent extraction, as well as the physical properties of the SLM and its environment [25, 45].

The permeation coefficient (P) is then defined as the flux through a unit area of the membrane.

$$P = \frac{J}{A} = \frac{dC}{Cdt} \times \frac{DV}{A} \tag{2.3}$$

The equation can be integrated to:

$$\ln\left(\frac{C}{C_o}\right) = -\frac{PAt}{DV} \tag{2.4}$$

where C_o is the initial feed concentration.

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Various investigators have illustrated the validity of this equation, particularly for stationary and batch experiments [8, 25-29, 46]. In these studies two distinct situations were identified; one for low solute concentration in the feed solution and the other for high solute concentration. The two concentration regions are governed by different limitations, and are described by different mathematical equations.

Low concentrations. Investigators showed that the diffusion of the solute in the SLM is about one order of magnitude lower than in the aqueous solutions [26, 47]. However, at low concentrations the chemical reactions which allow the solute to permeate into the membrane becomes rate-determining. Because the permeation is chemically controlled, the rate-limiting stage of mass transfer is the first stage (K_1). At low concentrations the restrictive movement of the solute through the membrane becomes negligible. The most typical factors that have been identified to influence the permeation rate in this stage are the chemical composition of the feed solution and the initial concentration of the solute in the feed solution.

Equation 2.5 was found to hold for low solute concentrations [28, 29, 47]:

$$\mathbf{J} = k\,\mathbf{C} \tag{2.5}$$

where k is a collective constant that depends on the geometry of the system. C is the initial concentration of the solute in the aqueous-organic interface (which for all practical purposes is equivalent to its concentration in the feed solution).

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These investigators studied closed SLM systems in which a flat SLM separates two stirred aqueous tanks. Equation 2.5 predicts that the flux will decrease linearly with time as the concentration in the feed solution decreases. The equation was found to hold for lower solute concentrations [6, 18, 26, 48, 49]. Matsuyama *et al* [28, 29] described the flux of cobalt through a DEHPA SLM as the product of the cobalt concentration and the concentration of the cobalt-extractant complex. They worked under conditions of low metal concentration, high pH, and high extractant concentration. They concluded that the diffusion of the metal in the stagnant layer of the feed solution was rate-determining.

They found that the calculated values were in agreement with theoretical values, and ascribed deviation from this equation to the formation of aggregates of the extractant. In feed solutions with low concentrations, fast interfacial reactions between the organic reagent and solute occur, and the effect of aqueous diffusion and chemical reactions can be expected to diminish. It can however, not be completely disregarded [49].

High concentrations. As the concentration of the solute increases, the amount of solute that can be accommodated by the SLM reaches a physical limit. If the concentration of the solute is sufficiently high, the amount of solute that permeates through the SLM, stage 3, becomes constant. For high concentrations the diffusion through the SLM is rate-controlling, and the

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flux becomes independent of the initial concentration of the solute in the feed solution. This flux is often defined as a facilitation factor, F, that describes the total mass transfer of the solute through membranes. The following equation which expresses the independence of the flux on the feed concentration applies:

$$J = J_{Max} = F \qquad (2.6)$$

The facilitation factor depends on both the physical and the chemical environment of the SLM. Chemical factors include the metal species that is transported, the degree of polymerisation of the metal with the extractant, and the composition and pH of the feed and stripping solutions. Deciding physical parameters include temperature, flowrate, viscosity of the liquid membrane, reagent concentration, membrane thickness, porosity, and tortuosity [5, 25-29, 48]. (Tortuosity is defined as a dimensionless parameter that compensates for the route that a specific solute must follow in its passage through a membrane. It is the length of the diffusion path divided by the thickness of the membrane.)

Various investigators found that the flux through SLMs is between 1,7 and 5 x 10^{-11} mol.dm^{-3} cm^{-2} s^{-1} for a membrane with a typical thickness of 50 to 200 μm. Cox [34] found that this value is about the same as the flux observed for Donnan dialysis for the same area and thickness of membrane. Kreevoy [6] states that: '...even with these best-case estimates it is hard to imagine a flux of more than 10^{-7} mol.dm^{-3} cm^{-2} s^{-1} for current commercial polymer membranes with a minimum thickness of approximately 2,5 μm...' . The concentration at which the permeation rate becomes constant depends on various factors, but

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was found to be surprisingly similar for different systems. The concentration at which this change in permeation behaviour was observed in several closed and stirred optimised SLM systems was close to 0,5 $g.dm^{-3}$ [3, 7, 18, 44].

Equation 2.5 can be extended to reflect individual parameters of a specific stationary system. For example, to study the effect of the concentration of the extractant in the organic phase on the extraction of a specific divalent cation, the following equation was suggested [50]:

$$J = k_m\{(C_T/2) - C_{ML}\} \qquad (2.7)$$

where k_m is the mass transfer coefficient, C_T is the total concentration of the extractant in the organic phase, and C_{ML} the amount of complexed extractant. All of these equations have been shown to describe stationary systems extremely well, but are not as successful in describing flowing systems.

2.2.5.2 Enrichment factors

The application of SLMs is often aimed at the enrichment of a solute as opposed to simple selective separation. The flux through the SLM and the attainable enrichment are closely related. In fact, enrichment can be seen as an application of the mathematical models of flux described earlier. These models were used to study the enrichment obtainable with SLM systems by various investigators [34, 41, 48]

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The enrichment (Y) of a species is defined by Sato *et al* [41] as the ratio of the concentration of the species in the stripping solution [S_s] to its initial concentration in the feed solution [S_f].

$$Y = [S_s]/ [S_f] \tag{2.8}$$

This definition will be used for most of the present study.

In most publications the surface area of the SLM system is identified as one of the more deciding factors for enrichment. The feed and strip solutions can be recycled to reuse the membrane area many times, and increase the effective enrichment. In emulsion liquid membranes a large surface area is attainable. Pre-concentration factors of 600 have been reported for the extraction of copper with a hydroxime emulsion.

Cox [34] and Nishiki [48] stated independently that the enrichment factor in SLM systems increases in a logarithmic fashion with contact time. Nishiki [48] studied enrichment of platinum with trioctyl amine in a batch SLM system. He found that an enrichment (Y) of 60 times was possible in 7 hours.

Sato *et al* studied enrichment in a flowing tubular SLM system, using DEHPA for the extraction of copper and zinc [41]. They found that if the flow of the stripping solution is kept constant, the enrichment factor (Y) increased linearly with increasing flowrate of the feed solution.

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Danesi gave an excellent summation of the factors and parameters that determines enrichment in a tubular SLM system [5]. He summarised the equations that described the transport as follows:

In a once through mode

a) Low metal concentration

$$C_{out} = C_{in} (\phi - 1)/ (\phi + 1) \text{ for } \phi > 1$$

$$\phi = RU/PL\varepsilon \qquad (2.10)$$

b) High metal concentration

$$C_{out} = C_{in} - [E]\ 2L\varepsilon/n\Delta_0 UR$$

$$[E]\ 2L\varepsilon/n\Delta_0 UR << C_{in} \qquad (2.11)$$

In a recycling mode

a) Low metal concentration

$$\ln Cin/C^o_{in} = -(A/V)\ Pt\ (\phi/ \phi + 1) \qquad (2.12)$$

$$\phi > 1$$

b) High metal concentration

$$C_{in} = C^o_{in} - [E]\ At/n\Delta_0 V$$

$$[E]\ At/n\Delta_0 V << C^o_{in} \qquad (2.13)$$

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where:

C_{in}	-	the concentration of the species at the entrance of the hollow fibre unit
C^{o}_{in}	-	the concentration at time zero
C_{out}	-	the concentration at the exit of the module
[E]	-	the total concentration of the extractant in the SLM
n	-	the number of metal ions bound to each organic reagent molecule at loading
R	-	the internal radius of the hollow fibre
L	-	the fibre length
U	-	the linear velocity of the feed solution
ε	-	the membrane porosity
P	-	the permeation coefficient
Δ_o	-	the membrane diffusional parameter
t	-	the time in seconds
A	-	the total internal area of the fibres
V	-	the volume of the aqueous feed solution.

2.2.5.3 Selectivity

Another important parameter in the evaluation of SLMs is selectivity. Reagents used for solvent extraction are seldom completely selective for any one solute. In conventional solvent extraction processes the differences in thermodynamic behaviour are used to obtain selective separations. In these extractions batch systems are used, and thermodynamic equilibria play

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a major role. Small differences in thermodynamic behaviour of compounds can be exploited for successful separation of species. Simple comparison of distribution coefficients is often sufficient to predict the success of a selective separation. However, it is not that easy to quantify the selectivity of a separation when using SLMs. Unlike solvent extraction, the rate of permeation of the respective species is based not only on thermodynamical equilibria, but also on kinetics. Kinetics can also be used to advantage. Differences in the kinetic behaviour of compounds can be exploited to achieve an even greater degree of selectivity.

Danesi [25] formulated equations, analogous to those used in solvent extraction, to establish the selectivity that can be expected when using closed SLM systems with stirred solutions. He postulated a modified permeability coefficient (P_{mod}) analogous to the K_d values used in solvent extraction. These coefficients indicate the selectivity of solutes.

P_{mod} is expressed as:

$$P_{mod} = \frac{K_d}{K_d\Delta_a + \Delta_o} \qquad (2.14)$$

where:

$$\Delta_a = \frac{d_a}{D_a} \quad \text{and} \quad \Delta_o = \frac{d_o}{D_o} \qquad (2.15)$$

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d_a and d_o represent the aqueous double layer (Nernstian layer 1) and membrane thickness respectively, D_a represents the aqueous diffusion coefficient of the metal species, and D_o represents the membrane diffusion coefficient of the complex formed between the metal and the carrier. Danesi found that (P_{mod}) depends inversely on the concentration of the unbound extractant, the pH value of the feed solution, and the diffusional parameters that describe the SLM transport process.

A separation can be achieved between two metal species if the modified permeability coefficients of the various metal species are sufficiently different. Danesi showed that the diffusion of europium through an SLM containing HDEHPA in n-dodecane was controlled by both the diffusion through the SLM and the diffusion through membrane aqueous stagnant layers (Nernstian layers). By increasing stirring rates in stationary solutions, he could shrink the diffusion layer to approximately 10^{-3} cm; the same order of magnitude as the SLM [26]. Danesi [25] also pointed out that the selectivity of an SLM depends more on the kinetic behaviour than on thermodynamic considerations and showed that a higher selective Co-Ni separation can be obtained than with solvent extraction . He also illustrated that the selectivity of extraction can be enhanced by decreasing the organic reagent in the SLM (with the associated decrease in flux) at higher solute concentrations in the feed solution. The reason for the higher selectivity was the competition of the two solutes for the extractant.

Selectivity (α) of one solute over the next has also been defined as the ratio of the respective enrichments obtained for the species [41]. Matsuyama defined selectivity between cobalt and nickel in terms of their respective fluxes as:

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$$S = \frac{J_{Co}}{J_{Ni}} \cdot \frac{[Ni_F]}{[Co_F]} \qquad (2.16)$$

He investigated three cases:

- where the metal loading is low and diffusional resistance in the feed phase negligible,
- where the metal loading is high and diffusional resistance in the feed phase negligible, and
- where diffusional resistance of the metal in the feed solution is rate-determining

The best separation for nickel and cobalt (S = 900) was achieved at low pH and low concentrations of the respective metals. He concluded that the resistance in the membrane phase was the determining factor for selectivity. It was also shown that the simultaneous transport of two metals can be achieved without the flux of one affecting that of the other [34].

2.3 APPLICATION

The applications reviewed demonstrated the tremendous potential of SLMs as a selective separation technique, albeit in the hydrometallurgical field. Also a close examination of the literature revealed a large diversity in mechanisms, rate laws, and rate constants for similar SLM systems [6]. Much of this apparent disagreement arises from small differences in the experimental conditions, for example the use of a different solvent. Also, existing

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experimental designs were limited in that they allowed only univariant investigation of parameters. Furthermore, swopping from one set of conditions to another is a tedious process - a most undesirable situation during development. These factors made optimisation of SLM systems a manual and time-consuming process.

Clearly, the approach adopted was unsuitable for the present investigation. In the application of SLMs to an analytical flow-based method, the requirements are quite different. Important criteria include:

- small dead volume
- adequate surface area
- convenient modification of the chemical and physical environment of the SLM
- simple design that is easy to use.

Flow-injection analysis (FIA) was found to offer an excellent solution to these requirements. A simple SLM unit was incorporated in a FIA manifold. This design allows both a theoretical and an empirical approach to the study of SLMs. Once this new approach had been developed for the study of SLMs, its wider application was immediately identified. This approach to the evaluation of SLM is proposed as a viable option to researchers investigating SLMs on the macro scale.

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2.3.1 Description of the apparatus

The SLM unit (*Figure 2.2*) was constructed from two pieces of clear polyvinylchloride (PVC) with a milled channel 0,5 mm deep, 1 mm wide and 240 mm long [51]. The support was placed between the two pieces of PVC. A flat sheet of polyvinylidene difluoride (Millipore, Durapore GVHP 090 50) was used as a support for the organic phase. The sides of the support were sealed in place with a latex gasket before the PVC pieces were secured together. The support formed the only separation between the two channels.

The organic solutions typically consisted of solvent, extractant and in some cases a modifier, and was loaded onto the support *in situ* by injecting 500 mm^3 of it into one end of the SLM unit. The lipophilicity of the support ensured that the organic solution was immobilised in the pores of the support. Excess organic phase was flushed from the unit with distilled water. When required, the organic phase could be removed from the support by injecting three 500 mm^3 portions of acetone into the channel and rinsing it with water.

The SLM unit was incorporated in the FIA manifold *(Figure 2.3)*. The manifold was assembled using polytetrafluoroethene (PTFE) tubing with an inner diameter of 0,5 mm. The role of the FIA manifold is to provide real-time monitoring of the solute concentration in either of the streams. By passing either of these solutions through an injection valve, a reproducible portion is injected into a flowing reagent stream, and carried to a flow-through detection system. Various detection systems can be implemented by a simple manifold change.

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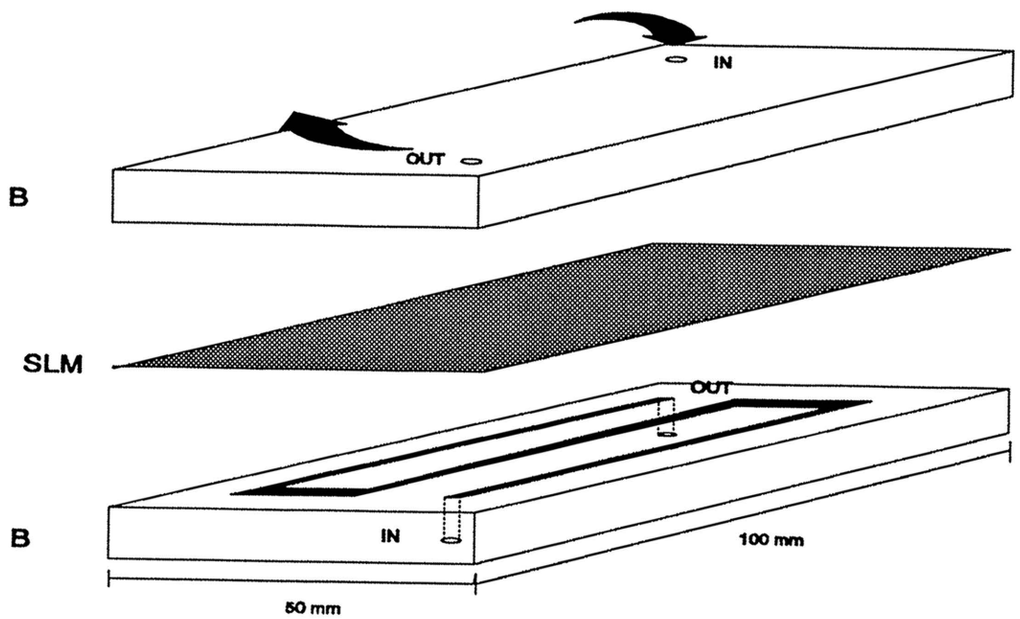

Figure 2.2: SLM Unit : B - Perspex body with a 1 mm x 0,5 mm x 280 mm channel.

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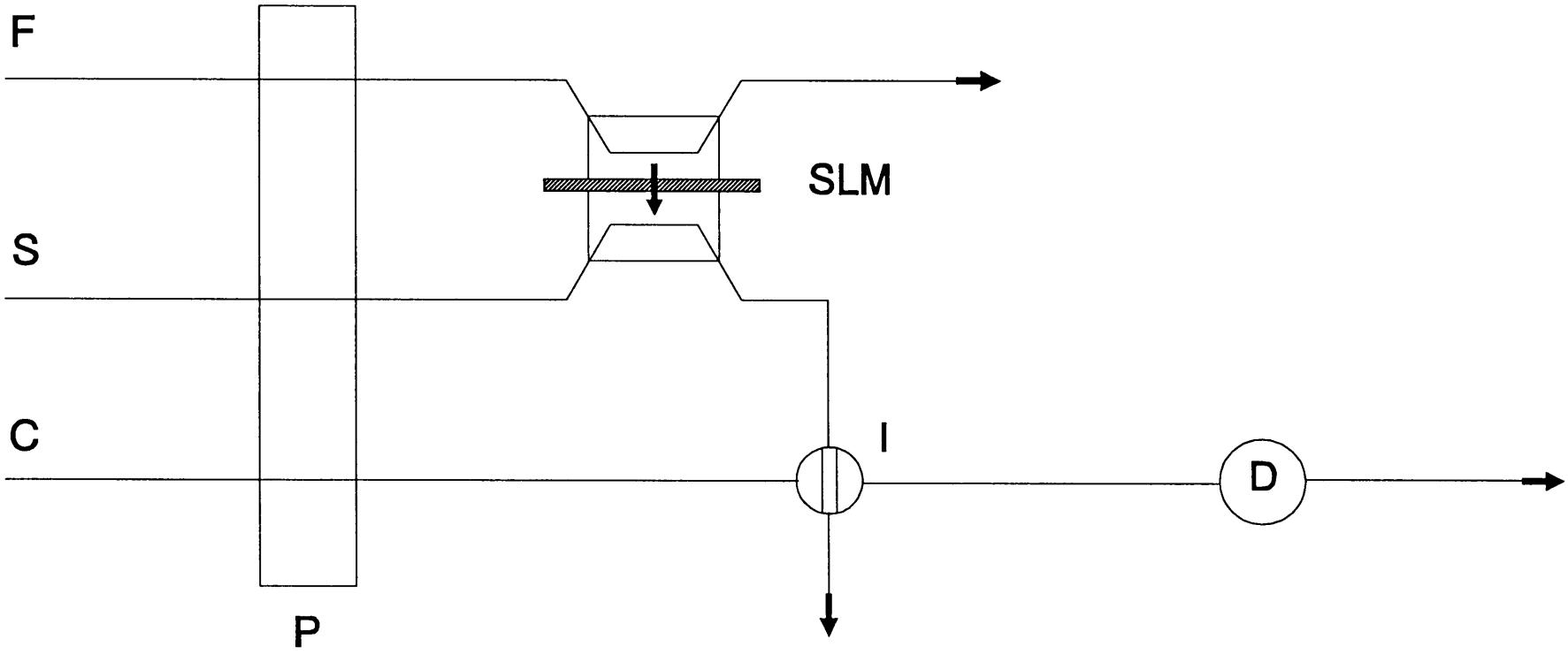

Figure 2.3: Flow-injection manifold. **F** - feed solution; **D** - detector; **P** - pump; **S** - stripping solution; **I** - injection valve; **C** - carrier solution.

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For this investigation a UV-spectrophotometer, an atomic-absorption spectrophotometer, and a flow-through anodic stripping voltametric cell were used. Analysis of the selected stream took less than 1 minute.

A feed solution of known concentration was used, and only the stripping solution was monitored. The feed solution containing the solute was pumped over the SLM. The solute complexes with the extraction reagent on the surface of the membrane, and the complex was then transported through the SLM. On the other side of the membrane, the solute was stripped into the stripping solution. The stripping solution was introduced into the FIA carrier solution at specific time intervals, and analysed.

The specific FIA manifold, and the detectors and reagents used for the determination of each of the individual solutes, will be discussed in the appropriate sections.

2.3.2 Construction of an SLM performance profile

Certain parameters that were identified in the previous sections for selecting a specific SLM such as selectivity, rate of permeation, and stability are easily evaluated with this FIA-SLM system. By determining the concentration of the solute in the stripping solution at various stages, a wealth of information on the behaviour of the SLM can be obtained.

First the SLM is formed as described above. The unit is washed for about 10 minutes by flowing water on either side of the membrane to rinse the excess of organic solution from the

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SLM surface. The selected feed solution and stripping solution are then passed over the SLM.

The initial concentration of the solute in the feed solution is known. FIA, being a fast analytical technique, allows the rapid analysis of the stripping solution. The concentration of the solute in the stripping solution is determined at regular time intervals (typically every 60 seconds) by injecting portions into the FIA manifold for analysis.

The concentration of the solute in the stripping solution is then expressed as a percentage ratio of that present in the feed solution. These percentages (permeation ratios) are plotted against time to give a performance profile as shown in *Figure 2.4*. The *y*-axis represents the permeation ratio and the *x*-axis represents time elapsed. The time that the feed solution comes in contact with the SLM is taken as the starting time for the performance profile.

2.3.3 Evaluation of the results

The solute is removed from the stripping side of the membrane at a constant rate. Also, the concentration of the solute in the feed stream is constant. Therefore the amount of solute in the stripping solution at a given time is an indication of its permeation rate through the SLM at that moment. Consequently, permeation rate and permeation ratio are used interchangeably under these conditions. It is therefore correct to refer to permeation ratio in terms of percentage permeation. (See *Figure 2.4*)

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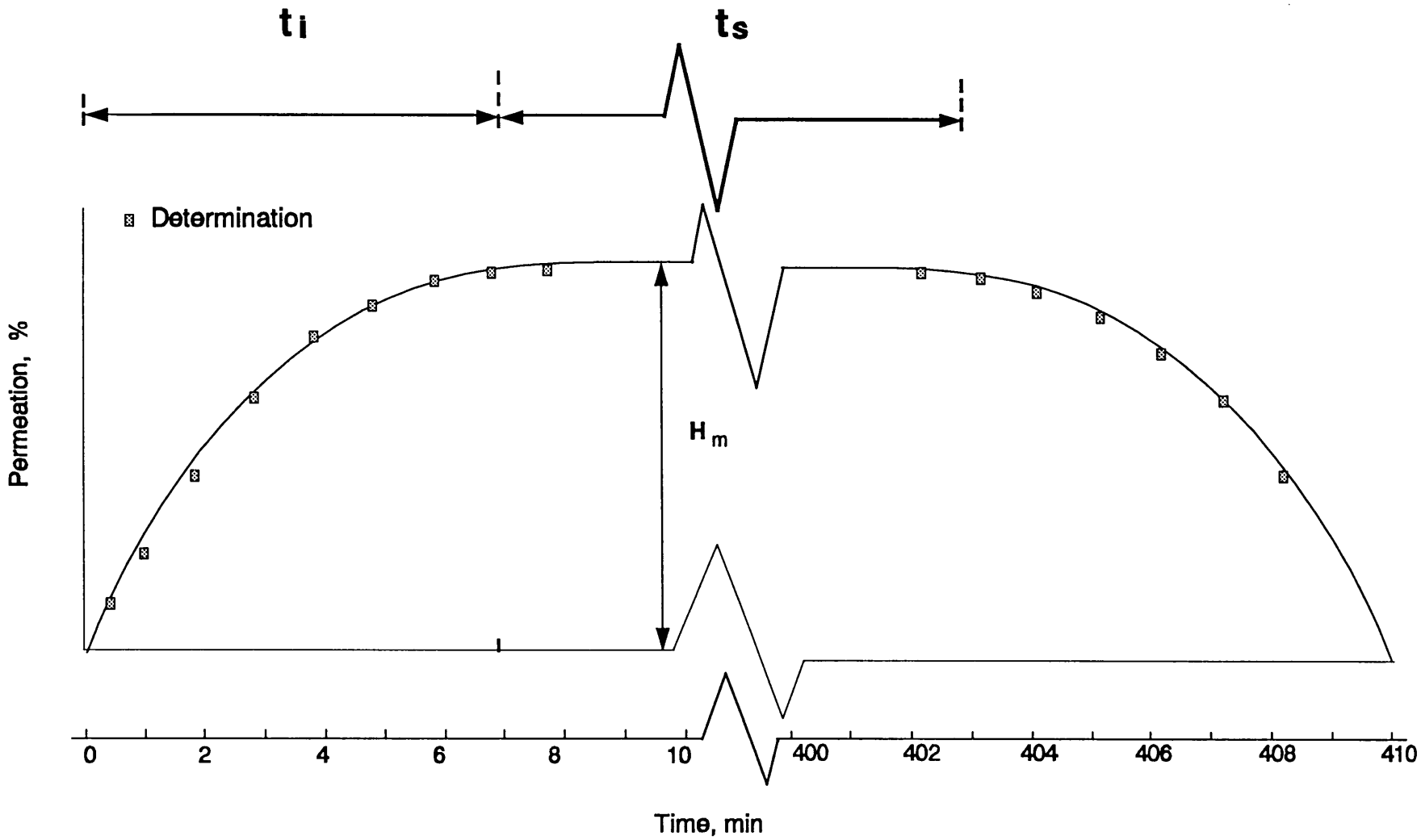

Figure 2.4 : Typical formation profile of a SLM. H_m - maximum permeation; t_i - initialising period; t_s - stability period (plateau).

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Three distinct zones can be identified in a typical performance profile:

- initial period (t_i)
- the plateau, and
- decay period.

During the initial period an increase is observed in the concentration of the solute in the stripping solution. During this time the solute is extracted into the SLM and, because the concentration of the solute in the SLM is increasing, the amount of solute that is available for back-extraction also increases. The concentration of the solute in the stripping solution will steadily increase during this period until a dynamic equilibrium is reached. The time required to reach the dynamic equilibrium state is indicated by t_i. This parameter reflects, to a certain extent, on the diffusion rate of the solute through the SLM.

When one of the five stages defined earlier becomes the rate-determining step a dynamic equilibrium is reached and the concentration of the solute in the stripping solution becomes constant. This is indicated in the performance profile as the plateau. The maximum permeation rate of the solute through a specific SLM is attained when the plateau is reached, and can be calculated from the height of the plateau H_m. This will be the rate of the slowest stage in the overall permeation. By changing the parameters recognised by Kreevoy [6] in a univariant manner, the rate-determining stage can be identified.

The time period for which the plateau is maintained provides information on the stability of a particular SLM, and is given by the time, t_s. This is the time that the maximum permeation

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is sustained. The suitability of the SLM for process application can be determined from this parameter. This parameter reflects on both the chemical and the physical stability of the SLM.

After an extended period (illustrated by the break in the profile) the concentration of the solute in the stripping solution starts to drop, indicating the failure of the liquid membrane.

The ease with which SLMs are formed and stripped in this system allows the investigator to compare different SLMs containing a variety of extractants or organic diluents. This approach can also be used to select a specific SLM with regard to slight differences in its composition. The performance profiles for different SLMs are easily obtained, and can be used to compare the relative stability (t_s) and flux (H_m) through the SLM. The shape of the profile during the initial period (t_i) reflects on the kinetic behaviour of the solute through a specific SLM, and can be used in evaluating selectivity parameters.

An important consideration in the evaluation of this approach to the study of SLMs is the flexibility afforded by the FIA monitoring system. Parameters that can be conveniently changed or varied include:

- the membrane used
- the composition of the organic solution
- the chemical composition of the feed and stripping solutions
- the geometry of the support
- temperature
- flowrate of the streams.

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The influence of these parameters on the permeation rate (H_m), stability (t_s), enrichment (E) and selectivity can easily be evaluated.

Furthermore, once a particular SLM system has been selected on this micro scale, the same FIA manifold can assist in the monitoring of pilot-scale or full-scale macro processes to further the optimisation. By substituting the experimental SLM unit with a full blown SLM process, both the feed and the stripping solution can be monitored and the data used to control the processes.

This development represents a major step forward in the study of SLM-based extraction processes for both the analyst and the hydrometallurgist.

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CHAPTER 3
SLMs AND SOLVENT EXTRACTION

The analytical chemist has made extensive use of solvent extraction as a powerful and selective separation technique. Over the years countless attempts have been made to automate this technique. These include Craig counter-current extraction unit [1], automated shakers, batch extraction with separation by centrifugation [2], and various flow methods discussed in Chapter 1. These attempts have met with mixed success.

In the hydrometallurgy field, SLMs have been suggested as an attractive alternative to solvent extraction. Several applications have been most successful. It was these successes that prompted this investigation of SLMs for the automation of solvent extraction under flow conditions in the analytical environment.

On the macro scale, the principles that apply to solvent extraction were found to hold to a great extend for extraction with SLMs. It is then not surprising that the development of SLM theory relies heavily on the theory of solvent extraction. It is therefore appropriate to address the similarities and the differences in the application of solvent extraction and SLMs.

3.1 BACKGROUND

The mass transfer through stages 2 and 4 (as defined in the previous chapter) is based on chemical reactions. The rates of these reactions are determined for stationary equilibrium conditions. In SLM sytems these equilibrium conditions seldom prevail; rather a dynamic equilibrium exists. Nevertheless the basic concepts established for equilibrium conditions in

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a solvent extraction environment were found to be extremely useful in developing and optimising an SLM system.

Of the concepts used in solvent extraction, extraction curves were found to be the most applicable to this investigation. In order to describe this concept, the following parameters need defining:

- the partition coefficient
- the distribution ratio, and
- the percentage extraction.

Partition coefficient. The partition coefficient (K_p) of a solute (z) describes the distribution of the solute between two immiscible liquids at equilibrium for a given ionic strength, temperature and pressure. In the simplest case it is the ratio:

$$K_p = [z]_o / [z]_w \qquad (3.1)$$

Subscripts (w) and (o) refer to the aqueous and organic phases. The main determining factor is the relative solubility of the solute in the two phases. However, it is seldom this straightforward.

In solvent extraction an extractant is often used. The distribution of the solute in such a system depends on the partition coefficients of both the extractant and the solute. If other molecules are involved in the reactions responsible for the extraction, the partition coefficients of these molecules also determine the degree of partitioning. To complicate matters even

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further, the concentration of all the participating chemical species in both phases could depend on secondary reactions such as dissociation. These dissociation constants or stability constants must also feature in any formula that describes the extraction. The partition coefficient might also include factors such as the basicity of the extractant, the nature of the donor atoms in the extractant, and the size and steric effects of the extractant. All this information is not always available, and therefore the partition coefficient is more of theoretical interest.

Distribution ratio. The distribution ratio of a specific solute is a more practical parameter. In contrast to the partition coefficient, the distribution coefficient is given by the same ratio, but take the chemical composition of the system into account. The distribution ratio, D, of a solute is defined as the equilibrium ratio of the total concentration of the solute in the organic phase to its total concentration in the aqueous phase [3]. This definition includes all the various forms that the solute can adopt, as well as the relevant partition coefficients.

The distribution ratio can change (in a restricted range) due to changes in the chemical composition of the phases. It also depends on all the equilibrium constants of the formal reactions taking place between the solute and the extractant. Sometimes more than one molecule of the solute or extractant is involved. This leads to a series of extraction constants, each which corresponds to a step in the formal reaction that takes place. The distribution ratio will contain the relevant reaction constants such as dissociation constants, equilibrium constants, dimerisation constants, and extraction equilibrium constants, as well as the concentrations of the extractant molecules that take part in the reaction, and the concentrations

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of all the products excluding those that contain the solute [4]. An example of a distribution coefficient is given in Section 3.2.

To achieve quantitative extraction of a solute with a typical solvent-extraction system, the distribution ratio of the desired solute must be greater than 10^3. For solutes to be separated from one another, the ratio of the respective distribution ratios should be greater than 10^6 [5].

Unfortunately, the distribution ratio can also be an extremely complex parameter to calculate, particularly when side reactions or other chemical reactions are involved in the extraction. Another limitation of distribution ratios is that they are defined for solutions that maintain a fixed volume in a closed vessel, either stirred or shaken.

Percentage extraction. Another parameter often used in solvent extraction is the percentage extraction. The percentage extraction (E) is defined as the amount of solute that is extracted into the organic phase at equilibrium [3]. This quantity is related to the distribution ratio (D) by the following equation [3]:

$$E = \frac{100\,D}{D + (V_w / V_o)} \tag{3.2}$$

where:

V_w is the volume of the aqueous phase

V_o is the volume of the organic phase.

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The percentage extraction, at a specific pH-value, is usually determined empirically. Equal volumes of the organic phase and an the aqueous phase with a known concentration of the solute are shaken together. The concentration of the solute in the aqueous phase is determined at equilibrium. The amount of solute in the organic phase is determined by difference, and the percentage extraction for that specific pH value is calculated.

3.2 EXTRACTION CURVES.

Extraction curves are used to relate the percentage extraction (E) of a solute to pH value. These extraction curves are usually constructed by plotting the respective percentage extraction versus the equilibrium pH-value at which it was determined. The concentration of the solute is kept constant in such a series of experiments. These curves are extremely useful to both the conventional and SLM application of solvent extraction. A closer examination of the theory behind these curves explains why they are widely used [4, 5].

In solvent extraction the solute is extracted as a neutral complex. If we assume that:

- the extractant and the solute exist in an unassociated form in both phases,
- the reaction between the solute and the extractant is exclusively responsible for the extraction - solvation plays no significant part in the extraction, and
- the extractant is an uncharged molecule,

then, in the simplest case the extraction reaction can be represented as follows [4, 6]:

$$M^{n+} + nR^{-} \rightleftharpoons MR_n \qquad (3.3)$$

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The dissociation of the complexing reagent into the aqueous phase can be describe by the reaction:

$$HR \rightleftharpoons H^+ + R^- \tag{3.4}$$

The following thermodynamic constants express the relevant equilibria :

Dissociation constant of the complex, $K_c = [M^{n+}]_w [R^-]_w^n / [MR_n]_w$ (3.5)

Dissociation constant of the reagent, $K_r = [H^+]_w [R^-]_w / [HR]$ (3.6)

Partition coefficient of the complex, $p_c = [MR_n]_o / [MR_n]_w$ (3.7)

Partition coefficient of the reagent, $p_r = [HR]_o / [HR]_w$ (3.8)

The distribution ratio of the solute is given by:

$$D = [MR_n]_o / [MR_n]_w + [M^{n+}]_w \tag{3.9}$$

which reduces to [6]:

$$D = K[HR]_o^n / [H^+]_w^n \tag{3.10}$$

where:

$$K = (K_r p_r)^n / K_c p_c \tag{3.11}$$

From equation 3.11:

$$D = K^* / [H^+]_w^n \tag{3.12}$$

where:

$$K^* = K[HR]_o^n$$

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The percentage extraction is usually determined for equal volumes of organic and aqueous phases. If the distribution ratio is converted to percentage extraction using equation 3.2, and the logarithm is taken on both sides, it can be shown that equation 3.12 transforms into:

$$\log E - \log (100 - E) = \log K^{*} + n\text{pH} \qquad (3.13)$$

Equation 3.13 describes a sigmoidal curve which is the same curve that can be obtained empirically for a specific set of conditions (*Figure 3.1*). The position of the curve along the x-axis is dependant on the magnitude of K^{*} (the collective constant that includes the distribution coefficients and partition coefficients of both of the reagent and the extractant). The position of the curve is also influenced by both the concentration of the extractant and the solute, as well as the volume ratios of the two phases. (This is due to the influence of these parameters on the respective reaction coefficients.) The slope of the curve depends on *n* (the charge on the solute). In more complex reactions, *n* is further dependant on the valence of the solute, as well as the number of solvent and extractant molecules involved in the extraction.

Figure 3.1 shows the extraction curves of selected cations with hydroxyquinoline [7]. These curves illustrate the effect of the charge of the cations on the slope of their respective extraction curves. (The curve for La is adjusted to the left by two pH units for comparison.)

The pH value at which 50 per cent extraction is obtained is defined as $pH_{1/2}$.

From equation 3.13 it follows that:

$$pH_{1/2} = - 1/n \log K^{*} \qquad (3.14)$$

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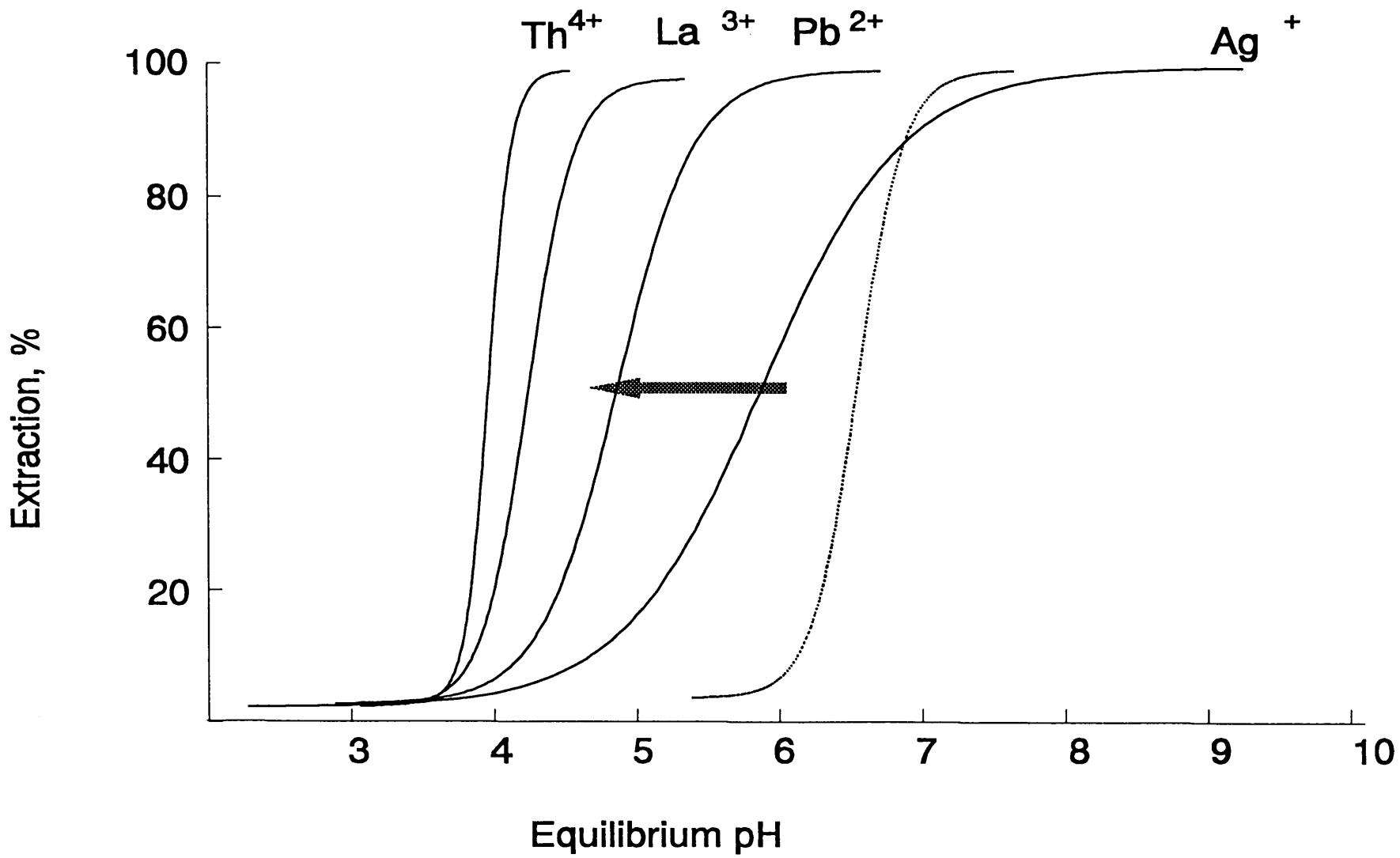

Figure 3.1 : The extraction curves for monovalent Ag^{+}, bivalent Pb^{2+}, trivalent La^{3+} and tetravalent Th^{4+} using 0,1 $mol.dm^{-3}$ 8-hydroxyquinoline in chloroform [5].

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In solvent extraction, the difference in the $pH_{1/2}$ values of two solutes is also a measure of the separability of the solutes. This will be shown to be true for SLM extractions as well.

3.2.1 Kinetic parameters

The attainment of equilibrium in the chemical reactions that control the extraction of a solute does not depend only on the concentration of various reagents, but also on their diffusion through the various phases. Diffusion rates have been accelerated in conventional solvent-extraction systems by shaking and stirring. Little has been done in classical solvent extraction to exploit the differences in kinetic behaviour of solutes for selective separation.

The use of SLMs in flow systems allows closer control of the kinetic parameters. The concentration of the solute in the feed and stripping solutions can be controlled to some extent by means of flow control. By changing flow conditions the dynamic chemical equilibrium can be changed to favour the selective extraction of a specific solute. In addition, by utilising optimised geometries in flowing systems, turbulence can be increased and the thickness of the interfacial layers between the phases (Nernst layers 1 and 2) can be minimised. This increase in diffusion can also be utilised to discriminate between solutes.

3.3 CLASSIFICATION OF EXTRACTANTS

Complexation reactions are usually responsible for extractant-facilitated solvent extraction. The complexation reaction can occur in combination with other ions to result in a neutral ion-association that favours the organic phase. Classification of these extractants is not simple,

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as there are a host of reactions whereby the solute can be complexed and extracted into the organic phase. Various classification systems have been proposed. This study uses a classification based on the solute that is extracted.

Such a classification is an oversimplification, but eliminates the confusion that is eminent in a more generic classification according to mechanisms such as ion association, ion exchange, complexation, chelation or liquid ion-exchangers, and the grey areas between these. Such a classification would give rise to another complication, since most compounds actually behave in a way that cannot be completely described by only one mechanism. The classification of extractants has attracted much attention and several proposals. In this investigation, a classification on the basis of the charge on the solute is used. The choice of this classification does not reflect on the validity of other systems, but rather allows for a logical presentation of the research findings.

A classification according to the charge on the solute results in three classes:

- extractants for anions
- extractants for cations
- extractants for neutral solutes.

The tables supplied for each of the three classes list a few examples of extractants applied as SLMs. The tables are meant for quick reference, and although they are extensive they are by no means complete. They do serve as a starting point for a study of SLMs.

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3.3.1 Anion extractants

The extractants in this class will extract anions and are almost exclusively hetero-organic compounds that contain a nitrogen group. The nitrogen acts as a Lewis acid (electron acceptor) during the extraction. This class includes both the aliphatic amines (primary, secondary, tertiary, and quaternary amines), the aromatic amines (such as aniline, *p*-nitro-aniline, *p*-toluidine), the heterocyclic amines (such as pyridine, quinoline, piperidine and *o*-phenantroline) and the derivatives of these compounds. In addition, the phosphorus-containing compounds are sometimes used for the extraction of anions, and include extractants such as trialkyl phosphonates, trialkyl phosphoric acids, the phosphine oxides and phosphonates.

Table 3.1 lists applications of these extractants in an SLM environment. It is evident that only a fraction of the extractants available for the extraction of anions have been used in an SLM environment, suggesting that SLMs are underutilised.

3.3.2 Cation extractants

This class includes all extractants that form complexes with cations. These extractants are usually Lewis bases (electron donors). They are organic compounds which usually contain an electron-rich hetero atom (N, O, P, S or a combination of these) that can donate electrons to an electron-poor solute to form an extractable complex. The extraction mechanism often involves the exchange of the hydrogen ions of the extractant for the cation in the feed solution, and the back-extration is achieved when the reaction is reversed. These extractants are also sometimes referred to as liquid cation exchangers. *Table 3.2* lists applications of these extractants in an SLM environment.

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Table 3.1 (1)
SLM systems for the extraction of anions

Element	Feed	Extractant	Diluent	Modifier	Strip	Geometry	References
Am	HCl	CMPO	DEB	-	HCOOH	Flat Sheet	8
Am	HCl	CMPO	DEB	-	HCOOH	-	9
Am	Acid Waste	CMPO	Decalin	TBP	0,5 mol.dm^{-3} citrate	Tubular	8, 10
Cd	2 mol.dm^{-3} NaCl/ 0,1 mol.dm^{-3} HCl	TLACl	TEB	-	NaAc/ NaCl	Stirred flat sheet	11
Cd	HCl	Alamine 336	Xylene	-	NaAc	Capillary membranes	12
Cd	HCl	Alamine 336	Xylene	-	NaAc	Flat sheets	12
Cd, Zn	0,5 mol.dm^{-3} HCl	TLACl	TEB	-	NH_4Ac	Flat sheets	13
Cd	1 mol.dm^{-3} NaCl	Alamine 336	*n*-Heptane	-	0,5 mol.dm^{-3} NH_4Ac/ NH_4Cl	Flat sheet	14
Co, Ni	8 mol.dm^{-3} LiCl/ 0,3 mol.dm^{-3} HCl	TLAHCl	Decalin/ DIPB	-	pH 6	Composite membranes	15
Cr	-	Alamine 336	Escaid 350	-	-	Tubular	16
Cr	Acidic	Adogen 382	SHELLSOL K	-	NaOH	Hollow Fibre	17
Cr	Acidic	TBP	SOLVESSO 150	-	NaOH	Hollow Fibre	17
Cr	Acidic	Adogen 283	SHELLSOL K	-	NaOH	Hollow Fibre	17
Cr(VI)	H_2SO_4, pH 2	LA-2	*n*-Dodecane	-	0,1 mol.dm^{-3} NaOH	Stirred flat sheet	18
Cr(VI)	Water	Aliquat 336	Kerosene	-	LiCl	Stirred Flat sheet	19
Cr(VI)	-	Aliquat 336	Kerosene	-	4 mol.dm^{-3} LiCl	Flat sheet	14
Cr(VI)	H_2SO_4, pH 1,6	PDPP	Nitrobenzene	-	Ammonia	Multi-layer flat sheets	20
Cr(VI)	pH 4,7	TOMAC	*n*-Dodecane	2-Ethylhexyl alcohol	NaOH	Spiral type	21
Cr(VI)	pH 1,0 - 3,0	TOA	Shellsol AB	2-Ethylhexyl alcohol	NaOH	Spiral type	22
Cu	HCl	Oxime	Toluene	-	HCl	-	9
D-Glucosamine		ODOBA		-	-	Stirred flat sheet	23

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Table 3.1 (2)

Element	Feed	Extractant	Diluent	Modifier	Strip	Geometry	References
Fe	4 mol.dm^{-3} HCl	TBP	Toluene	-	0,05 mol.dm^{-3} HCl	Flat sheet	24
Fe	4 mol.dm^{-3} HCl	Aliquat 336	Kerosene	TBP/ decanol	0,05 mol.dm^{-3} HCl	Flat sheet	24
Fe, Ni, Co	LiCl	TLACl	Triethylbenzene	-	0,1 mol.dm^{-3} HCl	Stirred flat sheet	18
H	$NaNO_3$	TOPO	DEB	-	NaOH	-	9
H	$NaNO_3$	Primene	DEB	-	NaOH	-	9
H	$NaNO_3$	CMPO	DEB	-	NaOH	-	9
H	$NaNO_3$	CMPO	DEB	-	NaOH	-	9
H	$NaNO_3$	TLA	DEB	-	NaOH	-	9
H	$NaNO_3$	TLA	Dodecane	-	NaOH	-	9
HCl	HCl/ NaCl	TLA	*iso*-Propylbenzene	-	NaOH/ NaCl	Stirred flat sheet	25
NO_3	H_2SO_4, pH 2	LA-2	*n*-Dodecane	-	0,1 mol.dm^{-3} NaOH	Stirred flat sheet	26
Nd, Ce	0,2 mol.dm^{-3} HNO_3/ 3 mol.dm^{-3} $NaNO_3$	OPDIBCMPO	Decalin	-	pH 2	Composite membranes	27
Np	Acid Waste	CMPO	Decalin	TBP	0,5 mol.dm^{-3} citrate	Tubular	8, 10
Pt	HCl	TOA	Xylene	-	Na_2CO_3/ NaOH	Flat sheet	28
Pt	HCl	TOA	Xylene	-	Na_2CO_3/ NaOH	Flat sheet	29
Pu	Acid Waste	CMPO	Decalin	TBP	0,5 mol.dm^{-3} citrate	Tubular	8, 10
Te(VII)	H_2SO_4, pH 2	TLA	*n*-Dodecane	-	0,1 mol.dm^{-3} NaOH	Stirred flat sheet	26
U	0,1 mol.dm^{-3} H_2SO_4	TOA	Kerosene	-	Na_2CO_3	Stirred flat sheet	30

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Table 3.1 (3)

Element	Feed	Extractant	Diluent	Modifier	Strip	Geometry	References
U	pH 1	Alamine 336	Aromatic 150	-	2 mol.dm^{-3} Na_2CO_3	Tubular	31
U	Acid Waste	CMPO	Decalin	TBP	0,5 mol.dm^{-3} citrate	Tubular	8, 10
U	pH 1	Alamine 336	Aromatic 150	-	Formate or HAc	Flat sheet	32
UO2	HCl, pH 1	Alamine 336	Aromatic 150	-	NaAc	Flat sheets	33
Zn	pH 1	TOA	*n*-Dodecane	-	1 mol.dm^{-3} HCl	Tubular	10, 34
Zr	10 mol.dm^{-3} HNO_3	TBP	Xylene	-	-	Flat sheet	35

Adogen 283	Ditridecyl amine
Adogen 382	Tri-*iso*-decyl amine
Aliquat 336	Methyltricaprylyl ammoniumchloride
CMPO	Dihexyl-N,N-diethyl carbamoylmethylphosphine oxide
CMP	Dihexyl-N,N-diethyl carbamoylmethylphosphonate
CPAA	Chlorophenoxyalkanoic acid
LA-2	Dialkyl (C_{12} - C_{13}) amine
NPOE	2-Nitrophenyl n-octyl ether
Solvesso 150	Diluent containing 97% aromatic; 3% pariffin
OMTPP	Oxomolybdenum(V)-tetraphenylporphyrin
ODOBA	4-Octyldecyloxybenzalsehyde
PDDP	3-(4-Pyridyl)-1,5-diphenyl pentane
Primene	Alkyl (C_{18} - C_{24}) amine
TOA	Tri-octylamine
TOMAC	Trioctylmethylammonium chloride
TBP	Tri-n-butyl phosphate
TLA	Tri-n-laurylamine
TLACl	Trilaurylammonium chloride
TMAOH	Tetramethylammonium hydroxide

Aromatic 150	Diluent
DEB	Diethylbenzene
DIPB	Di-*iso*-propylbenzene
Escaid 350	Diluent containing 97% aromatic; 3% pariffin
HAc	Acetic acid
NaAc	Sodium Acetate
Shellsol A	Triethylbenzene
Shellsol K	High boiling aliphatic diluent (< 0,5% aromatic)
TEB	Triethylbenzene
PDIBCMPO	*n*-Octyl- N,N-di-*iso*-butyl carbamoylmethylphosphine oxide

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Table 3.2 (1)
SLMs systems using cation extractants

Element	Feed	Extractant	Diluent	Modifier	Strip	Geometry	References
Al	Cu solutions, pH 2 to 3,6	DEHPA	Escaid 200	-	2 to 5 mol.dm^{-3} H_2SO_4	Stirred flat sheet	36, 37
Amines	NaOH	DEHE	*n*-Undecane	-	H_2SO_4	Flowing flat sheet	38
Ag	$HClO_4$/ HAc buffer	TTD	*m*-Chlorotoluene		0,1 mol.dm^{-3} thiosulphate	Flat sheet	39
Ca	pH 11	D2EHPA	-	-	pH 1	Flat sheet	40
Ce	Acid perchlorate	D2EHPA	Nitrobenzene	-	No strip	Suspended PU-foam	41
Co, Ni	pH 6	DTMPPA	Decalin/ DIPB	-	8 mol.dm^{-3} LiCl/ 0,3 mol.dm^{-3} HCl	Composite membranes	15
Cr(III)	Water	DNNSA	*o*-Xylene	-	pH 4,5	Stirred flat sheet	19
Cr(III)	pH 4,2	DNNSA	*o*-Xylene	-	0,5 mol.dm^{-3} H_2SO_4	Flat sheet	14
Cu	-	LIX 64N	Paraffin	-	H_2SO_4	Flat sheet	40
Cu	0,5 mol.dm^{-3} HAc/ NaAc	LIX 64N	Kerosene	-	H_2SO_4	Stirred flat sheet	42
Cu	pH 5,0	LIX 64N	Dispersol	-	H_2SO_4	Flowing flat sheet	43
Cu	pH 2,5	LIX 70	Kerosene	-	Formic acid	Stirred flat sheet	44
Cu	pH 2,5	LIX 64N	Kerosene	-	Formic acid	Stirred flat sheet	44
Cu	NaOH	LIX 84	Decane	-	HCl, pH 2	Hollow fibre	45
Cu	-	LIX 65N	Kerosene	-	H_2SO_4	Flat sheet	46
Cu	NaOH	LIX 84	Kerosene	-	HCl, pH 2	Hollow Fibre	45
Cu	pH 2 to 4	LIX 64N	Decalin	-	2 mol.dm^{-3} H_2SO_4	Tubular	47
Cu	0.5 mol.dm^{-3} HAc/ NaAc	D2EHPA	Dodecane	-	1 mol.dm^{-3} HNO_3	Hollow Fibre	48
Cu	pH > 7	LIX 65N	Octanol	-	1 mol.dm^{-3} H_2SO_4,	Flowing flat sheet	49
Cu	pH 4	Agorga P5100	*n*-Decane	-	-	Tubular	16
Cu	pH 1 to 4	LIX 64N	Kerosene	-	H_2SO_4, pH 0,5	Stirred flat sheet	50
Cu	0,1 mol.dm^{-3} HAc	SME 529	Dispersol	-	2 mol.dm^{-3} H_2SO_4	Tubular	21

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TABLE 3.2 (2)

Element	Feed	Extractant	Diluent	Modifier	Strip	Geometry	References
Cu	pH 1 to 4	Acorga P5300	Kerosene	-	H_2SO_4, pH 0,5	Stirred flat sheet	50
Cu	$CuSO_4$, pH 5,5	LIX 65N	Kerosene	-	0,2 mol.dm^{-3} H_2SO_4	Tubular	10, 51
Cu	pH 1 to 4	Kelex 100	Kerosene	-	H_2SO_4, pH 0,5	Stirred flat sheet	50
Cu	pH 1 to 4	Acorga P5100	Kerosene	-	H_2SO_4, pH 0,5	Stirred flat sheet	50
Cu	pH 3	N 503	PC801	-	H_2SO_4	Flat sheet	52
Cu	HAc/ NaAc	DEHPA	Various	-	HNO_3	Flowing flat sheet	53
Cu	pH 2,5	Kelex 100	Kerosene	-	Formic acid	Stirred flat sheet	44
Cu	pH 2,5	Kelex 100	Kermac 470B	-	1 mol.dm^{-3} H_2SO_4	Tubular	31
Cu	HAc/ NaAc	ß-Hydroxy-oxime	Toluene	-	1 mol.dm^{-3} HCl	Sheet	54
Cu	pH 3,5	LIX 64N	Paraffin	-	NaAc	Stirred flat sheet	55
Cu		SME 529	Dispersol	-	2 mol.dm^{-3} H_2SO_4	Tubular	10, 22
Cu	pH 2,5	LIX 63	Kerosene	-	Formic acid	Stirred flat sheet	44
Cu	pH 4 to 6	LIX 54-100	Kerosene	-	2,1 mol.dm^{-3} H_2SO_4	Stirred flat sheet	51
Cu	pH > 7	LIX 64N	Octanol	-	1 mol.dm^{-3} H_2SO_4	Flowing flat sheet	49
Cu, Ni, Co	HAc buffer	PS-Diphenyl thiocarbazon	Chloroform	-	1 mol.dm^{-3} HNO_3	Sheet	56
Cu, Zn	pH 3	LIX 64N	Kerosene	-	pH 1	Hollow fibre	19
Cu, Zn	NaOH	D2EHPA	Kerosene	-	1 mol.dm^{-3} HCl	Stirred flat sheet	19
Cu, Zn	HAc/ NaAc	D2EHPA		-	HCl	Hollow fibre	57
Er	pH 3	DTMPPA	TMB	-	1 mol.dm^{-3} HCl	Stirred flat sheet	58
Eu	0,1 mol.dm^{-3} HNO_3	DIDPA	1-Octanol	1-Octanol	5 mol.dm^{-3} HNO_3	Flat sheet	59
Eu	HCl	D2EHPA	Xylene		1 to 2 mol.dm^{-3} H_2SO_4	Stirred flat sheet	60

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TABLE 3.2 (3)

Element	Feed	Extractant	Diluent	Modifier	Strip	Geometries	Reference
Eu	HCl, pH 2	HDEHP	*n*-Dodecane	-	1 mol.dm^{-3} HCl	Stirred flat sheet	61
Eu	1 mol.dm^{-3} $HClO_4$	CMP	Kerosene	1-Decanol	0,1 mol.dm^{-3} HNO_3	Flat sheet	62
Ga	-	IPE	*n*-Dodecane	-	HCl	Stirred flat sheet	43
Ga	-	2-Bromo-decanoic acid	*n*-Dodecane	-	HCl	Flat sheet	63
H	HCl, pH 2	HDEHP	*n*-Dodecane	-	1 mol.dm^{-3} HCl	Stirred flat sheet	61
In	-	TBP	*n*-Dodecane	-	HCl	Stirred flat sheet	43
In	-	DTPPA	*n*-Dodecane	Cyanex 272	HCl	Flat sheet	63
Ni	pH > 7	LIX 65N	Octanol	-	1 mol.dm^{-3} H_2SO_4	Flowing flat sheet	49
Ni	pH > 7	LIX 64N	Octanol	-	1 mol.dm^{-3} H_2SO_4	Flowing flat sheet	49
Ni	0,1 mol.dm^{-3} HAc	2EHPAM2EHE	*n*-Dodecane	-	3 mol.dm^{-3} HCl	Stirred flat sheet	64
Ni, Co	HAc	Cyanex 272	Decalin	-	HCl, pH 3	Hollow fibre	34
Ni-Co	HAc, pH 6	Dialkylphosphonic acid	Decalin	DIPB	HCl, pH 1	Fibres	65
Rare Earths	HAc	TBEP	Ethers	-	0,05 mol.dm^{-3} H_2SO_4	Flat sheet	66
U	$NaClO_3$	DEHPA/ TOPO	Kerosene	-	6 mol.dm^{-3} H_3PO_4	Flowing flat sheet	67
U	pH 4 to 5	LIX 63	Kerosene	-	0,1 mol.dm^{-3} H_2SO_4	Flat sheet	68
U	3 mol.dm^{-3} HNO_3	D2EHPA	Escaid 100	TOPO	$(NH_4)_2CO_3$	Flat sheet	40

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Table 3.2 (4)

Element	Feed	Extractant	Diluent	Modifier	Strip	Geometry	References
U(VI)	Various	D2EHPAM2EHE	Kerosene	1-Decanol	0,5 mol.dm^{-3} HNO_3	Sheet	59
U	3 mol.dm^{-3} HNO_3	D2EHPA	Shellsol 2046	-	Na_2CO_3	Sheet	69
U	0,5 mol.dm^{-3} HNO_3	DEHPA	Kerosene	-	5 mol.dm^{-3} H_3PO_4	Stirred sheet	70
U(VI)	HAc buffer, pH 4	Kelex 100	Kerosene	-	0,1 mol.dm^{-3} HNO_3	Stirred sheet	71
U(VI)	HAc buffer, pH 4	Kelex 100	Kerosene	-	0,1 mol.dm^{-3} HNO_3	Stirred sheet	72
Y	pH 3	DTMPPA	Trimethylbenzene	-	1 mol.dm^{-3} HCl	Stirred sheet	64
Zn	HAc buffer, pH 5	Dithiozone	Carbon tetrachloride	-	HCl, pH 2	Stirred sheet	73
Zn	pH 2	DEHPA	Kerosene	-	pH 1	Stirred sheet	74
Zn	pH 4,7 to 6,0	Cyanex 272	Dodecane	-	0,1 mol.dm^{-3} HCl	Stirred sheet	75
Zn	0,01 mol.dm^{-3} HCl	HDEHP	*n*-Dodecane	-	0,2 mol.dm^{-3} HNO_3/ 3 mol.dm^{-3} $NaNO_3$	Composite membranes	27
Zn	HAc/ NaAc	DEHPA	Chloroform	-	1 mol.dm^{-3} HCl	Flowing sheet	36

SME 529	2-Hydroxy-5-nonylacetophenone oxime	Ascorga P5100	5-nonyl-salicylaldoxime : nonylphenol (1:1)
Cyanex 471	Tri-*iso*-butyl phosphine oxide	PC 801	Diluent
Cyanex 272	Di-2,4,4-trimethylpentyl phosphinic acid	Kermac 470B	Diluent containing 12% Aromatic; 49% parrifin; 40% napthenes
DEHE	Diethylhexyl ester	TOPO	Trioctyl phosphine oxide
DIDPA	Di-*iso*-decylphosphoric acid	TMB	Trimethylbenzene
DIPB	Di-*iso*-propylbenzene	Escaid 100	Diluent containing 20% Aromatic; 57% parrifin; 23% napthenes
DNNPSA	Dinonylnaphtalenesulfonic acid	Escaid 200	Diluent containing 3% Aromatic; 52% parrifin; 45% napthenes
DNNSA	Di-N,N-sulfonamine	DTMPPA	Bis(trimethylpentyl)phosphonic acid DTMPPABis(trimethylpentyl) phosphonic acid
DEHPA	Diethylhexyl phosphoric acid	EHPAM2EHE	Ethylhexyl phosphoric acid mono-2-ethylhexyl ester
HDEPA	Hexyldiethyl phosphoric acid	HAc	Acetic acid
NaAc	Sodium Acetate	IPE	*iso*-Propyl ether
Kelex 100	7-Dodecenyl-8-quinolinol	Kryptofix 22 DD	Macrocyclic ether
N 503	N,N,Di-1-methylheptyl acetamide	LIX 54-100	ß-Diketone
LIX 63	5,8-Diethyl-7-hydroxy-6-dodecanone oxime	LIX 64	2-Hydroxy-5-dodecylbenzophenone oxime
LIX 64N	4-Dodecylsalicyl	LIX 65	2-Hydroxy-5-nonylbenzophenone oxime
LIX 65N	2-Hydroxy-5-nonylbenzophenone oxime	LIX 70	2-Hydroxy-3-chloro-5-nonylbenzophenone oxime
Shellsol 2064	Diluent	LIX 84	2-Hydroxy-5-nonylacetophenone

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The anionic extractants (used to extract cations) include oxygen-containing groups such as carboxylates, acetates, oxalates, salicylates, and ß-diketones such as LIX 54-100 (phenyl alkyl ß-diketone), oximes, oximates, oxines, phenolates, enolates and tropolone and its derivatives. Sulphur-containing cation extractants that are often used in solvent extraction include diphenylthiocarbazone, dithizone and its derivatives, dithiocarbamates and xanthates. The sulphur-containing group reacts similar to most popular cation exchange resins with the same active groups [76, 77].

The phosphor-containing cation extractants are often used in the extraction of the base metals and the lanthanides. They include monoalkylphosphoric acids, dialkylphosphoric acids, alkylarylphosphonic acids and diaryl-dithiophosphonic acids. The selectivity displayed by these extractants is quite different from those of the equivalent active group immobilised on resins [76, 77]. Of these di-(2-ethylhexyl) phosphoric acid is probably the most popular acidic extractant, and it was selected as the extractant for a case study later in this chapter.

This class of extractants also includes nitrogen-containing groups, illustrating the amphoteric nature of nitrogen. The nitrogen group is almost always accompanied by electron rich hetero atoms, such as sulphur or oxygen. Specific extractants are nitrosophenols, nitrosoaryl hydroxylamines (Cupferon), hydroxamic acids, 8-hydroxyquinoline and its derivatives, the azo-dyes (such as PAR, PAN and derivatives) and thiourea and derivatives.

3.3.3 Neutral extractants

There is also a intermediate class of extractants that extract solutes through an ion-association mechanism. The extractant is usually a bulky organic molecule which incorporates the metal

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in its extractant groups. The large complex dissolves easily in the solvent. These extraction are usually extremely selective. The metal-containing enzymes and proteins in biological systems are excellent examples. The metal ions are incorporated in these proteiens with high molecular mass, and the complexes solvate the metal in the organic solvent by forming colloidal aggregates. The organophilic parts of the salt are orientated towards the solvent, shielding the ionic part (metal) from the organic solvent.

This class also includes the macro-cyclic ethers (crown ethers) and their derivatives [78]. The macro-cyclic ethers resemble crown-like structures that fit around the monovalent ions, and were originally used to extract the alkali cations. By skillful engineering of selective groups onto the ring to selectively attract other cations, a whole new field of reagents has been discovered. The desired cation fit into the circle of the crown and selectivity is based on the attached groups, synthesized onto the ring. This fascinating field of selective extractants is an active area of current research.

The metal ions can also be solvated or coordinated by the solvent molecules in such a way that they are incorporated as an integral part of the solvent where the solvent molecules displaces the coordinated water molecules. The solvent is usually an electron-rich solvent that includes oxygen in its structure such as an alcohol, ether, ketone or an ester.

Examples of this extraction mechanism are the extraction of iron from hydrochloric acid by diethyl ether or the extraction of dicyanoaurate(I) ion-pairs by polar aprotic solvents such as hydrofuran or dialkyl ketones [79].

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Table 3.3
SLM systems using neutral extractants

Element	Feed	Extractant	Diluent	Modifier	Strip	Geometry	References
Amines	0,1 mol.dm^{-3} NaOH	Aliphatic solvents	-	-	0,05 mol.dm^{-3} H_2SO_4	Flowing flat sheets	80
Au, Ag	Potassium solution	Kryptofix 22 DD	Decanol	-	Distilled water	Stirred Flat sheet	81
CO_2	High pressure	Sodium carbonate buffer	-	-	Low pressure	Stirred flat sheet	82
CPAA	H_2SO_4	Aliphatic solvents	-	-	Phosphate buffer	Flat sheet	77
H_2S	High pressure	Sodium carbonate buffer	-	-	Low pressure	Stirred flat sheet	82
K	pH > 10	Crown ethers	NPOE	-	pH < 10	Flat sheet	83

CPPA Chlorophenoxyalkanoic acids
NPEO 2-Nitrophenyl-*n*-octylether
Kriptofix 22 DD Macrocyclic ether

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Other extractants in this class are oxonium, neutral trialkylphosphates, trialkylphosphine, oxides, triarylphosphine oxides, tetra-alkylalkylene diphosphine oxides, tetra-alkyl pyrophosphates and tetra-alkylhypophosphates.

3.4 APPLICATION

3.4.1 Cation extraction

The extraction curves (Section 3.1) are available for most commercially available extractants, and can aid in the selection of an SLM system. To illustrate the significance of solvent-extraction principles in the development of SLMs, the extraction of the common cation extractant DEHPA was arbitrarily chosen. The literature reveals that many cations can be extracted with this extractant both in solvent extraction [5, 84] and via SLMs [22, 41, 50, 60].

The extraction and back extraction are based on the reversible reaction between the solute and the extractant where the proton of the extractant can be substituted by the solute according to the following equation:

$$M^{n+} + nHA \rightleftharpoons MA_n + H^+ \qquad (3.15)$$

In the SLM system the extractant (A) is initially associated with a hydrogen ion in the organic phase. The extractant dissociates in the double layer in the aqueous feed solution adjacent to the SLM (Nernst layer 1), releasing the associated proton into the feed solution. The extractant combines with the solute according to reaction 3.15 and partitions into the organic phase. The complex permeates through the SLM, and on the stripping side the reaction is

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reversed in the second double layer (Nernst layer 2). The proton substitutes the solute in the extractant, and the solute diffuses into the stripping solution. The extractant is restored to its initial state and is available to repeat the process.

Figure 3.2 illustrates the extraction curves of selected cations that have been extracted with DEHPA [5]. These curves were used to select the pH value of the initial feed and stripping solutions for the SLM.

Consider the extraction curve for copper. The plateau where maximum extraction occurs, above a pH value of 4, specifies the pH region where the right-hand side of equation 3.15 is favoured. A feed solution at this pH value will support the formation of a copper/ extractant complex that can partition into the organic phase. The plateau of minimum extraction, at a pH value of below 2,3, indicates the pH region where the left-hand side of the reaction is favoured. The extractant will preferentially combine with a proton and the solute will partition into the aqueous phase. The pH value of the stripping solution will be selected from this range.

3.4.1.1 Experimental design

All reagents were of Analytical Reagent grade, and all aqueous solutions were prepared with deionised water. The FIA carrier solution, used for the determination of cations, contained 0,012 mol.dm^{-3} 4-(Pyridyl-2-azo)-resorcinol monosodium salt (PAR), dissolved in a buffered solution with a pH value of 4,5. The buffer contained 1 mol.dm^{-3} ammonia and 0,3 mol.dm^{-3} acetic acid.

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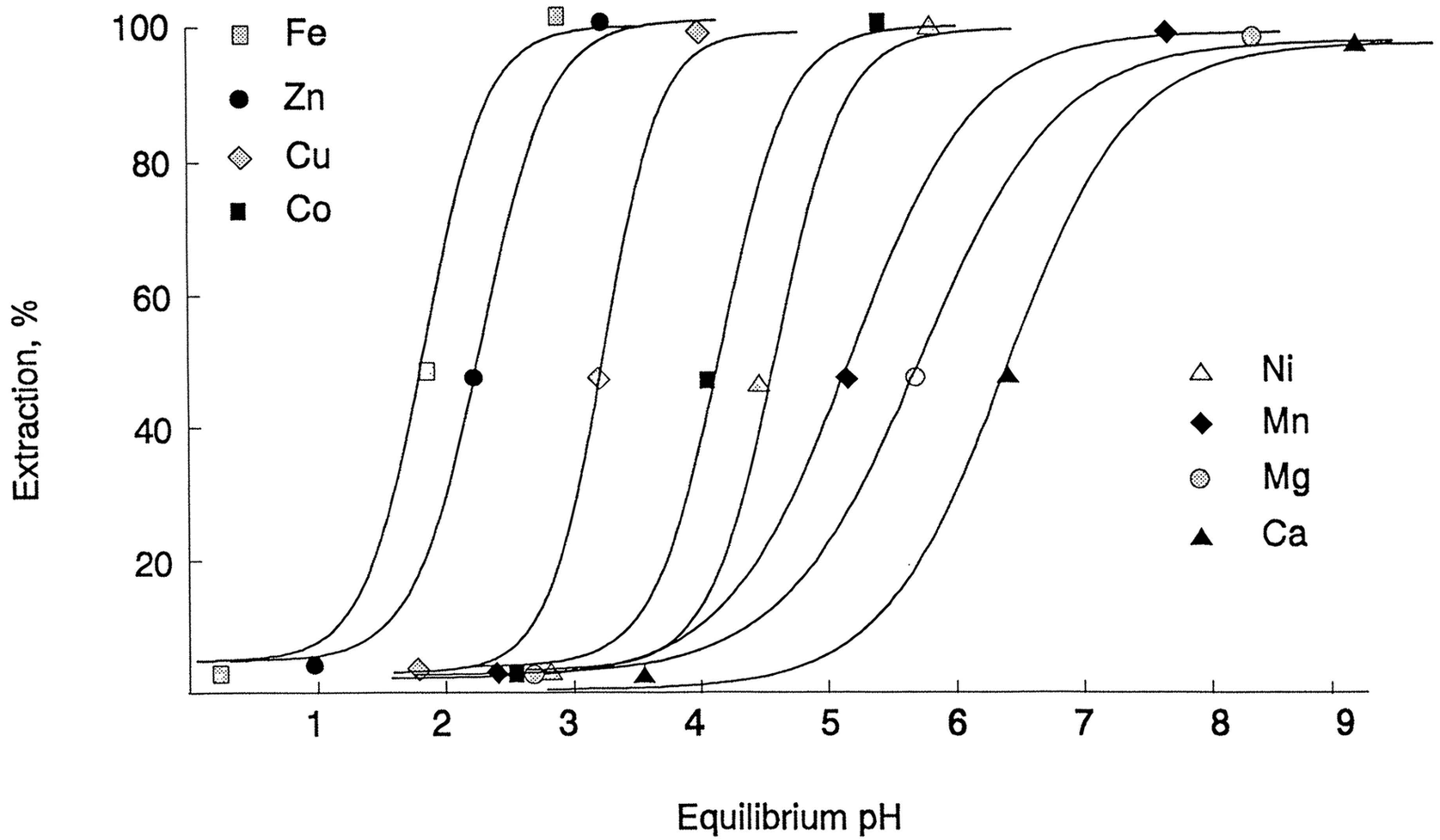

Figure 3.2 : Extraction curves of some selected metals from sulphate solutions using DEHPA.

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This solution was prepared on a weekly basis. The organic phase consisted of 40 per cent of the extractant, di-ethylhexylphosphoric acid (DEHPA), dissolved in diethylbenzene (DEB).

The FIA-SLM system described in Section 2.4.3 was used for this investigation. All solutions were propelled with an Alitea peristaltic pump (C4-XV). The SLM was prepared *in situ* by contacting a porous Durapore membrane with the organic phase.

An initial pH value of 2 was selected for the stripping solution and the feed solution was buffered at a pH value of 4. A reproducible volume of the stripping solution was introduced into the FIA carrier solution at specific time intervals using an injection valve. (Both Valco valves and 4-way, electrically-operated, air-actuated Dionex valves were used). Copper in the stripping solution reacted with the PAR in the carrier stream as it was carried to the flow-through detector. The resulting colour was detected spectrophotometrically at 520 nm with a Jasco Uvidec 100 spectrophotometer. The various performance profiles were obtained and evaluated according to the parameters discussed in Section 2.4.4.

3.4.1.2 Conditions that influence the extraction (feed)

According to *Table 2.1* the parameters on the feed side of the SLM that strongly influence the permeation of the solute (copper) are:

- the solute
- the concentration of the solute
- the pH of the feed solution
- the type of buffer
- the ionic strength of the feed solution .

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The concentration of the solute and the ionic strength of the feed solution were not investigated in this section, and will be considered later. First, the correlation between the extraction curves for various solutes and the SLM extraction was investigated in order to study the behaviour of a solute in the SLM environment. However, no attempts were made to test the selectivity of the system, because of the variety of metals that was favoured by this particular extractant. The investigation rather concentrated on the factors that control the permeation through SLMs. A univariant study of these parameters was carried out.

Different solutes. If we consider the extraction curves in *Figure 3.2* it is evident that the permeation of the respective solutes is dependant on the pH of the feed and stripping solutions. The behaviour of the various metal ions can be predicted fairly accurately from these extraction curves. When attempts were made to extract the various metal ions from an acetate buffered feed solution (pH 4), it was found that no magnesium or calcium permeated through the SLM. However, manganese, cobalt, nickel, copper, zinc, indium, lead, the lanthanides and uranium permeated through the SLM. (The curves for indium, lead, the lanthanides and uranium are not shown.) The results compare well with what one would expect from a study of the respective extraction curves. It was found that the heavier lanthanides were not completely back-extracted, and lowered the permeation of copper by masking the available extractant molecules. They were extracted, but could not be back-extracted. If higher concentrations of nitric acid were used in the stripping solution, some of these lanthanides were released into the stripping solution.

The influence of the type of buffer on the permeation of the solute were investigated next. For the investigation, copper was arbitrarily chosen from the list above.

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Type of buffer. The effect of the type of buffer, as well as the effect of the pH of the feed stream on the permeation of the solute, was investigated. Four buffers were used. The buffer solutions were prepared to cover the respective pH ranges.

- Buffer A (pH 3,8 - 7,8) : Acetate buffer containing potassium acetate and acetic acid.
- Buffer B (pH 1,2 - 5,0) : Citric buffer containing hydrochloric acid and disodium citrate.
- Buffer C (pH 9 - 12,6) : Citrate buffer containing sodium hydroxide and disodium citrate.
- Buffer D (pH 2,2 - 7,8) : Phosphate buffer containing sodium hydrogen phosphate and citric acid.

The feed solution contained copper at a known concentration ($1,5 \times 10^{-3}$ mol.dm^{-3}) and the appropriate buffer at a concentration of 0,1 mol.dm^{-3}. The stripping solution was 0,5 mol.dm^{-3} nitric acid. The performance of the various buffers and the effect of the pH-value of the feed solution are illustrated in *Figure 3.3*.

The figure illustrates the importance of the choice of buffer. It is not wise to assess the effect of pH when different buffers are used. Different buffers affect the reactions that govern the extraction of copper in different ways. The extraction reactions depend on the respective interactions of the buffer and the solute, and also on the interaction between the buffer and the extractant in the SLM. The reactions of the buffer with the various solutes present in the feed solution need to be considered when selecting a buffer.

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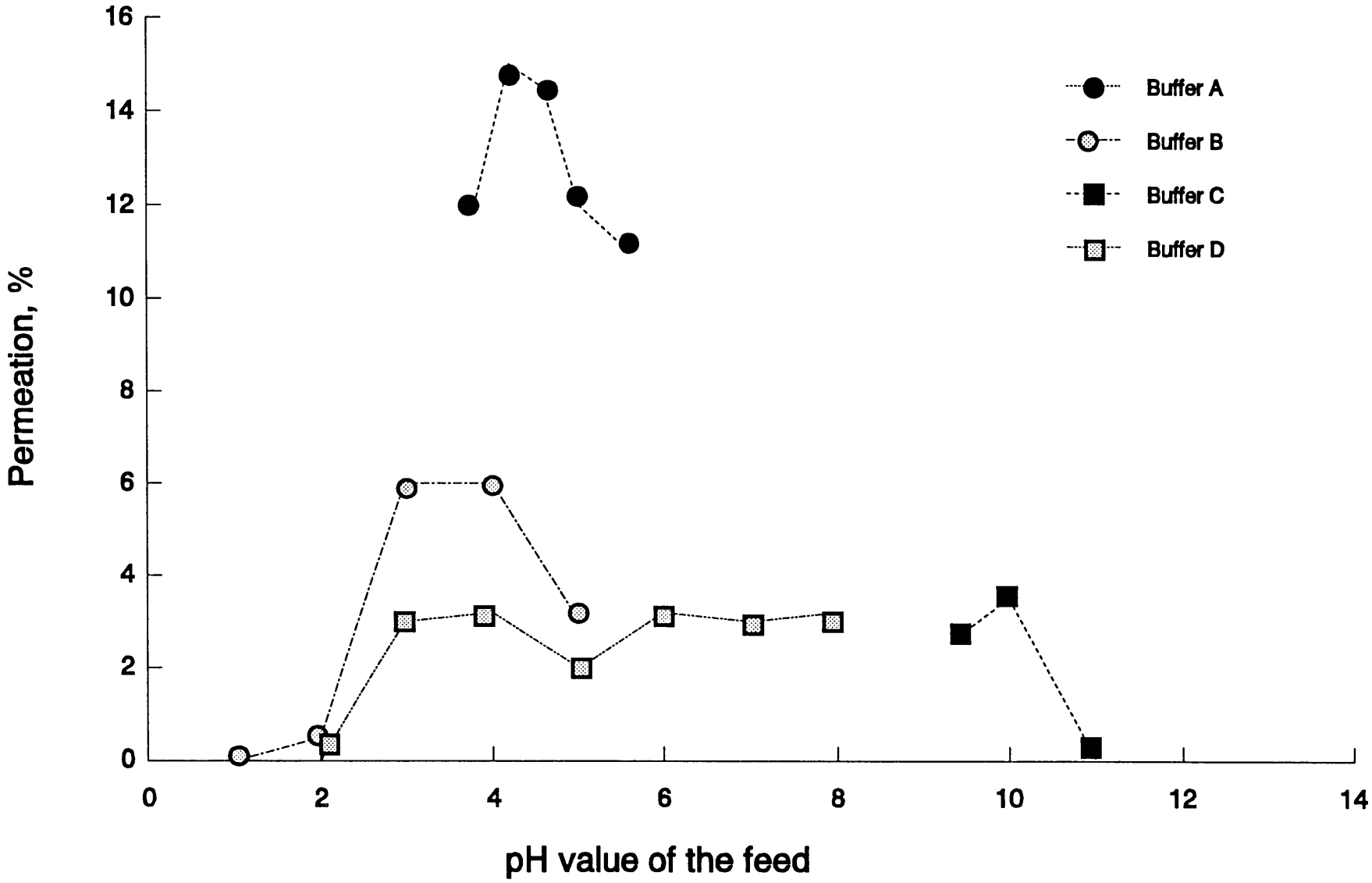

Figure 3.3 : The effect of different pH-buffers on the permeation of copper through a DEHPA SLM.

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The buffer that gave the highest permeation rate for copper was an acetic acid/ acetate buffer (pH 4). Based on this, the concentration of this buffer was chosen for further investigation.

Concentration of the buffer. In order to study the effect of the concentration of the buffer on the permeation, an acetic acid buffer with a molar ratio of 1:4 acetic acid : sodium acetate was used. *Figure 3.4* show the buffer concentration versus permeation. The maximum permeation (H_m) was obtained with a buffer concentration between 0,02 and 0,04 M. At lower buffer concentrations the buffering capacity of the buffer is not sufficient to compensate for the protons released into the feed solution. At higher concentrations of the buffer, the permeation also dropped.

A possible explanation for this latter observation is two-fold. It might be due to reactions that are inhibited by large concentrations of acetate buffer; the undissociated acetic acid might partition into the organic phase, thereby changing the existing extraction mechanism. Alternatively, the decrease might be due to the increase in the concentration of hydrogen ions on the feed side of the SLM, thus repelling the protons from the stripping side.

Attempts to use an unbuffered solution on the feed side of the SLM were unsuccessful. A buffered solution (0,25 $mol.dm^{-3}$) showed a drop in pH value from 4,5 to 3,5 as the feed solution travelled through the SLM unit (24 cm). This drop in pH is due to the counter-permeation of H^+ from the stripping solution to the feed solution. This drastic change in the H^+ concentration observed in buffered solutions will under the conditions of unbuffered solutions change the pH of the feed solution. If the pH of the feed solution drops to below 2,5, the extraction stops.

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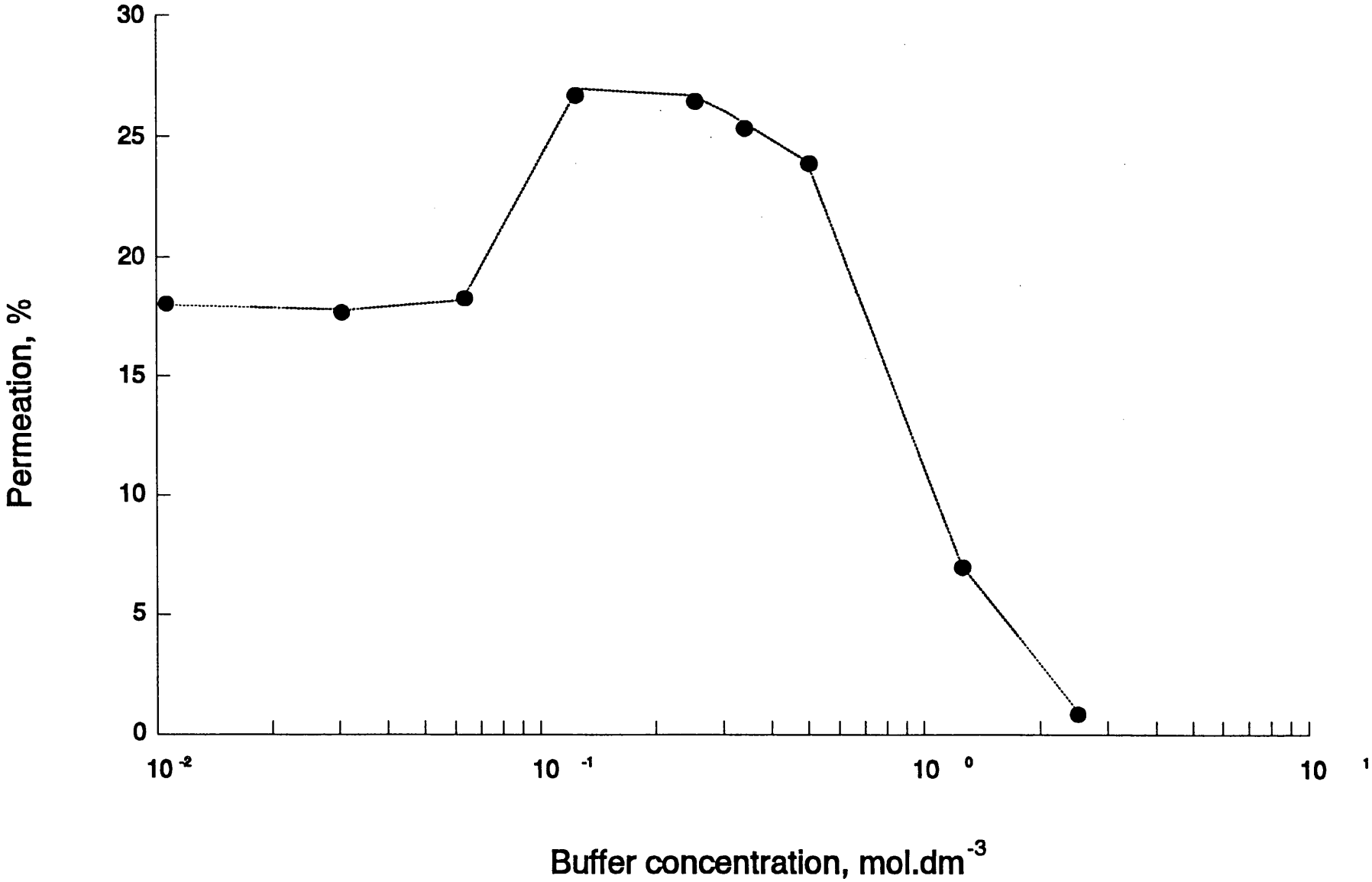

Figure 3.4 : The effect of the concentration of the buffer on the permeation of copper.

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3.4.1.3 Conditions that influence the back-extraction (Stripping)

The parameters that influence the back-extraction on the stripping side of the SLM according to *Table 2.1* are:

- the counter-ion
- the concentration of the counter-ion
- the pH of the stripping solution
- the type and presence of a buffer
- the ionic strength of the stripping solution.

The counter-ion in this particular system was the proton, other counter-ions were studied, and neither was the effect of the ionic strength. The concentration of counter-ion and the pH are equivalent, and will be studied next.

pH of the stripping solution. The influence of the concentration of the protons in the stripping solution on the permeation of copper was investigated first. Nitric acid was arbitrarily chosen as the source of protons in the stripping solution. *Figure 3.5* shows the percentage permeation (H_m) versus the concentration of nitric acid used in the carrier solution. As expected from the extraction curve for copper, the permeation dropped in a sigmoidal fashion for stripping solutions with pH values between 2 and 4. The maximum permeation was obtained at pH values between 0,2 and 1 (acid concentration between 0,1 and 0,75 mol.dm^{-3}). The permeation drop for acid concentrations higher than 1 mol.dm^{-3} can be explained by the high permeation of the protons to the feed side of the SLM, effectively changing the pH of the feed solution, and this will influence the extraction reaction.

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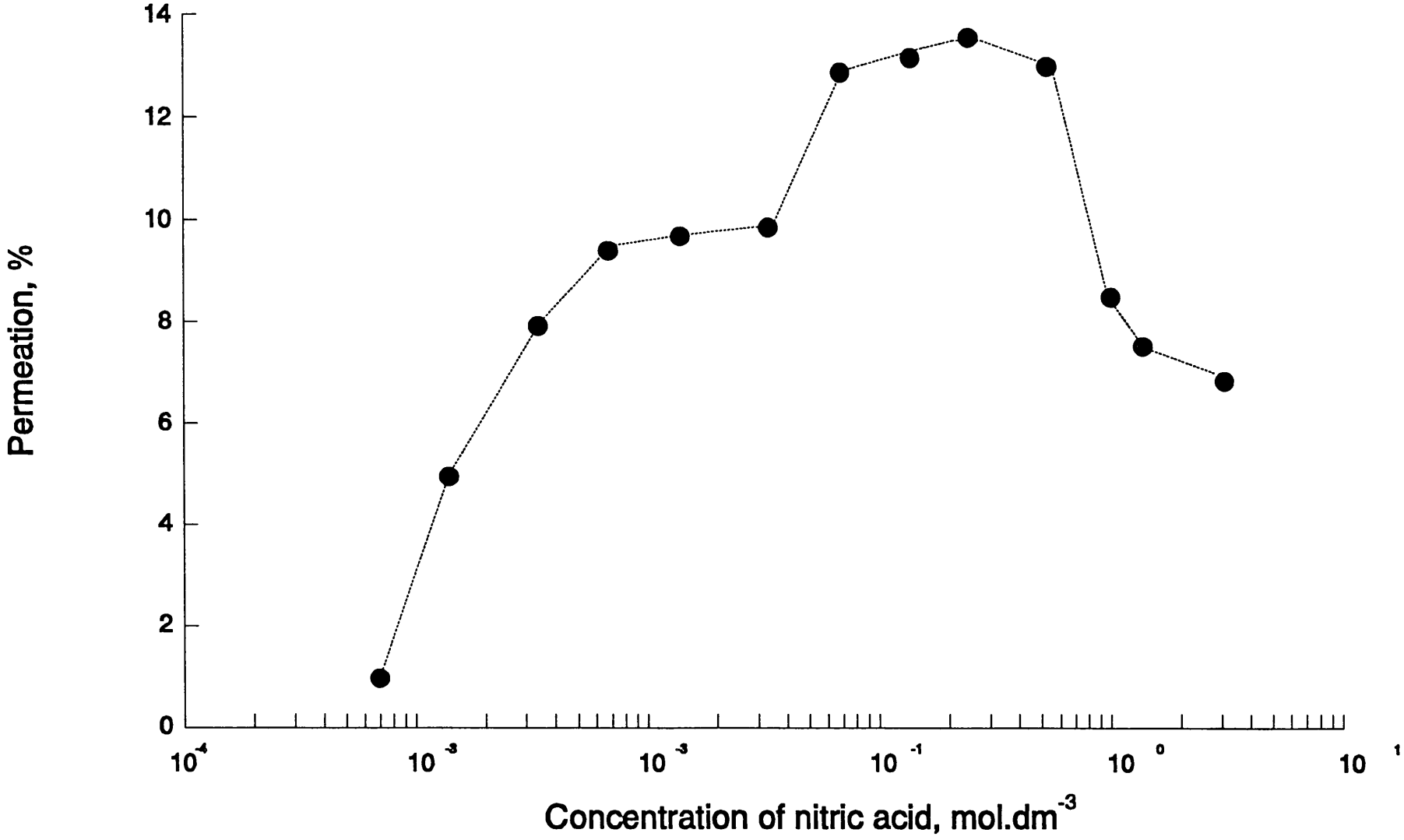

Figure 3.5 : The influence of the concentration of nitric acid in the stripping solution on the extraction of copper.

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Type of acid. The effect of the different inorganic acids, over the concentration range 0,2 to 1 mol.dm^{-3}, on the permeation rate (H_m) of copper through the SLM was investigated. Solutions used as stripping solutions included inorganic acids (hydrochloric, nitric, phosphoric, and sulphuric acids - *Figure 3.6*) as well as buffered solutions (citric acid, phosphate, and citrate buffers - *Figure 3.7*).

The type of acid seemed to be irrelevant, although the concentration was found to be more significant. When sulphuric acid was used *(Figure 3.6)*, there was a marked difference. With sulphuric acid as the stripping solution, the permeation rate steadily decreased over a period of two to three hours. This suggested a different interaction between the SLM, copper and the sulphuric acid. This was confirmed by the fact that the SLM was stable for a shorter period. Two possibilities exist: either the sulphuric acid attacked and degraded the organic phase, or the sulphate interfered with the stripping mechanism.

The back-extraction with strong acids was more effective than that of the buffered solutions, which, as expected from the extraction curves, became less effective with increasing pH value. The permeation of copper obtained with buffered stripping solutions, even at high pH values, seems odd. The fact that the buffers might play an alternative role, such as secondary complexation or changing the extraction mechanism, it might explain the unexpected result.

3.4.2 Anion extraction

The use of SLMs for the extraction of anions was also investigated. In this case, the extraction of dicyanoaurate(I) ($Au(CN)_2^-$) was investigated.

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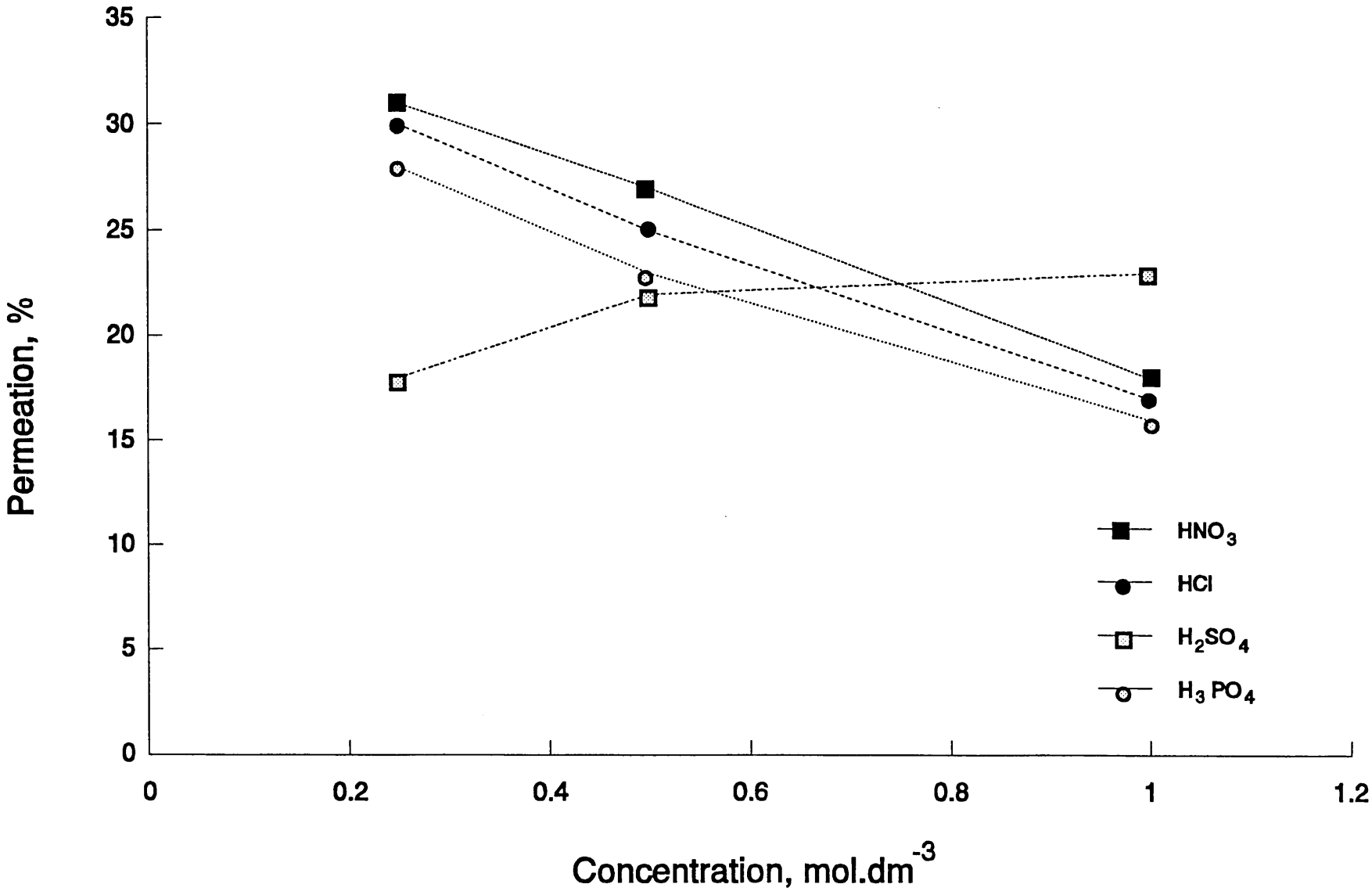

Figure 3.6 : The influence of different inorganic acids as stripping solutions on the permeation of copper through a DEHPA-SLM.

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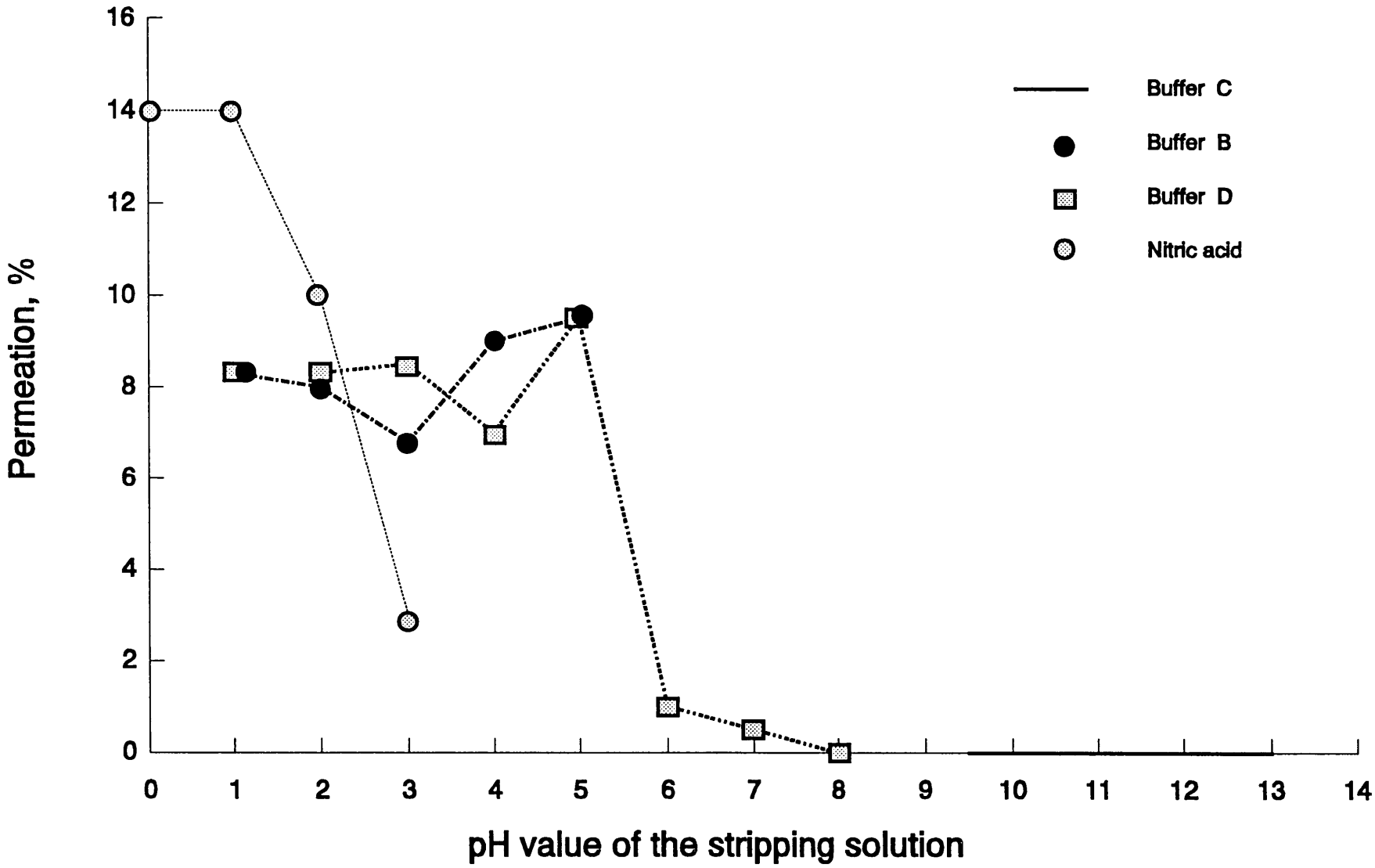

Figure 3.7 : The effect of various buffer solutions used as the stripping solution on the permeation of copper through a DEHPA-SLM.

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The detection of gold in process solutions is a topic of considerable importance, particularly in South Africa. Several sensitive methods for the determination of gold are found in the literature [85-88]. These methods require either expensive and sophisticated instrumentation, or lengthy and labour-intensive preconcentration techniques. These characteristics mitigate against automation and the development of process analysers. It was therefore decided to use the extraction of gold as a case study.

Solvent extraction has been employed by various researchers for the separation and concentration of dicyanoaurate(I) from alkaline cyanide solutions [89-92]. Economic considerations have prevented these successful laboratory-scale experiments from being extended to the process scale. Other reasons include limitations arising from the manipulation of large volumes of different phases, the loss of expensive extractants, and growing resistance to the handling of potentially harmful solvents.

The various potential extractants that were considered for the extraction of gold from alkaline process solutions can be grouped either as solvents, weak-base amines or strong-base amines.

The oxygen-containing solvents are known to extract gold from aqueous solutions [79, 93]. It was found that the capacity of these extractants for the extraction of dicyanoaurate(I) increases in the order [79, 94]:

ethers < esters < alcohols < ketones < aldehydes.

The extraction capacity for dicyanoaurate(I) also increases with increasing concentration of the acid and ionic strength of the aqueous feed solution. In this extraction, gold is present in the organic phases as a neutral solvated molecule, which is coordinated by between one and six extractant molecules [79]. It has also been found that the organic phosphorous modifiers

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are capable of selectively extracting aurocyanide from process solutions by solvation extraction [99]. Solvation extraction involves the transfer of a neutral species from the aqueous phase to the organic phase by the replacement of coordinated water molecules by extractant molecules. Due to its strong electron-donating or Lewis base nature, tri-*n*-butyl phosphate (TBP) is able to solvate the alkali cation-aurocyanide ion-pair by displacement of the weakly coordinated water molecules. This results in a hydrophobic ion-pair structure which moves into the organic phase [79]. TBP has been shown to exhibit high selectivity and a high loading capacity for gold. Back-extraction of gold into the aqueous phase is difficult since the solvation reaction is not pH-dependent [99].

Various nitrogen-containing compounds have also been used to extract dicyanoaurate(I). These compounds can be classed either as strong bases (completely dissociated at all pH values) or weak bases (partially undissociated depending on the pH of the solution). The extraction of dicyanoaurate(I) with strong-base amines is well documented, especially the extraction of gold with Aliquat 336. It is reported that it extracts the cyanide complexes of gold, copper and nickel over the pH range 1,4 to 11,5 [95, 96]. Selective extraction, is however, difficult. Back-extraction by a mere change in pH value is also difficult and the back-extraction is usually performed by acidic thiourea or thiocarbamate [95, 96].

Among the most common reagents used for the solvent extraction of gold from cyanide solution are the alkyl amines. Various amines such as Primene JM-T (primary amine), Adogen 283 (secondary amine) [98-98], and Alamine 336 (tertiary amine) [105, 98, 96] have been used for gold extraction. Since protonation of these amines is necessary for aurocyanide extraction, this normally occurs only from acidic solutions. Also of interest is the work of Mooiman on weak-base amines [98-102]. He conducted an excellent study of the solvent

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extraction of dicyanoaurate(I) from alkaline process solutions, using weak-base amines. Although aimed at batch-type solvent extraction systems, Mooiman's work proved to hold for flowing SLM systems as well. His findings were extremely useful, and warrant further discussion.

3.4.2.1 Protonation of weak-base amines

The primary, secondary, and tertiary amines are referred to as weak-base amines. These weak-base amines contain a nitrogen atom with an orbital bearing a lone pair of electrons, which allows the amine to accept a proton and become positively charged. Although protonation of the weak-base amines can be achieved by acidification of the aqueous feed solution, this option is undesirable in a flow manifold for at least three reasons. Firstly, at low pH values, the extraction becomes unselective. Secondly, process solutions almost always contain the gold as dicyanoaurate(I) in an alkaline medium. Acidification of typical plant cyanide solutions is hazardous because of the formation of free cyanide. Thirdly, the undesirable formation of bubbles occurs at low pH values, due to the presence of the carbonate in the process solutions.

Mooiman's work [97-102] addressed this problem and provides an elegant solution. He found that the use of these amines in conjunction with various organic phosphorous esters results in the modification of the amine basicity [98]. This allows the amine to remain protonated at higher pH values, commensurate with those of the process solution. The amine then behaves as a liquid ion-exchanger, extracting the aurocyanide anion into the organic phase. Mooiman suggested the use of the Lewis base modifiers in the organic phase. These modfiers alter the extraction characteristics of the weak-base amines [99]. He showed that the apparent basicity

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of these amines, with regard to the extraction of dicyanoaurate(I), could be altered by using these modifiers in the organic solution.

Figure 3.8 depicts the extraction curves of dicyanoaurate(I) using only a primary amine and a primary amine in the presence of the modifier. Dicyanoaurate(I) could not be extracted from solutions with pH values higher than 7 in the absence of the modifier. In the presence of a modifier, extraction of dicyanoaurate(I) was possible even at pH 10. At this pH value the extraction was about 40% of that found at pH 7.

The extraction curve for dicyanoaurate(I) using a modified extractant, shown in *Figure 3.8*, was used to select an appropriate pH value for the initial part of the study. It is possible to back-extract dicyanoaurate(I) from the organic phase by a mere pH change. The feed solution was a buffered solution (at either pH 7 or 10). The dicyanoaurate(I) was found to partition into the organic phase if contacted with an aqueous solution with a pH value of 10,5 and lower, and extraction will occur. A stripping solution with a pH value of 11 or higher favours the partition of the dicyanoaurate(I) back into the aqueous phase and back-extraction will result. The back-extraction is achieved with a stripping solution at a pH 12.

Mooiman was particularly interested in the selective separation of the gold complex from most of the metal cyanide complexes commonly found in plant solutions. He found that the apparent shift in basicity observed for dicyanoaurate(I) did not apply to the other metal cyanide complexes to the same extent [98].

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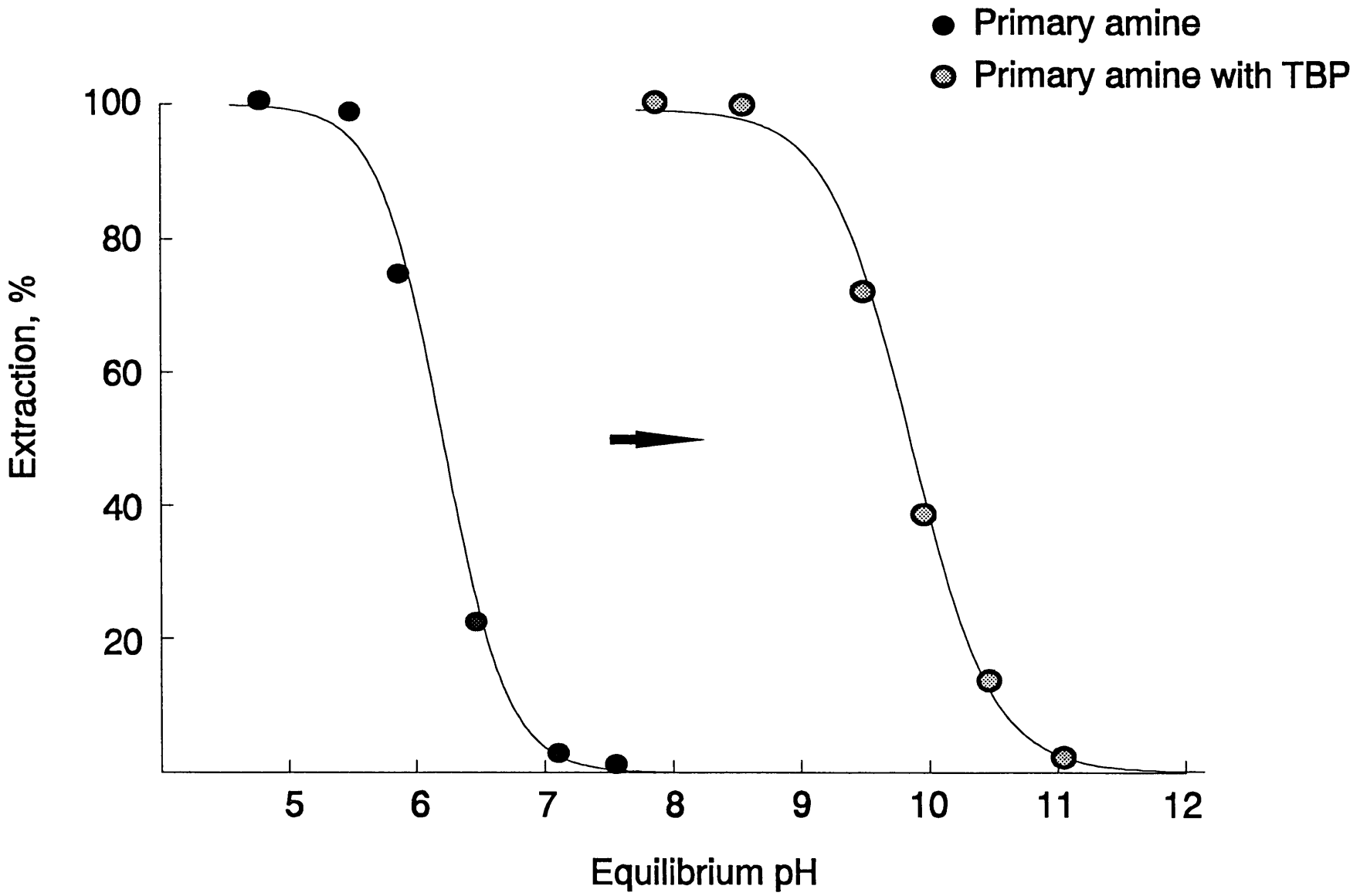

Figure 3.8 : Extraction curves for dicyanoaurate using a primary amine with and without TBP as 'modifier' [101].

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Figure 3.9 show the extraction curves for the various metal cyanide complexes most commonly found in cyanide process solutions [101]. These extraction curves are sufficiently separated to facilitate discrimination between dicyanoaurate(I) and the other metal-cyanide complexes.

3.4.2.2 Experimental design

Apparatus. The flow-injection manifold was similar to that used for the study on the extraction of copper, except for the selection of the solute.

Detection of dicyanoaurate(I). The dicyanoaurate(I) complex was studied using various detectors. Firstly, it could be detected spectrophotometrically at 240 nm. In this investigation, a Jasco UVIDEC or a Spectra-Physics 2000 spectrophotometer with a flow-through cell were used for these UV measurements. A linear calibration curve was obtained for the gold complex in the concentration range 5 to a 100 $mg.dm^{-3}$. Some of the organic solvents and reagents absorb strongly at 240 nm and interfered with the UV detection of gold. A Varian Spectra 10/20 or a Philips SP-9 atomic-absorption spectrophotometer (AAS) was used for the detection of gold in tests where interference was experienced. The instrumental conditions used were as specified by the manufacturers. Deuterium-arc background correction was applied, and the resulting response was directed via the on-board microprocessor to a chart recorder or to the controlling PC. The working range for AAS determination was 0,5 to 50 $mg.dm^{-3}$.

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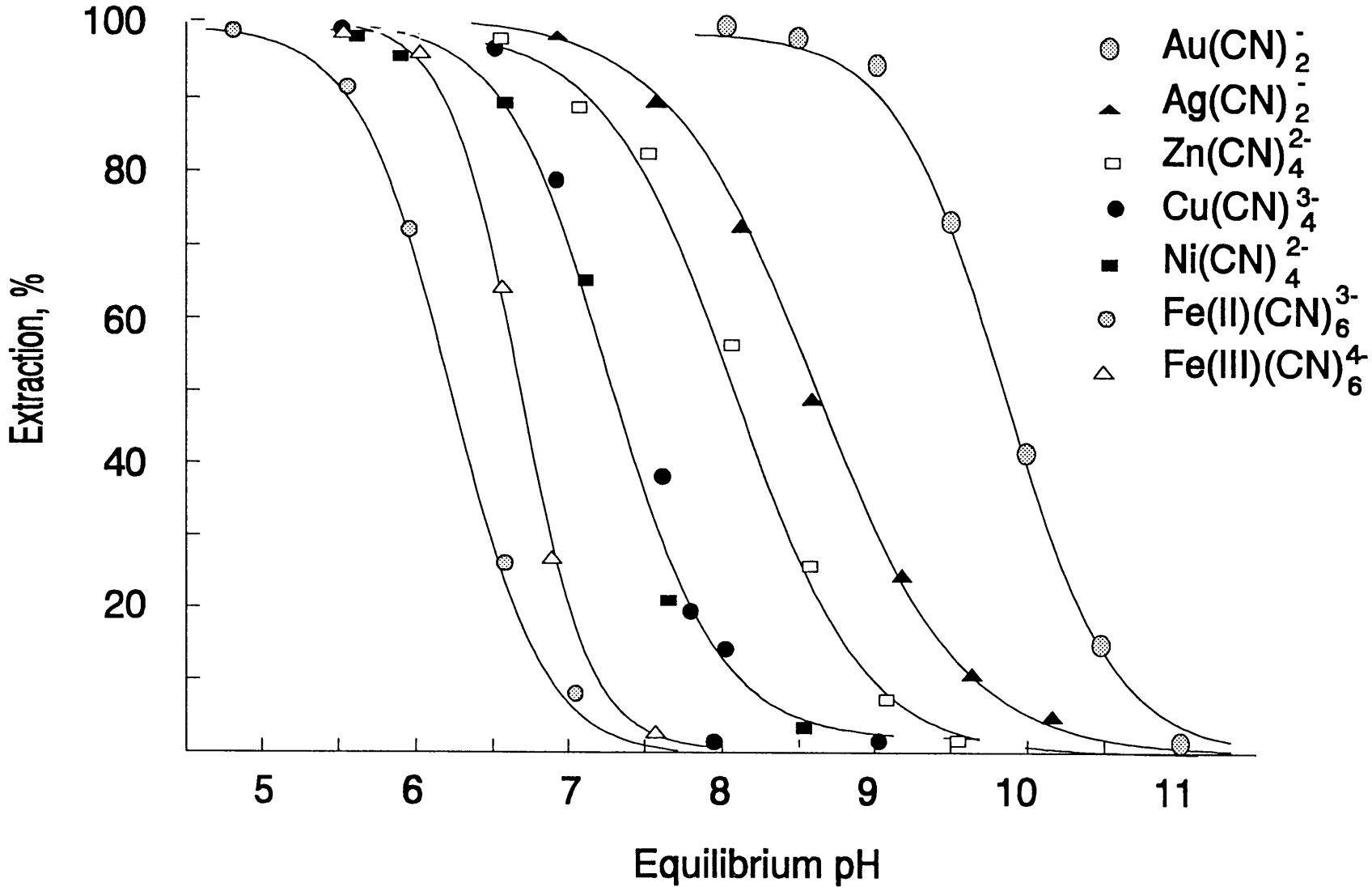

Figure 3.9 : Extraction curves for the metal cyanide complexes using a 'modfied' primary amine [101].

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In certain tests the various metal cyanide complexes in the stripping solution were separated by reverse-phase ion chromatography. A high-performance liquid chromatographic (HPLC) method that has been described for the separation and determination of the metal cyanide complexes [88] was used. This method was used for experiments aimed at the selectivity of the SLM extraction towards the base metal complexes. Chromatographic separations were performed at room temperature using a Spectra-Physics pumping system, a Dionex reverse-phase column and injection valve fitted with a sample loop of 50 mm^3, and a Jasco spectrophotometer model UVIDEC-100-IV or a Spectra-Physics scanning UV-VIS spectrophotometer. Chromatograms were recorded on a Spectra-Physics integrator. The injection was controlled by a software package FlowTEK [100] developed at Mintek. The metal cyanide complexes was detected at 214 nm.

Reagents. All reagents were of Analytical Reagent grade. Deionised water was used to prepare all aqueous solutions. The extractants evaluated for the SLMs included primary, secondary, tertiary and quaternary alkyl amines in various solvents. A stock solution containing 1000 $mg.dm^{-3}$ of the gold-containing complex and 200 $mg.dm^{-3}$ sodium cyanide was prepared. Appropriate dilutions were made from this stock solution to prepare the buffered feed solutions. Two buffers were used. A phosphate buffer, with a pH value of 7, was prepared from potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate ($Na_2HPO_4.2H_2O$). A carbonate buffer with a pH value of 10 was prepared from sodium carbonate (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$). The strength of the buffer in the feed solution was 0,1 $mol.dm^{-3}$.

The stripping solution for the SLMs containing the weak-base amines was 0,1 $mol.dm^{-3}$ sodium hydroxide. For the quaternary amines, the stripping solution was 1 $mol.dm^{-3}$ thiourea

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(DBBP), when tested by these workers in a solvent-extraction system, were found to behave similarly. Although TOPO gave marginally better extraction efficiencies, TBP was selected as the modifier in the present investigation due to its more favourable solubility characteristics in both aqueous and organic solutions over the chosen pH range. Furthermore, it did not interfere in the UV determination of gold.

The permeabilities of several SLMs containing primary amines with different chain lengths were compared. All SLM which contained weak-base amine (for the primary amines only those with carbon chain lengths of less than ten) were prepared by dissolving 10% (v/v) of the appropriate amine in 40% (v/v) heptane and 50% (v/v) TBP. Tridecyl amine (TDA), pentadecyl amine (PDA) and heptadecyl amine (HDA) are all waxes and are sparingly soluble in heptane. However, it was possible to dissolve 1% (m/v) TDA in heptane. Saturated solutions of PDA and HDA were prepared in a 50/ 50 (v/v) heptane/ TBP mixture for the permeability tests. The maximum permeation ratio, H_m, for each of the tested amines is given in *Table 3.4*.

Table 3.4
Permeability of SLMs containing primary amines with different chain lengths

Extractant	H_m (%)	
	pH 7	pH 10
Ethyl	5	1,5
Propyl	7	2
Nonyl	11,5	1,7
Tridecyl	15	4
Pentadecyl	12	2
Heptadecyl	10	1

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The permeation rates increased as the chain length increased up to a chain length of thirteen, where an H_m value of 15% was obtained. The longer the chain length of the extractant, the more hydrophobic the ion pair formed between the solvent and the dicyanoaurate(I). This affects the extraction rate of the gold complex into the organic phase and accounts for the increase in permeation. The amines with shorter chain lengths are also more soluble in the aqueous solutions, which results in less stable SLMs. This is illustrated by the shorter t_s values (in the order of 30 minutes to 1 hour). The decline in the maximum permeation for SLMs that contain amines with more than thirteen carbon atoms might be due to the small amount of extractant in the SLM or to viscosity effects. TDA was chosen for further tests.

It is expected that the extraction of the gold will be favoured by feed solutions with lower pH values, owing to the basicity of the amine in the SLM. As expected, the permeation of gold from feed solutions at pH 10 is considerably less than from feed solutions at pH 7.

The secondary amines followed a similar trend to the primary amines with respect to the permeability of the SLM for gold (*Table 3.5*). A commercial extractant LA-2 (a mixture of secondary amines with chain lengths between 12 and 15) gave the best results (H_m = 10,5%). Generally, the secondary amines did not yield SLMs with the same high permeation rates as their primary amine equivalents.

The effect of TBP on permeation is depicted in *Figure 3.10* Higher TBP concentrations improved the extraction of gold from feed solutions with pH values of 7 and 10, and enhanced the permeation of gold through the SLM.

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At pH 7 a maximum H_m value of 13% was obtained for an SLM that contained 10% (v/v) LA-2 and 90% (v/v) TBP. It is important to note that the percentage of gold permeating through this SLM was doubled compared with an SLM containing no TBP as the modifier.

Table 3.5
Permeability of SLMs containing secondary amines with different chain length

Extractant	H_m (%)	
	pH 7	pH 10
Diethyl	2,9	0,3
Dipropyl	3,3	0,3
Dihexyl	3	1
LA-2	10,5	2,4
Adogen 283 (ditridecyl)	9	5,2

Tertiary amines. The permeation of gold through the SLMs was lowest when tertiary amines were used *(Table 3.6)*. The same trend was observed with respect to the carbon chain length. The highest permeation (H_m = 9%) was obtained with a commercial amine, Alamine 336 (tricaprylyl amine).

Table 3.6
Permeability of SLMs containing tertiary amines with different chain lengths

Extractant	H_m (%)	
	pH 7	pH 10
Trimethyl	1,8	0,2
Triethyl	2	0,2
Tributyl	3,6	0,2
Trioctyl	5,5	0,4
Alamine 336	9	2

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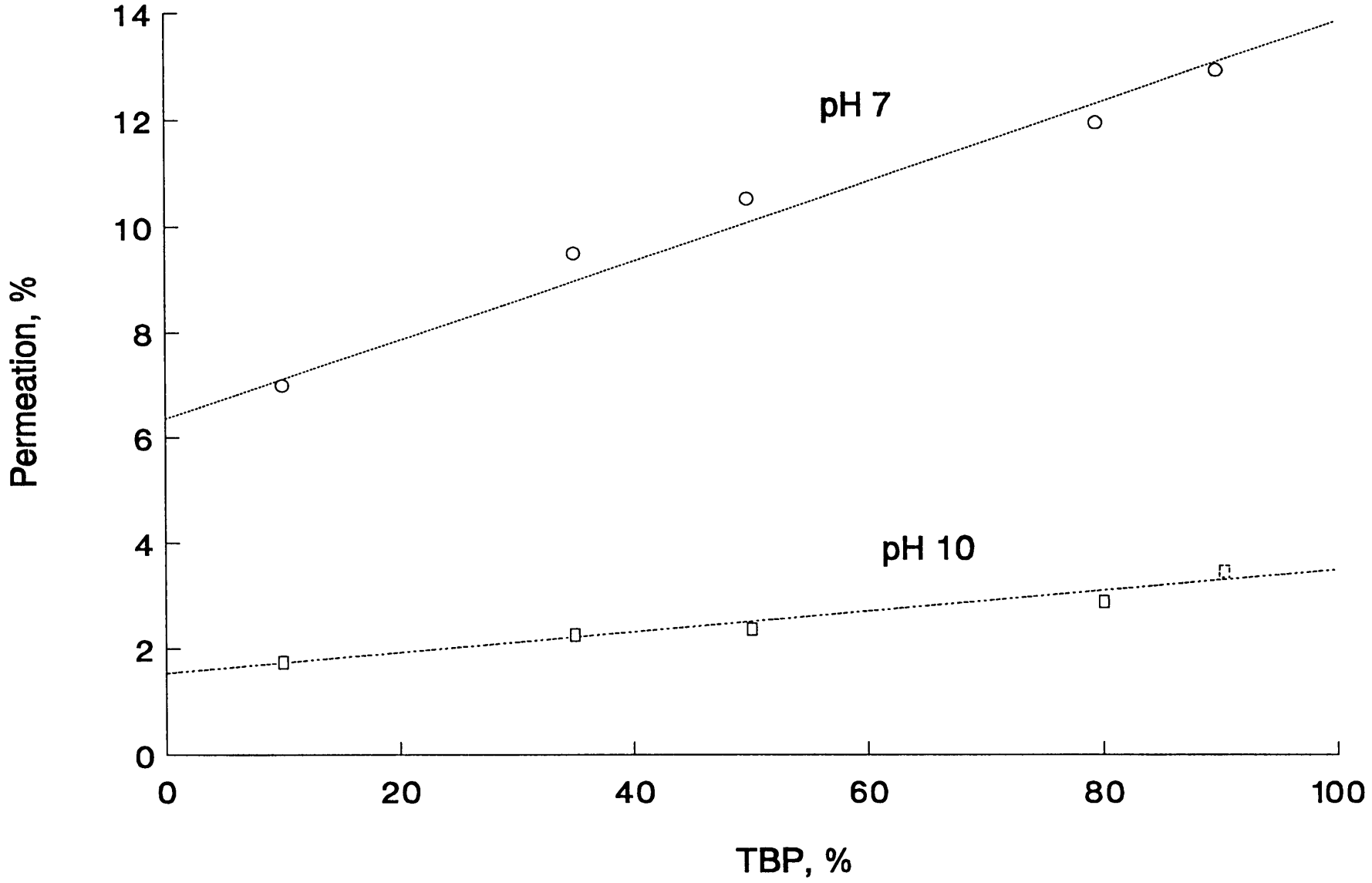

Figure 3.10 : The effect of the percentage TBP on the permeation of gold through a LA-2 SLM. The respective organic phases contained 10% (v/v) LA-2, the respective amount of TBP, made up in heptane.

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Strong base amines. The strong base amines include quaternary amines (R_4N^+ OH^-) and is like all strong acids and bases, completely ionized, regardless of the pH of the solution. The reaction can be described by the following equation (overlining indicates a compound in the organic phase):

$$\overline{R_4N^+} + Au(CN)_2^- \rightleftharpoons \overline{R_4N^+Au(CN)_2^-} \qquad (3.16)$$

The mechanism of extraction with strong-base SLMs is quite different to that of the weak-base amines. The gold complex forms an ion pair with the strong-base amine irrespective of the pH value of the feed solution. Of course, a mere change in pH value will not accomplish the required back extraction.

In conventional solvent extraction, thiourea has been used to strip the gold from an organic phases solution containing quaternary amines such as Aliquat 336 [90].

$$\overline{R_4N^+Au(CN)_2^-} + 2H_2NC(=S)NH_2 + 2H_2SO_4 \rightleftharpoons \overline{R_4N^+HSO_4^-} + Au(H_2NC(=S)NH_2)_2^+ + HSO_4^- \qquad (3.17)$$

The thiourea ligand competes with the cyanide for the gold. The addition of acid to the stripping solution assists the formation of the thiourea complex and destabilises the gold cyanide complex, thus enhancing the stripping of gold from the organic phase.

This extraction was applied in an SLM system. The SLM consisted of 20% (v/v) Aliquat 336, in a 50/50 (v/v) mixture of TBP and heptane. The feed solution contained 50 $mg.dm^{-3}$ dicyanoaurate(I) buffered at pH 7 (to allow comparison with the weak-base amines). The

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stripping solution consisted of 1 mol.dm^{-3} thiourea in 0,25 mol.dm^{-3} sulphuric acid. Due to the absorbance of thiourea in the UV spectrum, the colorimetric method could not be used for the determination of gold. AAS was therefore chosen as the method of detection.

Two SLMs containing quaternary amines were tested, a short chain tetrabutylammonium hydroxide (TBAOH) and a commercial amine Aliquat 336 (methyltricaprylyl ammonium chloride). A high gold permeation (a H_m value of 17,5%) was achieved for the Aliquat 336 SLM. An SLM containing TBAOH gave a similar H_m value. However, the SLM containing Aliquat 336 displayed better reproducibility and stability than the one containing TBAOH. This is due to the lower solubility of Aliquat 336 in the aqueous phase.

For the evaluation of an SLM it is not enough to only consider its permeation behaviour to a selected solute. The selectivity is also of major importance. The selectivity of the three extractants that gave highest permeation of the dicyanoaurate(I) in their respective classes (TDA, LA-2 and Aliquat 336) was compared in the next suite of experiments.

3.4.2.4 Selectivity

The constituents of the three organic solutions considered, are given in *Table 3.7.* These organic solutions were used to prepare the respective SLMs.

The SLMs were evaluated with respect to their enrichment of gold and were tested for two plant solutions labelled A and B. Gold-bearing plant solutions typically contain between

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0,01 and 20 mg.dm^{-3} dicyanoaurate(I). The concentrations of the other base-metal cyanide complexes (*viz.* iron, silver, nickel, copper and cobalt) vary considerably but are usually below 10 mg.dm^{-3}.

The pH value of these plant solutions is normally between 10 and 11. The two filtered plant solutions were spiked with the respective cyanide complexes so that they contained 10 mg of each metal per litre. In addition 10 mg.dm^{-3} of gold was added as the dicyanoaurate(I) complex. The sample solutions were buffered to avoid changes in permeation, due to changes in the pH value of the feed solution while it travels through the SLM unit. The same buffered sample solution was used for all three SLMs to allow comparison between the systems.

Table 3.7
Constituents of the organic solutions used in the selectivity tests (%)

	SLM 1 (TDA)	SLM 2 (LA-2)	SLM 3 (Aliquat 336))
Extractant	1 (m/v)	17,5 (v/v)	20 (v/v)
TBP	49,5 (v/v)	41,25 (v/v)	40 (v/v)
Heptane	49,5 (v/v)	41,25 (v/v)	40 (v/v)

The manifold used for these tests is shown in *Figure 3.11* A 250 cm^3 portion of each of the adjusted plant solution was passed, in a once-through mode, on one side of the SLM. The gold was collected in 25 cm^3 of a suitable stripping solution, which was circulated on the other side of the SLM. Both solutions were pumped at a flowrate of 1,5 cm^3.min^{-1}. When TDA and LA-2 SLMs were used, the stripping solution was 0,1 mol.dm^{-3} sodium hydroxide. For the Aliquat 336 SLM, 1 mol.dm^{-3} thiourea in 0,25 mol.dm^{-3} sulphuric acid was used as the stripping solution.

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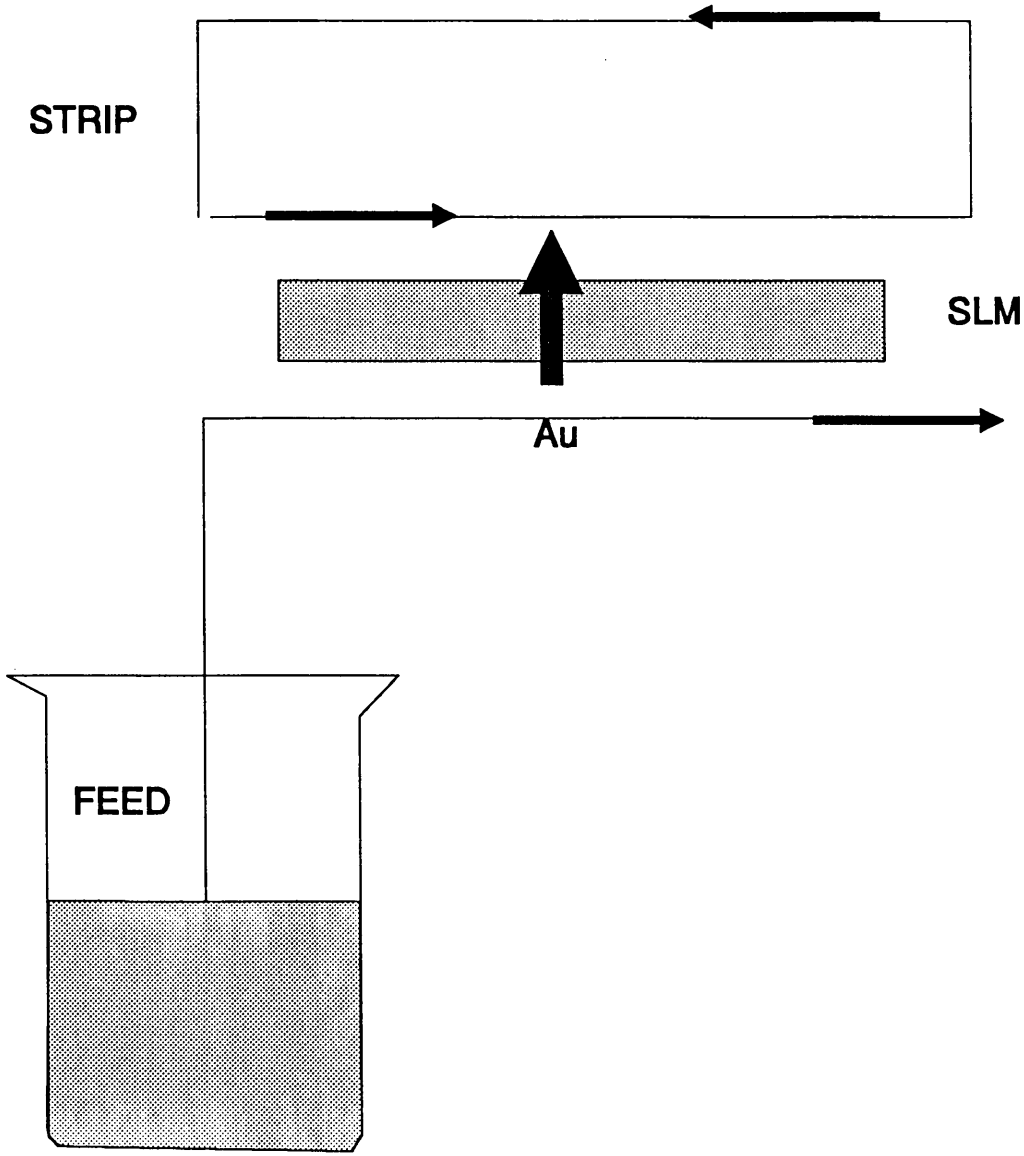

Figure 3.11 : Manifold for investigating the selectivity of various SLM systems.

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Aliquots of the two spiked sample solutions and the various stripping solutions were analysed by ICP-MS, with some of the results being cross-checked by AAS. Enrichment was determined from these results and confirmed by ion-interaction chromatography with photometric detection [88].

Sample A was a concentrate of repulped filter cake and sample B was a waste solution. Gold plant A uses sodium cyanide in the cyanidation step, while plant B uses calcium cyanide. For all the experiments sample A was buffered at pH 7 without any difficulty. When an attempt was made to buffer sample B, both at pH 7 and pH 10, the calcium precipitated. In the SLM system using Aliquat 336, it is not necessary to buffer the feed solution. However, calcium was found to precipitate in the present system when it came into contact with the sulphuric acid in the stripping solution. To prevent the precipitation of calcium, EDTA was added to sample B, which was buffered at pH 10 and used for the selectivity tests. Precipitation still occurred at pH 7, even in the presence of EDTA.

The results of the selectivity study are shown in *Figure 3.12* A and B. The *y*-axis displays the ratio between the concentration of the metals in the stripping solution to that in the feed solution.

Although the SLM that contained the Aliquat 336 resulted in the highest enrichment of gold for both samples, it also gave the poorest selectivity. From sample A, considerable enrichment of silver, and also of copper was evident.

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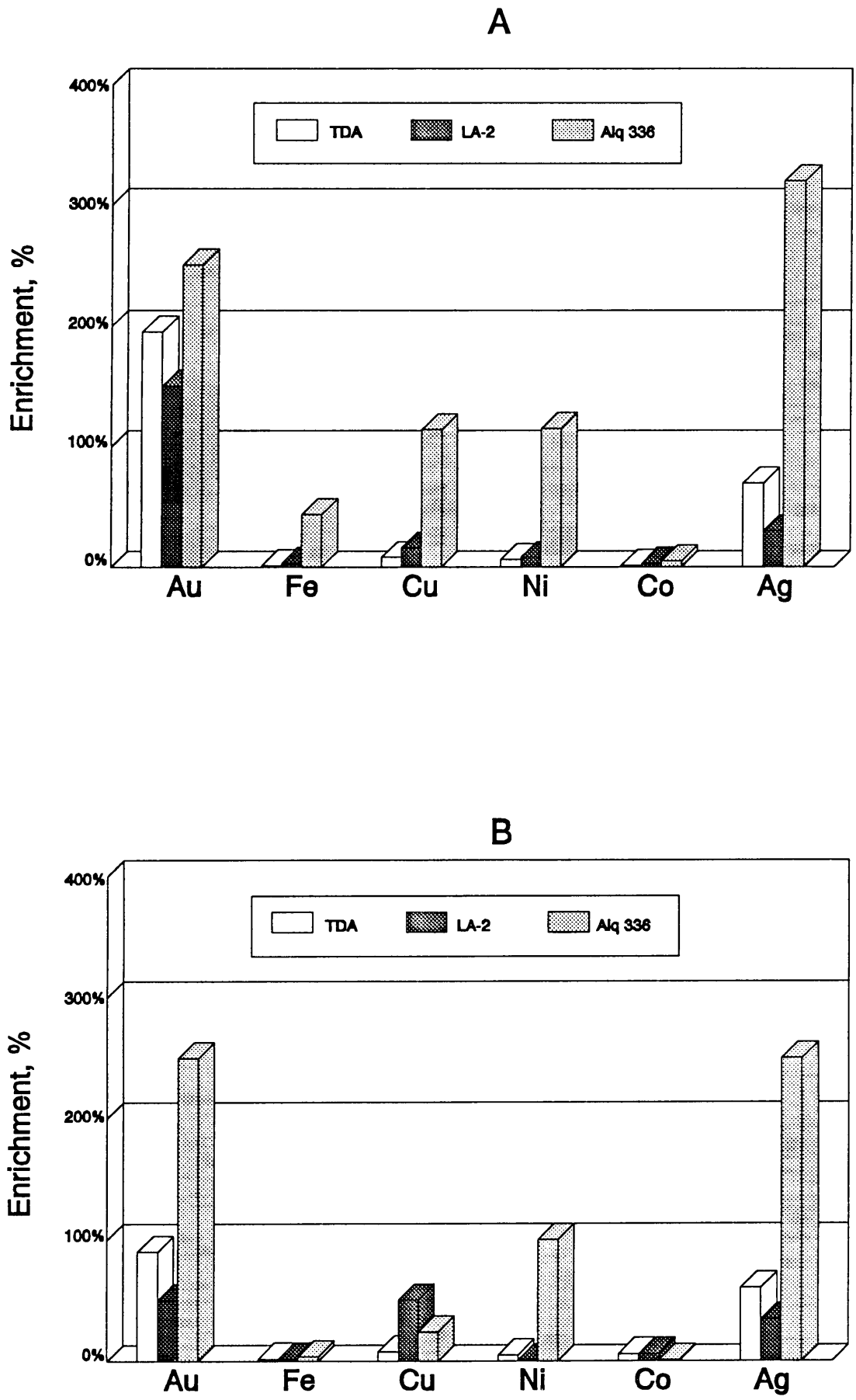

Figure 3.12 : The selectivity of various SLMs towards gold enrichment in two process solutions.

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Both elements were considerably less extracted from sample B, (possibly due to the presence of the EDTA). Nickel was found to co-extract to a similar extent from both solutions. A very small amount of iron was extracted from sample A, and even less from sample B. A negligible amount of cobalt was extracted from both samples.

The enrichment of gold by extraction with an SLM containing TDA was considered next. Enrichment factors for sample B were expected to be lower than those for sample A, due to the higher pH value of the feed solution B (pH 10). Compared to the SLM with Aliquat 336, gold was enriched to a lesser extent, but very little of the base metals were co-extracted. Only silver was co-extracted in significant amounts in both tests.

The SLM containing LA-2 was inferior with respect to enrichment, for both samples tested. It gave the lowest enrichment factor for gold, and although it was more selective than the SLM prepared from Aliquat 336, it was not as selective as the SLM containing TDA. Again, significant co-extraction of silver was experienced. In sample B both silver and copper were co-extracted.

3.4.3 Observations

Even in the small test unit used in this investigation, it was essential to buffer the aqueous solutions, specifically the feed solution. This was neccesary to keep the pH conditions fixed during the permeation process. In general, it was observed that the optimum concentration of the buffer and the acid solutions was 0,25 mol.dm^{-3}. Care should be taken in the choice of a buffer to ensure that it only provide a source of the co-, or counter-ions. Any possible alternate reactions as a result of the buffer must be considered.

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It should further be noted that the manifold used was designed for the quick scanning of various extractants, and the ratio of surface area to volume was not optimised. However, the fact that 15% of the gold could be extracted by an SLM with such a small area (2.4×10^{-4} m^2) was considered encouraging.

Although the primary reason for the investigation was the evaluation of various extractants for their inclusion as SLMs in a simple method of analysis, the findings could benefit plant-scale studies as well, particularly the findings for the extraction of dicyanoaurate(I) [53].

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CHAPTER 4
SLMS AND MEMBRANES

In this chapter the membrane characteristics of SLMs will be studied. Since the largest application of SLMs has been in the field of solvent extraction, one would intuitively regard the chemical reactions, and their respective rates, as the most dominant factors in determining diffusion rates. However, in certain cases the chemical factors can become a secondary consideration, while the physical processes of diffusion (stages 1, 3, and 5) dominate the rate (and thus the selective permeation) of species. In these cases the static equilibrium parameters becomes very much a secondary consideration. A holistic approach, in which the SLM is viewed as a single entity comprising support, solvent and extractant, will be adopted.

The SLM will be viewed as physical barrier through which chemical species permeate by a solution-diffusion process. This part of the study concentrates less on the specific chemical reactions that take place in the system, and more on the membrane as a whole, the driving forces for permeation, and the effect of the physical environment on diffusion.

To enable a measure of perspective, an overview of membrane science in general is included. A classification of the membrane separation techniques and a description of the available materials currently used for SLMs is also provided.

4.1 BACKGROUND

Membrane separation is a vital process in life itself, and mankind has used filtration for centuries. Consider how nutrients are extracted from digestive systems, or how oxygen

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diffuses from the environment into various organisms. In plants, essential minerals salts are concentrated from soil into the roots of the plant and in various biological systems membranes are responsible for the removal of toxins. Membranes are also used to good effect in a variety of industrial separations; particles from liquids, dissolved solids from liquids, and gases from liquids.

Londsdale has given an excellent overview of the development of the field of membrane science [1]. An interesting study of the discriminating capabilities of membranes mentioned by Londsdale was reported as early as 1748. The French Abbé, Nollet placed 'spirits of wine' in a vessel, the mouth of which was closed with a animal bladder and immersed in pure water. Because it was permeable to water and not to the components of the wine, the bladder swelled and eventually burst, due to the permeation of water under osmotic pressure.

In 1855 Fick published his laws of diffusion, which are still used to study first-order diffusion through membranes. He also prepared and studied the first artificial semipermeable membrane. It was made from an ether/ alcohol solution of cellulose nitrate, called *collodion.* Fick used these membranes for an extremely important membrane technique that was later termed dialysis by Graham [2]. As early, as 1861 Graham drew a distinction between compounds according to their physical size. He distinguished between colloids such as proteins, gums and polysaccharides; and crystalloids which are substances with lower molecular mass. It is generally accepted that colloids range in diameter from 10 Å to 10 000 Å (0,001 to 10 μm). Particles larger than 10 μm can easily be seen with a microscope, and are considered beyond the colloidal size-range. He also described different diffusion rates for

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various gases through rubber. The following developments mentioned by Londsdale [1] were particularly noteworthy:

- Osmosis was studied in the late 1800s by Traube, Pfeffer, and van't Hoff.
- Microporous membranes were mentioned by Zsigmondy in the early 1918s, and introduced the fields of ultrafiltration and microfiltration.
- Reverse osmosis was studied in 1920 by Manegold.
- Donnan dialysis was described in 1934.
- Dialysis was applied for the first time in an artificial kidney by Kolff in 1940.
- In 1950 the first microfiltration and dialysis membranes became commercially available.

The proliferation of membranes in recent years is staggering and one just has to look at the patent catalogue to see the rate at which membrane technology is being developed. The applications of membranes are extremely diversified, and include disciplines from biology to physics. Two approaches to membrane classification shed new light on this burgeoning field of research: physical classification, and the mechanism by which permeation takes place.

4.2 MEMBRANE MATERIALS

Synthetic membranes are traditionally not regarded as being highly selective for chemical separations. Rather they are associated with physical separations. Manufacturers use a classification based on pore size.

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Figure 4.1 shows the boundaries between the various membrane techniques, based on particle size discrimination, as proposed by Porter [3]. These classes are:

- filtration
- microfiltration
- ultrafiltration
- dialysis (electro-dialysis and heamo-dialysis)
- osmosis
- reverse osmosis.

The dividing lines are not well defined [1].

The literature frequently refers to membranes according to their molecular weight cut-offs (MWCOs). Converting MWCO to pore size is not straightforward, especially in macromolecules, where molecular shape is an important consideration when defining size [1]. *Figure 4.1* also indicates the approximate relationship between MWCO and pore size.

Filtration. Most commercial filtration membranes are made of compacted cellulose and filter particles larger than 10 μm from solutions [1]. These membranes are generally hydrophilic, as they are used mostly to separate solids from aqueous solutions. They are not, therefore, really suited to being supports for organic liquids. (An interesting possibility, however, would be to use them as inert supports for an aqueous phase between two organic phases.) Also their pore size is usually too large and irregular to function as a supports for an SLM.

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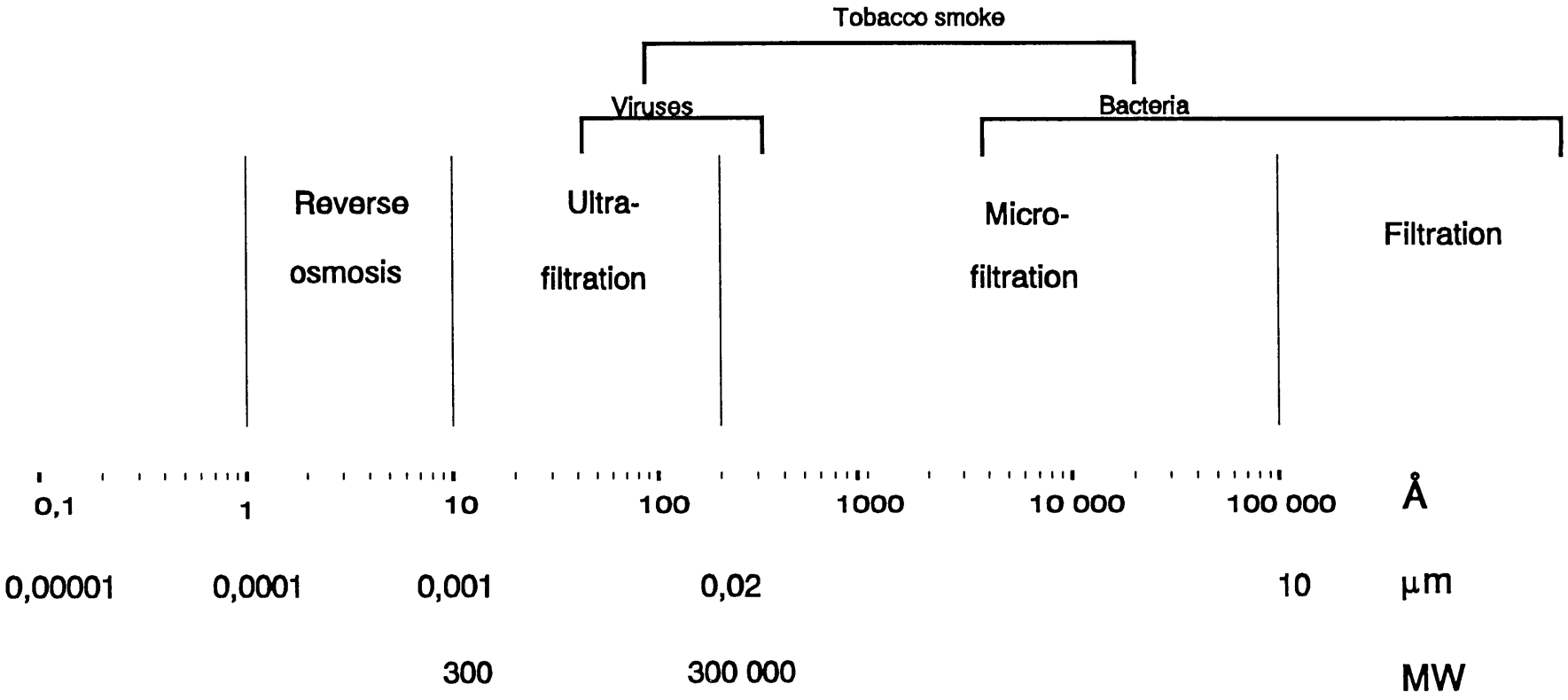

Figure 4.1 : Classification of membrane separation techniques according to the particle size they affect.

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Microfiltration. The first porous membranes that were used for microfiltration were finely porous cellulose-nitrate/ cellulose-acetate membranes. The development of these membranes is associated with the detection of biological warfare agents during World War II. The origins of the Millipore company [1], currently one of the main suppliers of membranes, can be traced to this period. The current trend is to use lipophilic, materials for microfiltration.

Materials used for fabrication include pure cellulose nitrate, pure cellulose acetate, various polymers such as polyvinyl chloride, polyamide, polypropylene (PP), polyvinyl difluoride (PDVC or Durapore), polytetrafluoroethylene (PTFE) and Nylon, as well as acrylic co-polymers such as Nafion, and ion-exclusion membranes.

Most membranes used for microfiltration and those used for ultrafiltration have a pore size of between 0,1 and 2 μm [4, 5]. Theses membranes are most frequently used as supports for SLMs.

Ultrafiltration. Ultrafiltration membranes retain species larger than 10 Å (MWCO range between 300 000 and 300). These membranes are typically made of cellophane, cellulose acetate, polycarbonate, polyvinyl chloride, poly-amides, polysulphone, polyvinylidene fluoride, co-polymers of acrylonitrile and vinyl chloride, poly acetal, poly acrylate, poly electrolyte complexes, and cross-linked polyvinyl alcohol [1].

Dialysis. Dialysis membranes are usually hydrophilic membranes with a MWCO of between 14 000 and 3 000 (0,003 to 0,01 μm), and can be viewed as a special application of ultrafiltration.

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Osmosis. The membrane processes in which only the solvent diffuse through the membrane, but not the dissolved salts, is called osmosis. Most animal bladder membranes, parchments, or vegetable tissues, exhibit osmotic behaviour. Synthetic osmotic membranes are formed by diffusing $Fe(CN)_6^{3-}$ and Cu^{2+} from opposite sides into each other through a dialysis membrane. An insoluble film is formed that is not permeable to ions, but allows aqueous solution to pass through.

4.3 CHEMICAL CLASSIFICATION OF MEMBRANES

With recent development in membrane science, the use of membranes has advanced from separations based on physical parameters, to separations based on chemical properties. This section will deal with the mechanisms that control diffusion through the membrane. The terms phase I - the first aqueous phase; phase II - the membrane; and phase III - the second aqueous phase; will be used to avoid any inferences to the mechanism by terminology.

4.3.1 Unfacilitated transport

If solutions of different composition are brought into contact with each other, the solute molecules will flow from the solution with the high concentration to the one with the low concentration. The membrane can be viewed as a partition between two such aqueous phases. The flux through the membrane is then controlled by the concentration difference of the solute in the two aqueous solutions.

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Fick's first law of diffusion describes the mass transport or flux (J) through these simple membranes in terms of a concentration difference of the solute. He saw the concentration difference as being the driving force for permeation [4, 6]:

$$J = \frac{dn}{dt} = -DA\frac{dc}{dx} \qquad (4.1)$$

where D is the diffusion coefficient of the solute through the membrane, A is the membrane area, *dn/dt* is the mass flow diffusion rate, and *dc/dx* is the concentration gradient of the solute. It is important to note that with the following approach some inherent assumptions are made. These include:

- diffusion in the membrane is the slowest (rate determining) step;
- phase and chemical equilibrium prevail at the phase boundaries;
- the membrane represents a plane-parallel boundary interface.

The concentration difference can be viewed as a concentration gradient across the membrane and is depicted in *Figure 4.2A*. The x-axis indicates the distance from the membrane. The y-axis indicates the relative concentration of the solute and in facilitated transport the co-, or counter-ion. The diagram illustrates the initial concentration of the components. The concentration gradient is defined as the difference between the concentration of the solute in the two solutions divided by the thickness of the membrane.

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To analyse the effect of the concentration gradient on the flux, it is convenient to substitute the diffusion coefficient (D) for a composite diffusion coefficient, D_A in equation 4.1. D_A incorporates all the physical parameters of the system, such as membrane area, temperature, electrical effects, pressure, flowrates of the solutions, geometry, viscosity, porosity, and tortuosity of the membrane.

Equation 4.1 becomes:

$$J = \frac{D_A}{x} . \Delta[A] \qquad (4.2)$$

$$\Delta[A] = [A]_I - [A]_{III}$$

where the subscripts I and III denote the respective phases.

In simple membrane techniques, such as dialysis, unfacilitated transport takes place, and equation 4.2 describes the permeation through the membrane. Solute A will move through the membrane, in an attempt to equalize the concentration in phase I and III. As time elapses the concentration gradient will decrease, and therefore the rate at which permeation takes place will decrease until the concentration of A is equal on both sides of the membrane, and permeation stops.

This simple case has three limitations:

- the changing permeation rate
- the solute cannot be concentrated in phase III to a level above its concentration in phase I.
- selective separation of the solute on a chemical basis is not possible.

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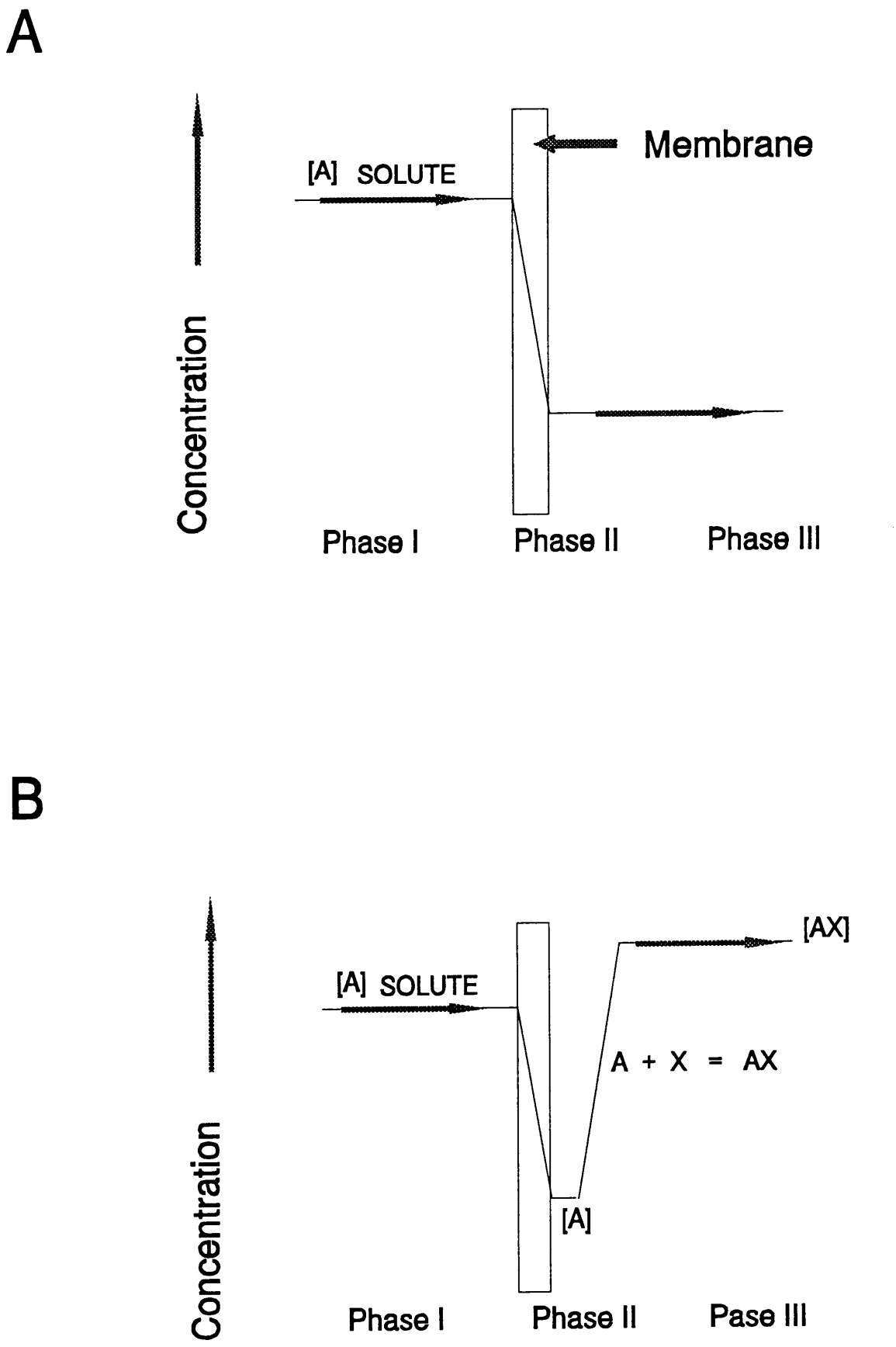

Figure 4.2 : Permeation models for unfacilitated permeation. A - simple permeation; B - permeation with secondary reaction.

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4.3.2 Unfacilitated transport with chemical reaction

Figure 4.2B illustrates a system in which the abovementioned limitations can be overcome to a certain extent. The solute is removed from phase III, and so the effective concentration of the solute stays constant in phase III (close to zero), thus ensuring continued transport across the membrane until it is depleted from phase I. Furthermore, if phase I is a flowing stream, the concentration of the solute is kept constant in phase I, thus keeping the flux through the membrane constant.

The solute can be removed from phase III by various reactions. Chemical methods include the addition of an auxiliary reagent (X). The auxiliary reagent can be either a complexing reagent, or a reducing or oxidising reagent. The solute can also be physically removed from phase III by precipitation or ion exchange. This removal of the solute (A) is indicated in Figure 4.2B as the complex (AX). Enrichment of the solute is possible. The concentration of the solute can be much higher in phase III, where it is present either as a complex (AX) or in a different oxidation state. A measure of chemical selectivity can be obtained by removing only the solute of interest from phase III.

4.3.3 Facilitated transport

The concept of selective permeation of oxygen through the lung membranes inspired even the earliest inventors. These researchers relied totally on artificial membranes to perform the separation between gases. Membranes that can affect gas separation are natural rubbers,

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silicone rubbers (polydimethyl siloxane), and even porous glass (used for the separation of azeotrope mixtures by pervaporation). Microporous polypropylene (PP) and microporous tetrafluoroethylene (PTFE or Teflon) have also been examined for the oxygenation of blood in a medical application.

These researchers required that the membranes had to be perm-selective to certain gases and also that they should have a high flux or permeation rate. These two requirements are often contradictory. In general, the more permeable a membrane is, the less perm-selective it becomes [1]. Various ingenious developments have almost perfected the permeation of oxygen through membranes.

In FIA, the approach to gas separation was somewhat different. Investigators relied more on the chemistry than the membrane to perform the separation. In the past ten years, porous hollow tubes of various materials have become commercially available. These hydrophobic tubes, have a typical pore size of between 4 and 2 μm and a typical wall thickness of between 0,5 and 1 mm. Gas can permeate through these tubes, while their hydrophobic nature repels the aqueous phase sufficiently to keep it from escaping from the tube. This characteristic has made the tubes invaluable as a degassing unit in FIA [7-10].

The tubes have also been used for low temperature distillation of the gas-forming compounds. The pH of the solution on one side of the membrane can be adjusted to force the gas-forming compound into its gaseous form. The evolved gas permeates selectively through the wall of the tube, and can be collected as the gas, or as a redissolved solution with the required pH

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value, on the opposite side of the membrane. These methods rely on the chemistry on opposite sides of the membrane for selectivity. Methods have been developed for the detection of ammonia, cyanide, sulphide, and thiocyanate, as well as for the hydride-forming elements [7-10]. Thicker hydrophilic tubes (silicon rubber) have also been used to achieve the same selective gas separation for the permeation of cyanide and sulphide [9].

In the lungs, the chemistry is an integral part of the membrane, and a mechanism of facilitated transport is employed. The lung membranes, which are not really perm-selective in themselves, are saturated with blood that contains haemoglobin. The haemoglobin acts as a complexing reagent, complexing the oxygen in the air and transporting it into the blood system. The reaction is reversed for carbon dioxide. The function of the haemoglobin is to facilitate the transport of the oxygen through the membrane. The importance of this facilitated transport was emphasised by Scolander in 1960 [11], who illustrated how the presence of haemoglobin in a membrane mediates an eightfold increase in oxygen passage.

The mechanism of facilitated transport is illustrated in *Figure 4.3*. The use of an extractant in the membrane renders the solute more soluble in the membrane (phase II) than in phase I. In the figure this enhancement in solubility in phase II is shown by the increase in the effective concentration of the solute in the membrane on the side of phase I. This causes an increase in the concentration gradient, and leads to an higher flux or mass transfer through the membrane.

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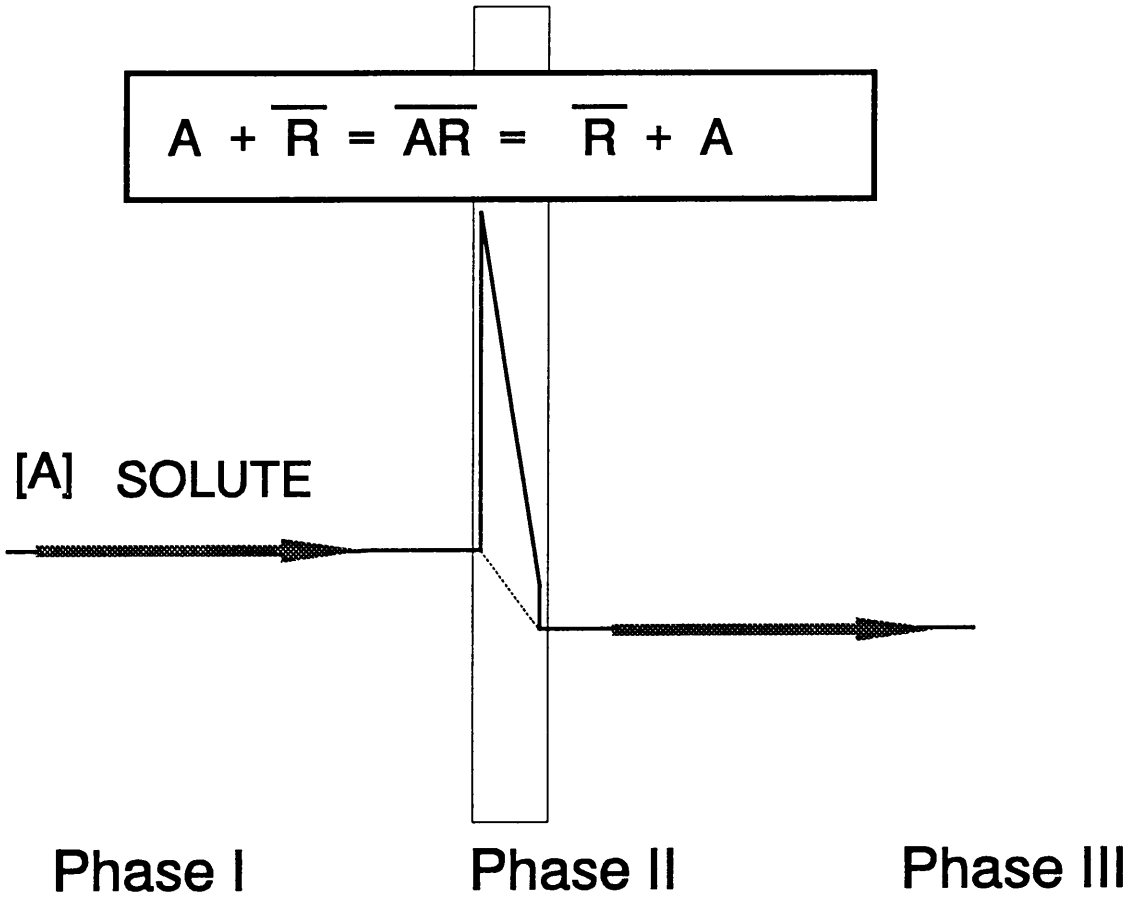

Figure 4.3 : Permeation model for facilitated transport.

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This is indicated in equation 4.3 by incorporating the distribution coefficient in the diffusion coefficient D which now becomes D_{AR}. D_{AR} for a solute is sometimes up to several orders of magnitude greater than D_A for solutes that are not complexed by the extractant. D_{AR} usually includes the partition or distribution coefficient used in solvent extraction.

$$J = \frac{D_{AR}}{x}. \Delta[A]$$

$$D_{AR} > D_A \qquad (4.3)$$

By selecting an appropriate extractant, the permeation of selected solutes through the membrane is enhanced.

It is important to note that the use of an extractant in the membrane serves the same function as a catalyst; it accelerates the permeation to equilibrium without being consumed. Permeation stops once the concentration of the solute is equal on both sides of the membrane. This mechanism cannot be used for solute enrichment, rather it accelerates the transfer of the solute across the membrane; a most vital process in the lungs.

4.3.4 Facilitated transport with secondary reaction

As for unfacilitated transport, the solute can be removed from phase III after facilitated transport to achieve enrichment. Section 3.3.2 illustrates the mechanism of facilitated

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transport with secondary reaction. The dicyanoaurate(I) is more soluble in the organic phase when it contains a quaternary amine. On the other side of the membrane the dicyanoaurate(I)-amine complex is destroyed by complexing the gold with thiourea. In the process, the gold complex changes its charge from (-1) to (+1) and dicyanoaurate(I) is thus essentially removed. Permeation of gold through the membrane will, however, continue against its own actual concentration gradient.

4.3.5 Facilitated coupled transport

The principles of facilitated transport have recently been extended to include facilitated coupled transport. Facilitated coupled transport is a technique based largely on the principles of solvent extraction.

This particular application of facilitated transport provides a measure of chemical selectivity to membrane separations as well as enrichment of the solute in phase III above its concentration in phase I. Selectivity is introduced by incorporating reagents in the membrane that selectively facilitate the transport of a chosen solute across the membrane. The extractants traditionally reserved for solvent extraction are used as these facilitating reagents. In addition, the compositions of phases I and III are also carefully selected to aid the selective complexation of the solute.

These membranes consist of an immiscible organic solution that contains the extractant on a support. Transport through these membranes is based on extraction and back-extraction. On

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the one side the solute is extracted from phase I, and on the opposite side it is back-extracted into phase III.

Owing to the nature of the extractants used in solvent-extraction, facilitated coupled transport can be classified according to whether it relies co-transport or on counter-transport, depending on the ion-association. As a rule of thumb, counter-transport takes place if cations are to be extracted, and co-transport takes place if anions are to be extracted.

4.3.6 Facilitated coupled counter-transport

The mechanism of counter-transport is illustrated in *Figure 4.4*. It represents by far the majority of published applications of facilitated coupled transport. The cation extraction used in Section 3.4.1 is an excellent example of this mechanism of transport.

The acidic extractant (HR) is dissolved in the organic phase that constitutes the membrane. In phase I the reversible reaction between the solute (A) and the extractant (R) is favoured. The complex diffuse through the membrane to the other side. In phase III the reverse reaction is favoured, and the complex in the acid form permeates to the opposite side for the next cycle.

The overall effect is that the solute moves from phase I to phase III and the co-ion, in this case the hydrogen ion, moves in the opposite direction from phase III to Phase I. The driving force for this reaction is not the only the concentration of the solute, but that of both

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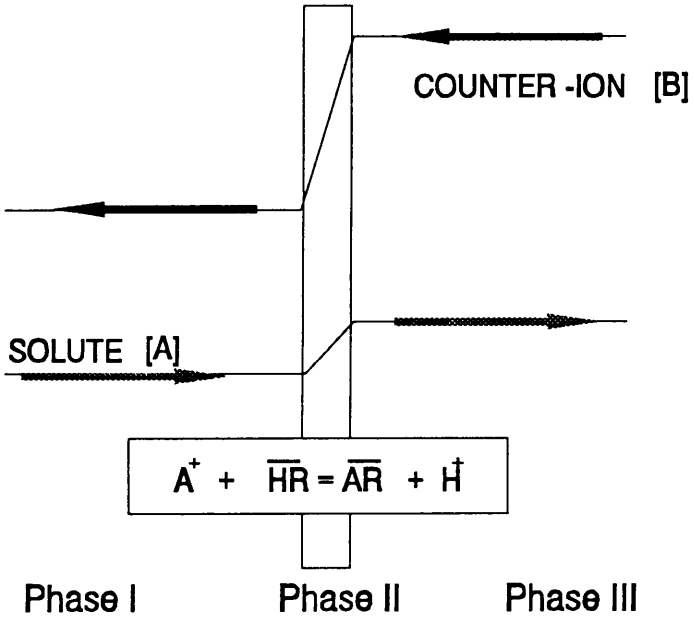
A



B

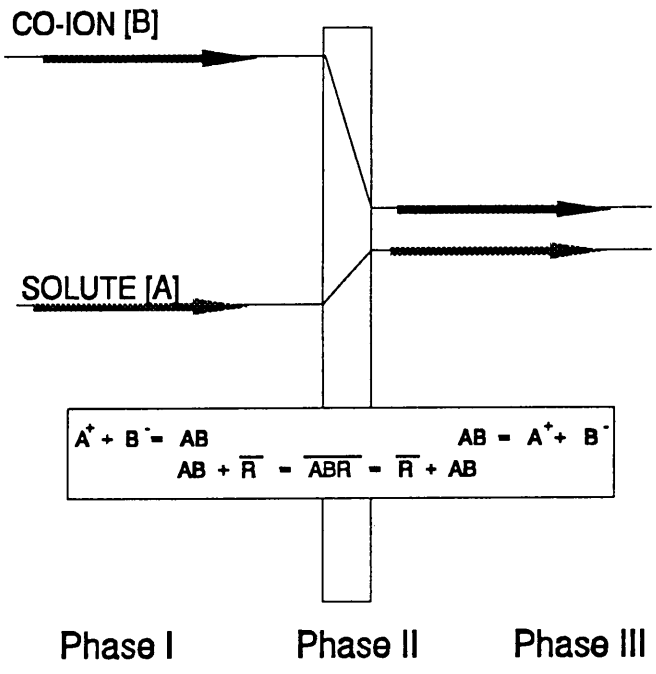


Figure 4.4 : Permeation model for facilitated permeation using extractants: A - counter-transport; B - co-transport.

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species. In fact, if the concentration of one of the species is much higher than the other, the concentration gradient of this species will determine the rate and extent of the extraction. The equation that describes the flux is:

$$J = \frac{D_{AR}}{x}.\Delta B$$

$$[B] \gg [A] \tag{4.4}$$

In the case of the copper permeation through the HDEPA membrane (Section 3.4.1) the co-ion is the proton. Use of the concentration of the hydrogen ion (pH) as the rate-determining species is convenient, as pH buffers of a specific concentration and pH value are easily prepared. In addition, by the very nature of buffers the pH is maintained by secondary complexation of the proton.

In the application of this technique, a concentrated acid is used in phase III to keep the proton concentration at an excess. A buffered solution is used in phase I to keep the concentration of hydrogen in phase I constant. The correct choice of these two solutions ensures a constant gradient of hydrogen ions across the membrane. The solute is then enriched against its concentration gradient.

4.3.7 Facilitated coupled co-transport

In facilitated coupled co-transport, the two species involved are transported in the same direction. *Figure 4.4B* illustrates the mechanism. By way of discussion, the example in

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Section 3.4.2.3, which deals with the extraction of dicyanoaurate(I) with modified primary amines, will be considered. In this example, the extraction potential is again supplied by the concentration of hydrogen ions. This time, however, it is phase I that has the lower pH value. A simplified view of the chemistry of extraction suggests that on the side of phase I, the amine is protonated in Nernst layer 1 according to equation 4.5:

$$\overline{R_3N} + H^+ \rightleftarrows \overline{R_3NH^+} \qquad (4.5)$$

The positively charged amine complexes with the dicyanoaurate(I) in phase I:

$$\overline{R_3NH^+} + Au(CN)_2^- \rightleftarrows \overline{R_3NH^+Au(CN)_2^+} \qquad (4.6)$$

The complex is then extracted into the organic phase, and is transported through the membrane. On the opposite side of the membrane, the complex is rendered unstable by the prevailing high pH value (the extractant is stripped from its proton), and the dicyanoaurate partitions into phase III:

$$\overline{R_3NH^+Au(CN)_2^-} + OH^- \rightleftarrows R_3NH + H_2O + \overline{Au(CN)_2^-} \qquad (4.7)$$

The concentration gradient of the co-ion (the proton) can be selected to be much higher than the solute concentration, in which case equation 4.4 holds. The concentration gradient of the proton is kept constant in phase I by buffering this phase. In phase III its concentration is maintained by choosing the hydroxide concentration to be a comfortable excess. The solute

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will keep on diffusing against its own concentration gradient until the concentration of the protons is equalised.

4.4 MANUFACTURING PROCESSES

Polymeric membranes are most frequently used as the supports for various SLMs. The process whereby porosity is engineered into the polymeric membranes is important because it has a direct impact on the physical characteristics of the final SLM. One of two processes is typically employed for the manufacture of porous polymeric membranes.

4.4.1 Wet processes

In the first process, the initial organic solution is prepared by dissolving the polymer in a suitable hot solvent. The solvent is typically a mixture of two liquids that are immiscible at lower temperatures but miscible at elevated temperatures. On casting, the solution cools and separates into two continuous phases. The pores are formed by the immiscible liquid which is removed from the membrane. Various final effects are obtained in the casting step of the process.

Solvent casting onto a solid. This process entails the casting of the polymer solution onto a suitable solid surface. The solution is gelled by slow exposure it to humid air. The water from the humid atmosphere causes the film composition to change in such a way that a porous membrane results.

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Materials that are cast in this way include cellulose nitrate, cellulose acetate (CA), acrylic copolymers (ACP), polyvinyl chloride (PVC), polyvinylidene fluoride (PVF), polyolefine such as PP or polyethylene (PE), polyamide (PA), and Teflon. An example of this type of membrane is Accurel, a product of the Membrana corporation.

These membranes are usually asymmetrical, with a thin skin on the one side and a high degree of porosity (60%). Although the evaporation can be accurately controlled, this process results in a distribution of pore sizes even in one membrane. The pores are typically between 0,1 and 10 μm and the size is ontrolled by the rate at which the solvent is cooled. The structure of the membranes resembles a sponge, and the interconnecting cells in the membranes form a tortuous route through the membrane.

Casting on liquid. Instead of casting the membrane on a solid surface, the membranes can be cast on a liquid surface. In this way the organic solution is quenched by the non-solvent (usually water) and annealed in water [1]. The resultant membranes are also anisotropic or asymmetrical, with smaller pores on one side of the membrane. These membranes can also be cast as hollow fibres, and are available in a number of polymers such as CA, PC, PVC, PA, PVF, ACP, polysulfone, copolymers of acronitrile and vinylchloride, polyacetal, and crosslinked polyvinyl alcohol.

This process results in extremely thin membranes, and the pores are more evenly sized than those obtained by casting on a solid. The interconnecting cells resembling elongated cells, and the membranes have a lower tortuosity.

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An example of these membranes is the polysulfone hollow fibres used in the Harp cross-flow filters [12]. These hollow fibres are hydrophilic and can effect separations between 10 Å and 200 Å. The Landolt-Blodgett (LB) process is also based on this technique. LB membranes are extremely thin membranes, typically silicone-polycarbonate copolymers or polyphenylene oxide, which are used for their perm-selectivity to oxygen [1].

4.4.2 Dry processes

In the second class, dry processes are employed.

Etching. The process that Nuclepore uses is based on a patent by Price and Walker (in Londsdale [1]), which produces microporous mica by the radiation-track-etch method. The membranes are made by irradiating thin polymeric (PC) films with a field of α-particles, followed by chemical etching to dissolve evenly - shaped circular pores from the bulk.

These membranes are more uniform in thickness and mass, and are 1/10 of the thickness of the equivalent membranes that result from casting the solvent on a solid surface. The resultant pores have a precisely defined pore size that penetrates the membrane in well-defined straight lines, and the tortuosity of the pores is essentially unity. Porosity is, however, much lower than that of membranes manufactured by other techniques. These membranes range in pore sizes from 0,03 to 8 μm. The main uses of these membranes are in aerosol filtration and particle size classification.

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Stretching. Two techniques that use stretching are described.

- Cellgard
- Gore-Tex.

Cellgard is a product from the Celanese Corporation. It is made from PP and is water-repellent. Surface-treated membranes that are water-wettable are also available. These membranes are made by exposing a manufactured polymer film to consecutive steps of cold stretching, hot stretching, and heat setting. This results in a series of permanent 'micro-tears' in the film.

These tears are quite uniform and are present in the layers of the membrane material. The tears do not always coincide from one layer to the next. The tortuosity of these membranes is greater then those of Nuclepore membranes but less than membranes prepared by solvent casting. These membranes are available in 0,02 and 0,04 μm rated pore sizes (MWC0 of about 100 000) in the form of 1 mm thick films or 100 to 400 μm ID hollow fibres.

Gore-Tex is a class of membranes that is made by the controlled cold stretching of Teflon, both uniaxially and biaxially. The resultant membranes are similar to those of Cellgard, and are available with pore sizes in the range 0,02 to 10 μm.

Factors such as the thickness of the membrane (δ), the percentage porosity of the membrane (ε), and the tortuosity of the membrane (ξ), is important for the selection of a support membrane [4, 5, 13]. An ideal membrane should be quite porous, have a low tortuosity factor, and should be as thin as possible.

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4.5 APPLICATIONS

The rate of permeation of a solute through the SLM, the selectivity of the SLM towards the solute, and the stability of the SLM are important factors to consider when selecting an SLM. The selectivity is mainly determined by the extractant (Chapter 3). In this chapter, the effect of the composition of the membrane on the permeation rate and stability of the SLM will be evaluated by considering several applications. The SLM systems discussed in Chapter 3 (*i.e.* extraction of copper and dicyanoaurate(I)) are used as case studies. An SLM comprises a solid support and the liquid membrane. First the support was considered and then the liquid membrane.

4.5.1 Support material

Audunsson [5] tested a wide range of Millipore filters which were prepared by the wet preparation technique where the membranes are cast on a solid. The resulting membranes are highly porous (between 60% and 85%). Audunson found that the SLMs behaved essentially like a single thin film of liquid. This he ascribed to the fact that the various membranes all showed similar tortuosity (the solute permeated via the shortest routes through the membrane). He also found that membranes with pores of > 3,0 μm leaked aqueous phase, and are unsuited as supports for SLMs. The importance of selecting a rigid membrane that does not deform into the flow channels was also stressed.

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Danesi and Rickert evaluated SLMs on different Accurel polypropylene hollow fibres [14]. They were interested in the influence of the pore size and wall thickness on the permeation rates and the lifetimes of the membranes. They found very little difference in the six membranes tested. They attributed this to the fact that all the membranes had a porosity of about 75%.

From the literature, it seems that the supports that perform best have a porosity of 70% or more, and are hydrophobic. For our purposes, we decided to use a membrane from Millipore (GVHP 090 50). This particular membrane was made from PVDC, which was chemically and physically inert to the conditions used in the test unit. It has a thickness of 125 μm, and is rigid enough not to deform into the flow channels. It had an average pore size of 0,22 μm which is sufficiently small to prevent physical leakage of the aqueous phases. The porosity of 75% ensured a large surface area for the SLM.

Table 4.1 provides a list of membranes evaluated by other investigators.

4.5.2 The extractant

Two factors were considered when evaluating the extractant:

- the selected extractant
- the concentration of the extractant.

The selection of a particular extractant is covered in detail in Chapter 3. This section focuses on the amount of extractant in the organic phase.

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Table 4.1
Various membranes used as supports for SLMs

Membrane	Membrane thickness (μm)	Percentage porosity	Pore size (μm)	Material	Geometry	Manufacture	Ref.
Acurrel BS7C	48	50		PP	Sheet	Armak. Co.	15, 16
Acurrel 4	160	75	0,2	PP	Sheet	Am. Enka Comp.	17
Celgard 2400	25	45	0,05	PP	Sheet	Celanese Plastic Co	18-26
Celgard 2500	25	38	0,075	PP	Sheet	Celanese Plastic Co	17, 18, 27-29
Celgard 2402	50	45	0,02	PP	Sheet	Celanese Plastic Co	30
Celgard 2502	50	38	0,04	PP	Sheet	Celanese Plastic Co	30, 31
Celgard K801	50	65	0,500	PE	Sheet	Celanese Plastic Co	18, 24, 32-39
Celgard 4410	175	45	0,05	PP	Sheet	Celanese Plastic Co	24
Celgard 4510	175	38	0,075	PP	Sheet	Celanese Plastic Co	24
Cell Pore NWO1	150	70	1,0	PO	Sheet	Sekisui	19, 39, 40
Durapore GVHP	125	75	0,220	PVDC	Sheet	Millipore Inc.	5, 41-45
Fluore Millipore	50	75	0,650	PTFE	Sheet	Millipore Inc	18
Fluoropore FP-005	45	45	0,050	PTFE	Sheet	Millipore Inc.	5
Fluoropore FP-010	60	57	0,100	PTFE	Sheet	Millipore Inc.	5, 46-48
Fluoropore FP-022	60	65	0,220	PTFE	Sheet	Millipore Inc.	5
Fluoropore FP-045	80	75	0,450	PTFE	Sheet	Millipore Inc.	5, 49-52
Fluoropore FP-100	100	80	1,00	PTFE	Sheet	Millipore Inc.	4
Fluoropore FP-150	100	80	1,50	PTFE	Sheet	Millipore Inc.	53
Fluoropore FS	125	85	3,000	PTFE	Sheet	Millipore Inc.	5
Fluoropore FH	145	85	0,500	PTFE	Sheet	Millipore Inc.	5
Fluoropore FG	175	70	0,200	PTFE	Sheet	Millipore Inc.	4, 54
Fluoropore FG	175	85	0,200	PTFE	Sheet	Millipore Inc.	5
Fluoropore FA	200	85	1,000	PTFE	Sheet	Millipore Inc.	5
Gore-Tex	13	98	10,00	PTFE	Sheet	W.L Gore and Assc.	45
Gore-Tex S10485	20	67	0,400	PTFE	Sheet	W.L Gore and Assc.	18
Gore-Tex	25	95	3,0	PTFE	Sheet	W.L Gore and Assc.	45
Gore-Tex 4C5	57	76	0,530	PTFE	Sheet	W.L Gore and Assc.	18
Gore-Tex	60	78	0,2	PTFE	Sheet	W.L Gore and Assc.	45
Gore-Tex	75	85	0,500	PTFE	Sheet	W.L Gore and Assc.	18, 32, 55
Millipore RATF	145	82	1,200	MCE	Sheet	Millipore Inc.	5

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Table 4.1(2)

Membrane	Membrane thickness (μm)	Percentage porosity	Pore size (μm)	Material	Geometry	Manufacturer	Ref.
Mitex LS	125	60	5,000	PTFE	Sheet	Millipore Inc	5, 18, 56-58
Mitex LC	125	68	10,000	PTFE	Sheet	Millipore Inc.	5, 59
Nucleopore	10	13	0,4	PC	Sheet	Nuclepore	55
Questar	50	45	0,04	PP	Sheet	Questar	58
Ultipore N-66	100	80	2,0	PP	Sheet	Pall Trinity Micro Corp	60
A1	3	70		PP	Tube	Asahi Kasei	61
A2	3	81		PA	Tube	Asahi Kasei	61
Acurrel 4	150	75	0,2	PP	Tube	Am. Enka Comp.	19, 39, 62-65
Acurrel 3	200	75	0,2	PP	Tube	Am. Enka Comp.	19, 39
Acurrel 2	300	75	0,2	PP	Tube	Am. Enka Comp.	19, 39
Acurrel 1A	400	75	0,1	PP	Tube	Am. Enka Comp.	19, 39
Acurrel 1B	400	75	0,2	PP	Tube	Am. Enka Comp.	19, 39
Acurrel 1C	400	75	0,4	PP	Tube	Am. Enka Comp.	19, 39, 66, 67
Gore-Tex TA-001	40	50	2	PTFE	Tube	W.L Gore and Assc.	61
KPF-400	3	45	0,135	PP	Tube	Mitsubishi	61

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The SLM-FIA system described in Section 2.4.3 was used to evaluate the performance of different SLMs. SLMs were evaluated by comparing:

- the maximum permeation rate, H_m, which is an indication of the flux achieved at dynamic equilibrium,
- the stability of the membrane as determined by time, t_s, that this permeation could be maintained in a specific environment, and
- the time that the system takes to reach equilibrium, t_c, which reflects on the resistance of the membrane to mass transfer.

(See *Figure 2.4* for details on the determination of these parameters).

4.5.2.1 Extraction of cations

Intuitively, one would expect that the higher the concentration of the extractant in the organic phase, the greater the facilitated transport rate. This was found to be true, although the effect of concentration was less than may be expected. As a rule of thumb, the optimum extraction of cations is achieved if the extractant comprise approximately 30-60% (v/v) of the total volume of the organic phase [61, 68-69].

The effect of the concentration of di-(2-ethylhexyl)-phosphoric acid (DEHPA) on the permeation of copper through the SLM was tested as an example of the extraction of cations. The optimum concentration was indeed found to be between 30 and 60% (*Figure 4.5*).

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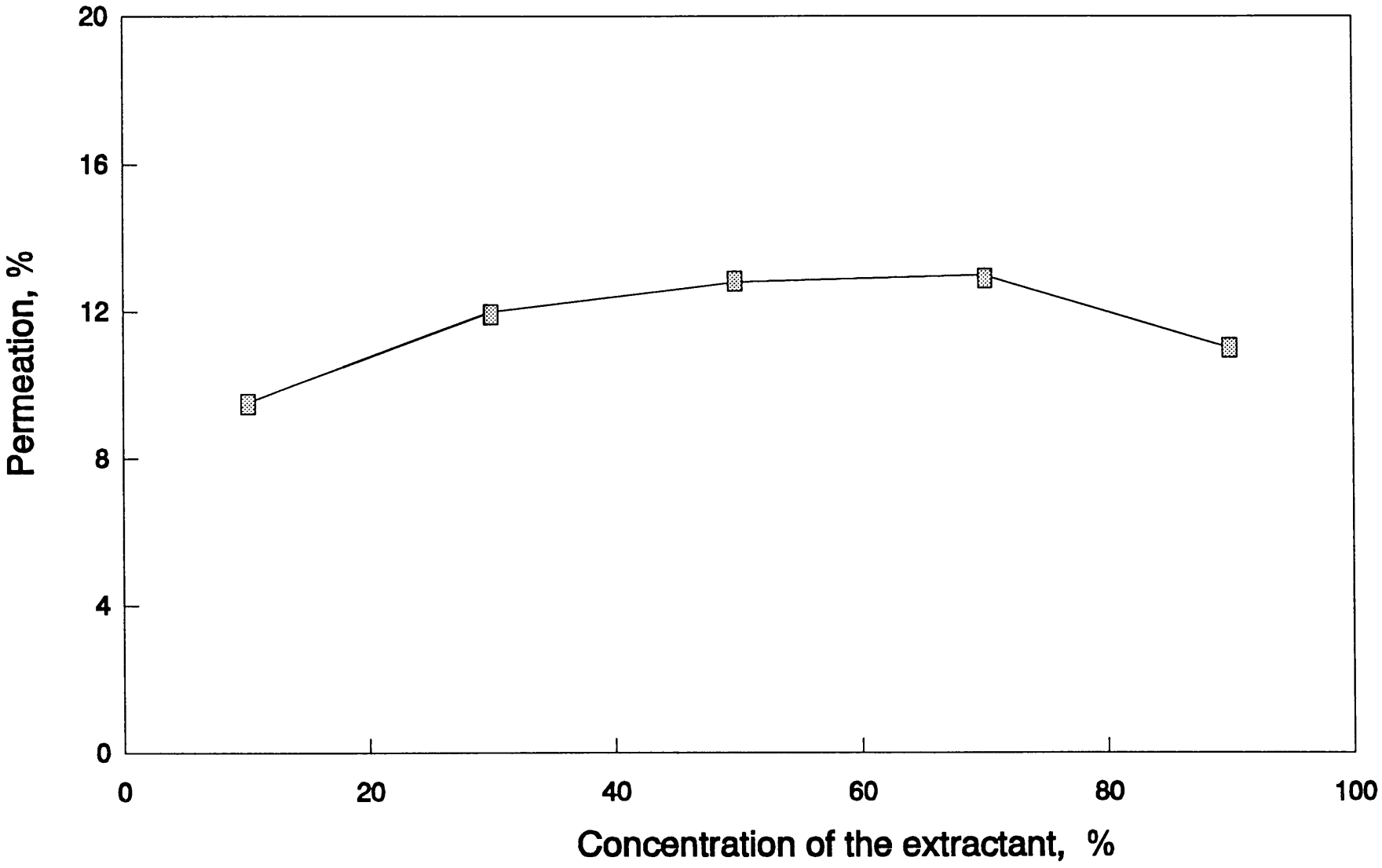

Figure 4.5 : Effect of the concentration of HDEHPA on the permeation rate of copper through a SLM.

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The observed curve is the result of the two competing phenomena. The first phenomenon is the complexation of the reagent with the solute. The higher the concentration of the extractant present in the organic phase, the faster the mass transport of the copper into the membrane. At the plateau, the extractant makes up a considerable fraction of the organic phase, and at higher levels starts to impact on the viscosity of the liquid membrane. When the viscosity of the solution increases the diffusion decreases, and the overall permeation rate drops.

4.5.2.2 Extraction of anions

An assessment of the literature on the use of SLMs for the extraction of anions, reveals that the optimum concentration of the extractant depends more on the underlying mechanism of transport than in the case of cation extraction.

The concentration of the extractant varies considerably from system to system and must be optimised for each individual system. The reported optimum concentration of the extractant was found to vary between 0,07 and 60% (m/v) [4, 70, 71] for different systems.

To study the effect of the concentration of the amine extractant, different concentrations of LA-2 were prepared in 50 % (v/v) TBP/ heptane. These organic solutions were used to make SLMs. The SLMs were tested in the FIA-SLM unit. The results are shown in *Figure 4.6*. The permeation rate increased with increasing amounts of LA-2, up to a maximum (H_m = 14,8%) at a concentration of 17,5 % (v/v) LA-2, and then decreased for higher concentrations of LA-2.

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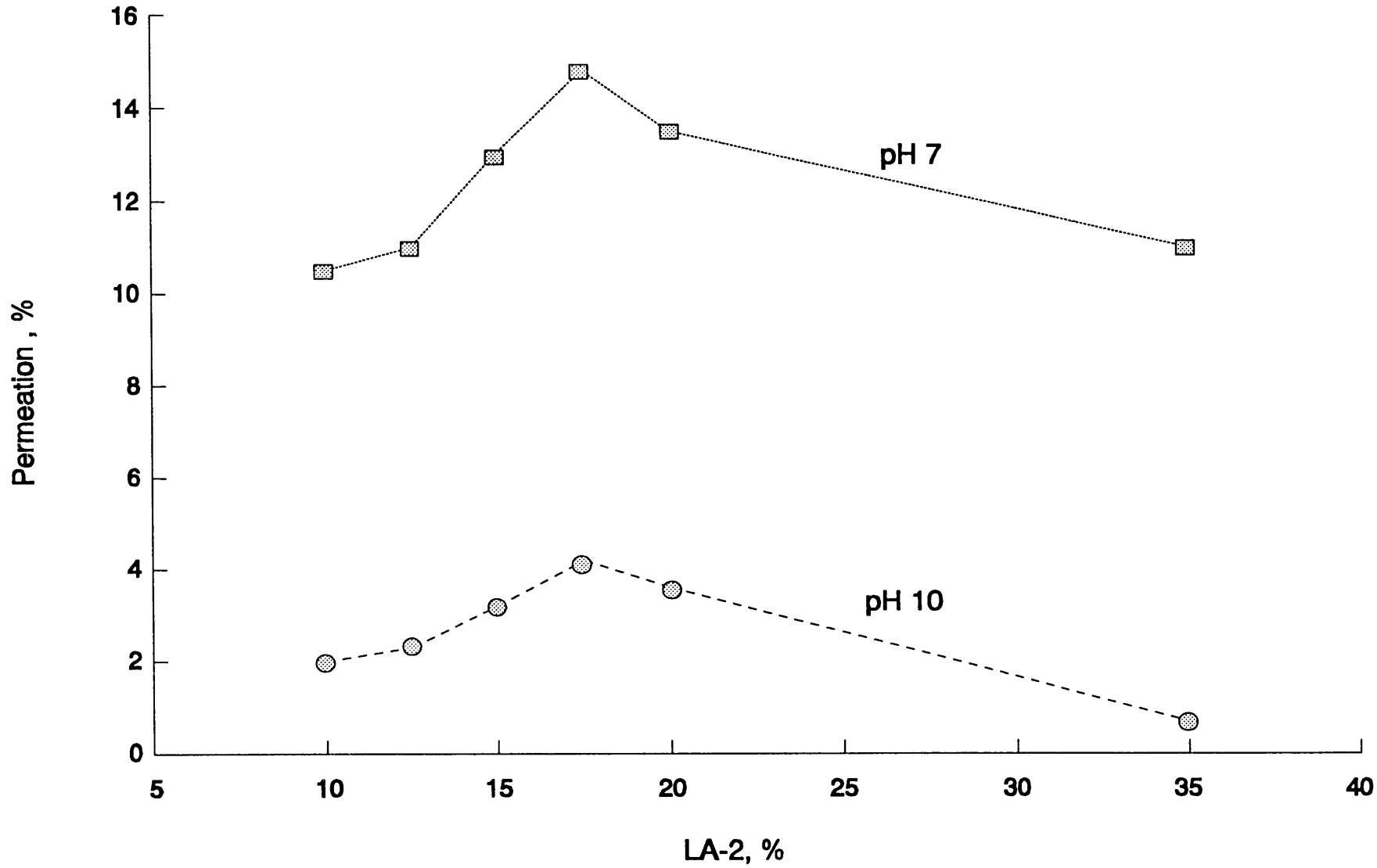

Figure 4.6 : The effect of the concentration of LA-2 in the organic phase on the permeation rate of dicyanoaurate through the SLM.

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Investigations also showed that the optimum concentration of a few other amines differed dramatically. It was found that the concentration of Aliquat 336 between 1% and 20% (v/v) did not affect the permeation of the gold through the SLM. Also, a concentration of 1% TDA was found to be optimum due to the solubility of TDA in the organic solution [72, 73].

The optimum concentration of the extractant also depends on the particular diluent employed, as described by Drioli *et al* [62, 65]. They found that, with the extraction of cadmium with tri-octyl amine, the optimum flux was achieved at a value of 60% and 30% respectively when xylene and o-xylene were used as diluents.

Another factor to consider is the mobility of the extractant in the organic phase. From our investigations it appears that the mono-substituted amines SLMs resulted in higher permeation rates than their higher substituted secondary and tertiary equivalents *(Figure 4.7)*.

4.5.3 The effect of the diluent

Various organic solvents are used as diluents in solvent extraction processes. In industry and also often for analytical purposes, the choice of organic solvent is usually based on economic considerations, availability, and more recently, environmental impact. In certain cases, minimum requirements based on factors such as low dielectric constant [74], hydrophobicity, and a low viscosity [75] are also considered. The choice of the organic solvent for an extraction process can be a vital parameter affecting efficient extraction. This is also true for SLM systems.

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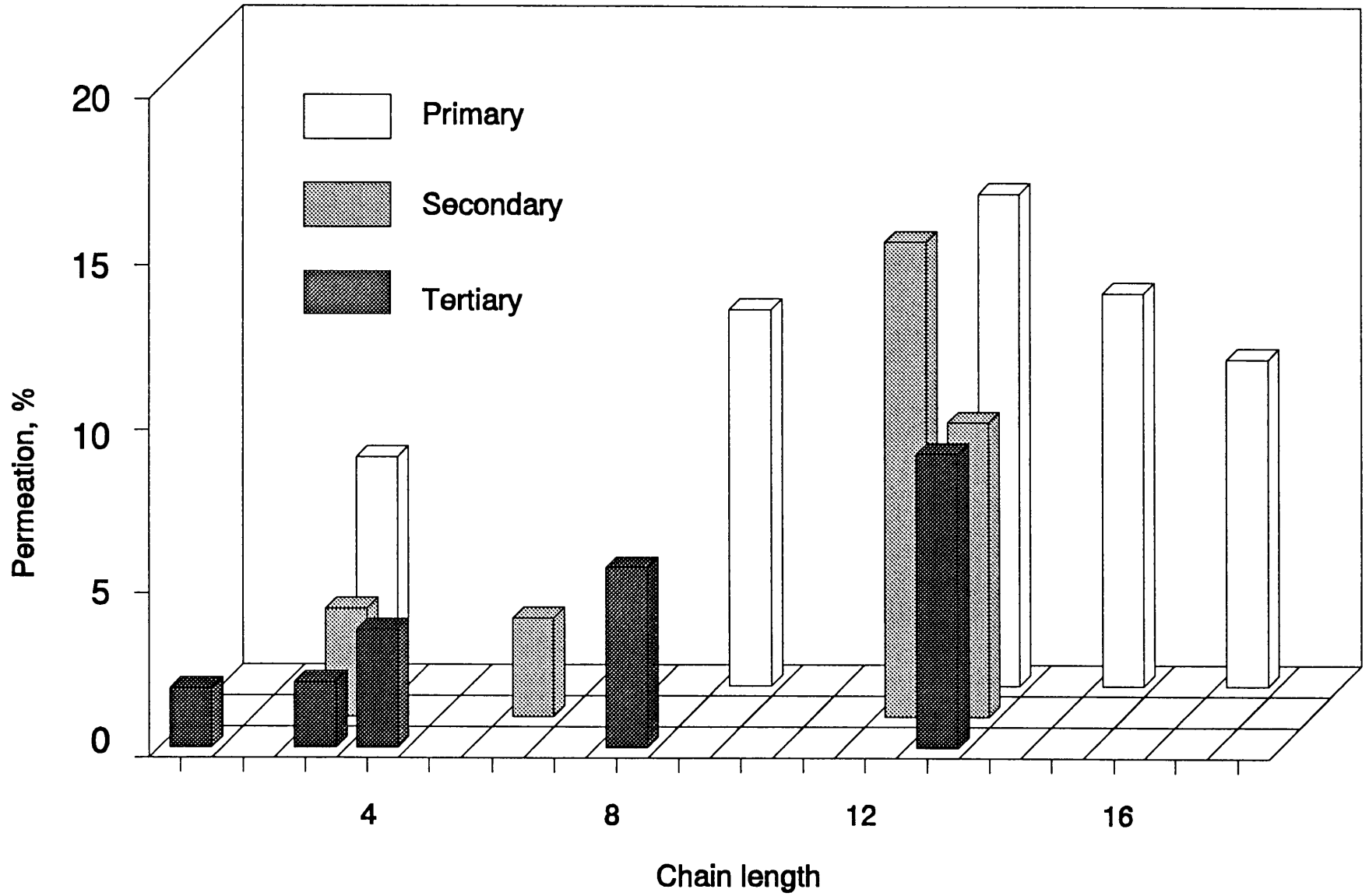

Figure 4.7 : Comparison of the respective permeation of various weak-base amine SLMs.

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The transport of a solute through the SLM relies heavily on the diffusion of both the extractant (back to the feed side) and the solute-extractant complex (to the stripping side). Therefore the viscosity would seem to be an important factor when choosing a diluent for an SLM system. A theoretical development for binary diffusion coefficients is based on a modification of the Stokes-Einstein equation [13, 25]. The modification relates the Stokes-Einstein equation and Ficks law. The flux through the membrane is also a function of the diffusion coefficient (D) [13]:

$$D = kT/6\pi r\tau \tag{4.8}$$

D is inversely proportional to the viscosity (τ) and the molecular radius of the extractant (r). The Boltzmann constant is given by (k), and (T) is the absolute temperature. The viscosity can be calculated as a composite of the membrane components [13]. The diluent comprises a large fraction of the organic phase in most SLM systems.

Other investigators [63] have shown that, except for factors such as the viscosity and the density of the organic phase, the porosity (ε) and tortuosity (Γ) also play a role in the effective diffusion coefficient (D_e) through SLM systems:

$$D_e = \varepsilon D/\Gamma \tag{4.9}$$

Although equations 4.8 and 4.9 give a general indication of the permeation, they do not explain the large differences in the behaviour of various similar SLM systems (see *Table 4.2*).

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Elhassi and co-workers mentioned that the function of the diluent is to increase the ability of the extractant to exist in monomeric, dimeric and trimeric forms in equilibrium with each other, and also to increase the extractant's ability to solvate polar molecules [13]. They concluded that viscosity effects are much more important in the small pores of an SLM support than in conventional solvent extraction. Danesi also pointed out that the stoichiometric coefficient for cobalt through a phosphoric-based SLM drops from 2 to 1,4 when the diluent is changed from aromatic to aliphatic diluents. He reasons that this is due to the non-ideal behaviour of the phosphoric acid dimers in alkanes in that they form aggregates [19, 39].

It soon became clear that the best organic solvent for a particular SLM cannot be easily predicted *a priori*. To add to the dilemma of choosing an appropriate diluent, the permeation rate of a single species is not the only determining factor for SLM extractions. The selectivity, or the difference in permeation of other co-extracting species, is also of the utmost importance. Furthermore, most organic solvents produced on a industrial scale vary in their composition [76]. At present, in solvent extraction, the choice of an organic solvent is usually made by trial and error or based on previous experience. Cussler states that the chief requirement for choosing an SLM diluent is a combination of intuition and good luck [77].

The proposed FIA-based SLM evaluation scheme described in Chapter 2, provides a simple and rapid method to evaluate various organic solvents. It was found that the tedious trial-and-error searches are made considerably easier with this FIA test module.

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4.5.4 Diluents used in cation extraction

Various organic solvents commonly used as diluents in solvent extraction were used to prepare the organic phase for SLMs described in Section 2.4.3. The feed solution was 1,57 x 10^{3} mol.dm^{-3} copper in an acetate buffer of 0,25 mol.dm^{-3} strength. The stripping solution was a 1,2 mol.dm^{-3} nitric acid solution. This stripping solution augmented the harshness of the conditions surrounding the SLM, thereby purposely accelerating the SLM degradation and allowing a greater number of stability tests to be carried out in a given time.

The permeation profiles of the various SLMs are displayed in *Figure 4.8 - 4.11*. The profiles are divided into the following four classes:

- ethers and ketones
- alkanes, alcohols, and fatty acids
- aromatics
- halo-alkanes.

The maximum permeation rate H_m can be used to judge the rate of loading and stripping of a particular SLM. It should be noted that the effective concentration of the analyte in the feed stayed the same during the entire experiment. The time required to reach H_m is indicated by t_c. This is an indication of the time taken for the specific system to reach equilibrium. The stability of a particular SLM is given by the time, t_s, for which the maximum plateau was maintained.

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4.5.4.1 Ethers and ketones

Ethers and ketones are commonly employed as extractants as well as diluents in analytical methods involving the separation of metal ions [78-80]. The permeability of SLMs, prepared with various common ethers and ketones and a constant amount of DEHPA, was evaluated. *Figure 4.8* depicts the permeation profiles for copper.

With the exception of di-*iso*-butyl ketone (DIBK), the permeation rate of the solute (copper) through the SLMs was very low, as indicated by the small H_m values. This can be ascribed to the fact that the oxygen-containing organic solvents are relatively more soluble in water than in most other organic solvents *(Table 4.2),* and they may have inhibited the successful formation of an SLM. This can be seen from the increasing permeation rate observed for the SLM containing DIBK compared with acetone and methyl-iso-butyl ketone (MIBK). This phenomenon is attributed to either the viscosity or to the lack of hydrophobicity. The time (t_c) needed to establish the maximum permeation rate of the SLM containing DIBK appears to be excessively long, and the maximum permeation rate was not maintained. Acetone, which is soluble in water, was used to displace all the other SLMs, and its profile is also included in *Figure 4.8.*

4.5.4.2 Alkanes, alkenes, and alcohols

In the hydrometallurgical field, alkanes, alkenes, and alcohols are often used for SLMs [29, 58, 61, 74, 81-83]. O'Hara found that an SLM containing kerosene was stable for as long as 14 days with continuous use [58].

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Table 4.2
Physical properties of selected diluents used in the organic phase of SLMs

Diluent	Viscosity (cP)	Solubility in water ($g.100cm^{-3}$)	Dielectric constant	Density ($g.cm^{-3}$)	t_c	t_s	H_m
Acetone	0,32	Miscible	21,4	0,79	3	0	2
Benzene	0,65	0,18	2,3	0,88	5	5	8
Carbon tetrachloride	0,97	0,008	2,2	1,80	10	∞	18
Chloroform	0,57	1,000	5,0	1,48	4	10	8
Di-*iso*-butyl ketone	-	5,000	18,3	0,93	28	15	15
Dichloroethane	0,79	0,900	10,6	1,25	5	10	5
Dichloromethane	0,43	2,00	9,1	1,32	15	10	4
Diethyl benzene	-	Immiscible	2,5	0,88	12	∞	23
Diethyl ether	0,32 (0,24)	6,040	4,3	0,74	11	15	4
Fatty acid mixture	-	Immiscible	2,7	0,90	30	15	32
Methyl-*iso*-butyl ketone	-	1,700	13,1	0,80	5	10	3
Pentane	0,23	0,010	1,84	0,61	3	40	37
Pentanol	3,5	2,200	14,7	0,81	10	10	4
Petroleum ether$_{(40° - 60°)}$	0,30	Immiscible	-	0,67	4	40	28
Pyridine	0,94	Miscible	12,4	0,98	2	3	3
Toluene	0,59	0,080	4,8	0,87	3	5	13
Triethylbenzene	-	Immiscible	-	-	9	∞	18

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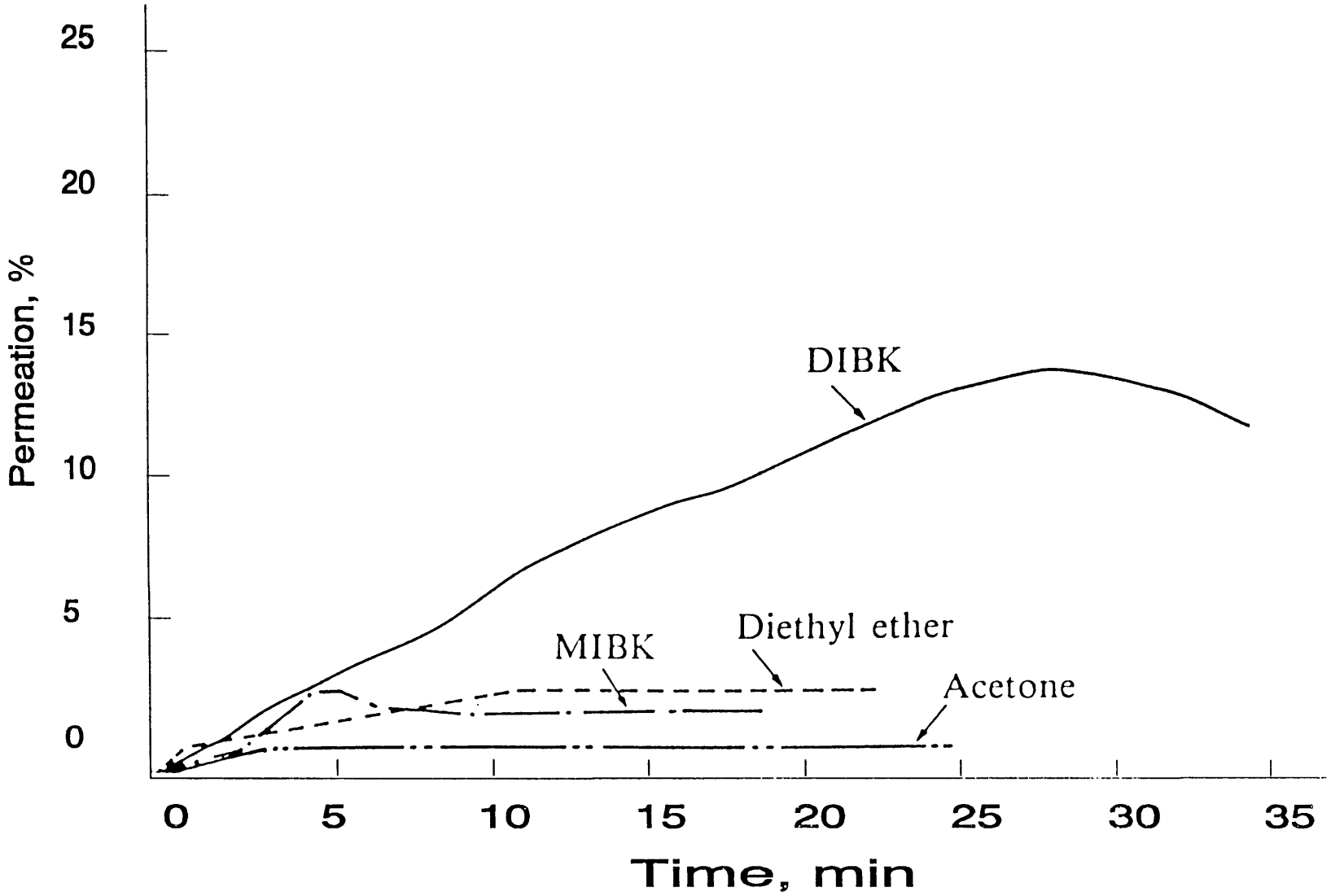

Figure 4.8 : Formation profiles of ethers and ketones.

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The analytical application of these solvents includes petroleum ether, *n*-hexanol, cyclohexane, and hexane for the extraction of metal complexes [78-80].

In *Figure 4.9* the performance profiles for pentane, petroleum ether, a fatty-acid mixture, and pentanol are shown. SLMs with pentane and petroleum ether rapidly reached their H_m values. Comparison of the t_c values of these two SLMs with the other diluents used indicated that the diffusion of the copper through SLMs containing paraffins, reach maximum permeation much faster than with SLMs containing other solvents. The maximum permeation, H_m, is also much higher in these membranes, indicating a faster transport through the membrane. This confirms the earlier statement that the unbranched molecules show faster diffusion.

A disadvantage of these SLMs is that they become washed out, as indicated by the short period t_s. This may be due to physical loss of the organic phase. Pentane has the additional disadvantage of a high volatility and a low boiling point (36°C), resulting in spurious bubbles in the system. In a plant environment, an SLM containing this diluent would need to be reconditioned often. As expected, pentanol did not form a satisfactory SLM due to its greater solubility in the aqueous solution. The fatty-acid mixture (long-chain unsaturated carboxylic acids) resulted an highly viscous organic phase. This SLM took a long time to reach its H_m value. The slower diffusion rate of copper through this viscous organic solution probably inhibited the initial mobility of the copper across the SLM.

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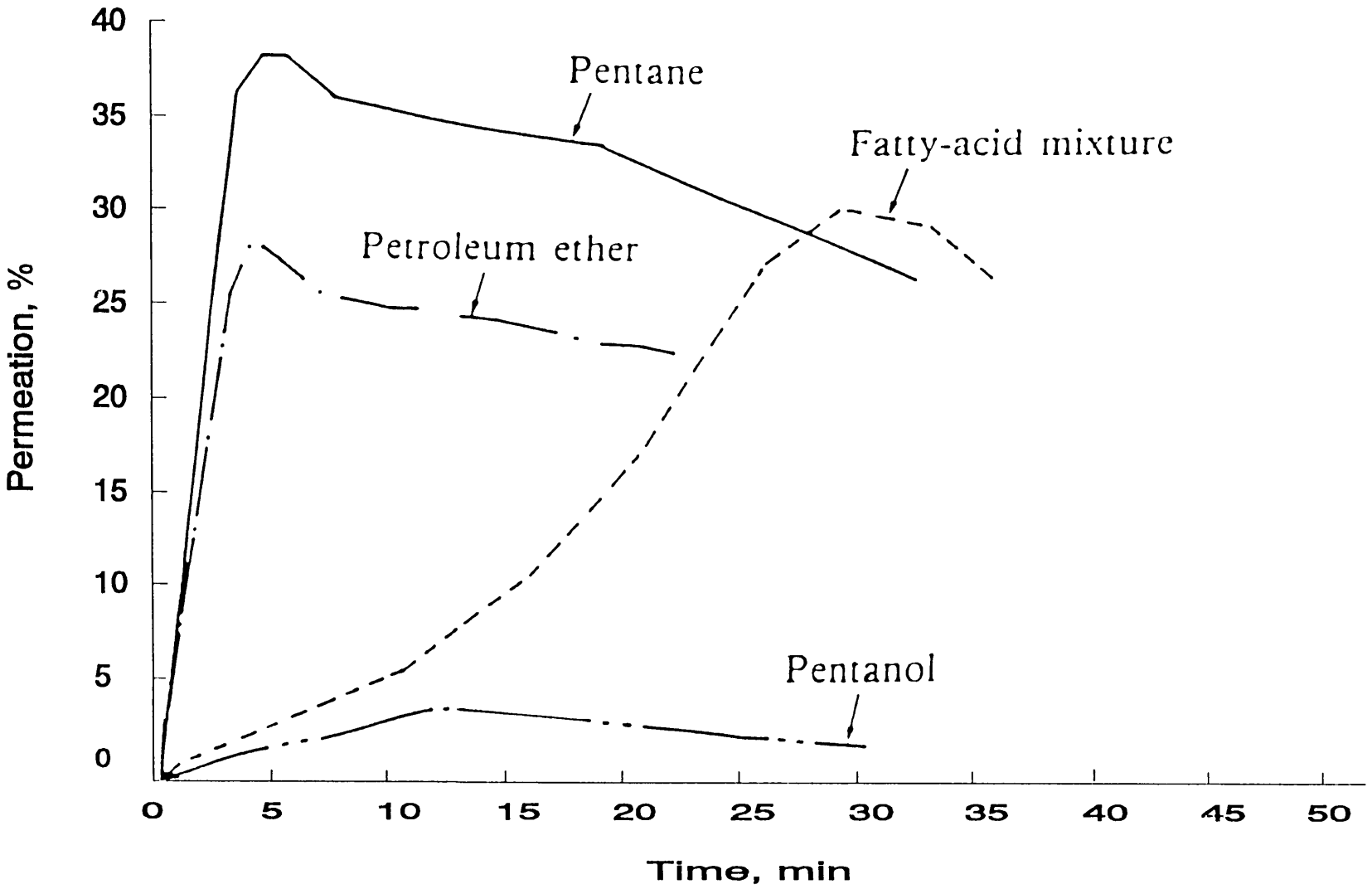

Figure 4.9 : Formation profiles of alkanes.

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4.5.4.3 Halo-alkanes

Halo-alkanes are often used in analytical chemistry for solvent extraction. In this class, Chloroform and carbon tetrachloride are the most commonly used substances in this class [78-80, 84]. However, the halo-alkanes have lost favour in recent years because of their carcinogenic properties.

The behaviour of SLMs containing the halo-organic solvents is depicted in *Figure 4.10*. Carbon tetrachloride forms a very stable SLM with a high permeation rate. SLMs containing the other halo-organic solvents degrade rapidly under the conditions used, and seem less suitable as diluents for SLMs. This may be due to their higher polarity, which makes them slightly soluble in water, thus affecting both the performance of the SLM and its stability.

4.5.4.4 Aromatics

Substituted-benzene organic solvents are frequently used in the metallurgical industry. Shellsol T, benzene, toluene, tri-ethyl benzene (TEB), di-*iso*-propyl benzene, decalin, phenylhexane, xylene, and di-ethyl benzene (DEB) have been used for the extraction of a variety of compounds from process solutions [18, 37, 75, 85, 86]. Aromatic solvents used for analytical applications include benzene and toluene for the extraction of metal complexes [78-80].

Figure 4.11 summarises the results obtained for SLMs prepared from a few organic solvents in this class.

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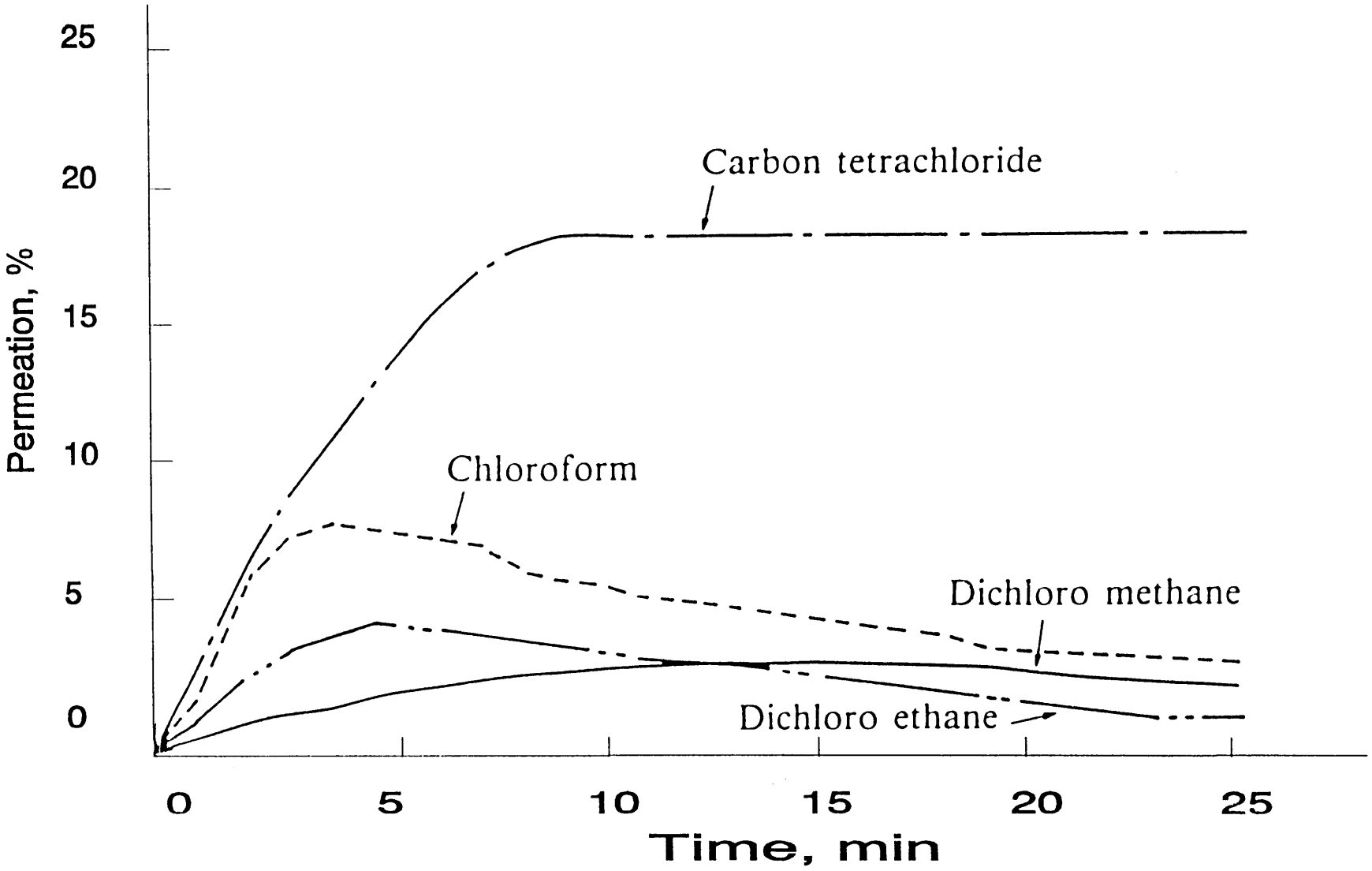

Figure 4.10 : Formation profiles of halo-alkanes.

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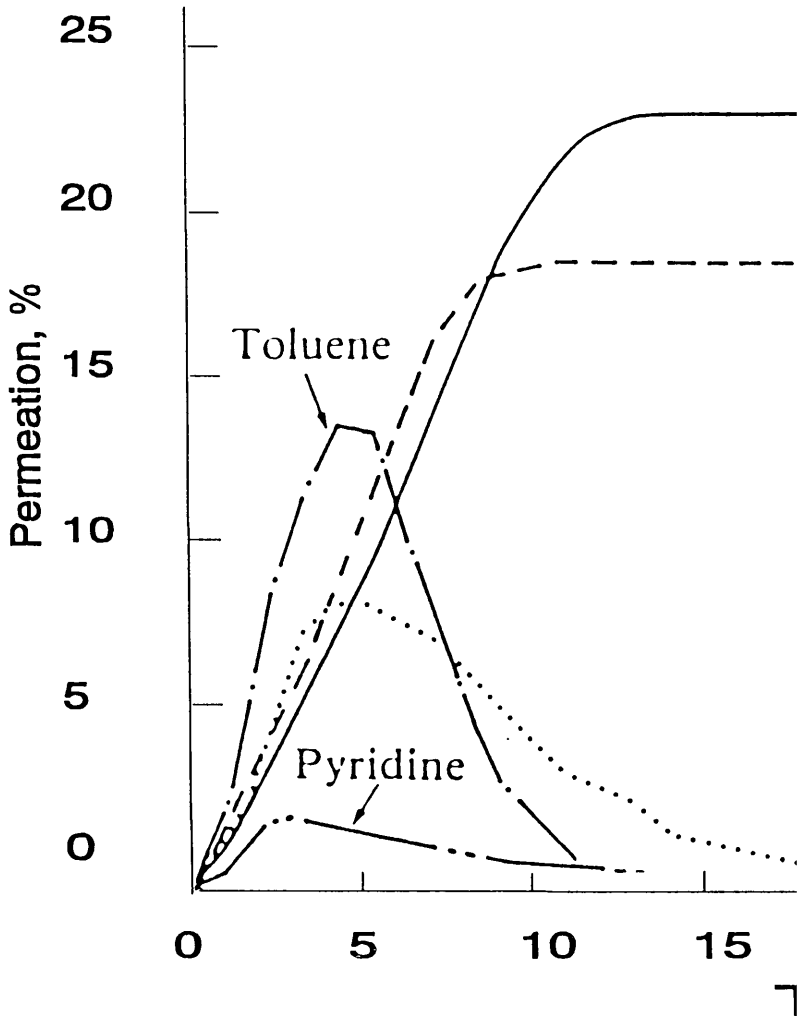

Figure 4.11 : Formation profiles of aromatics.

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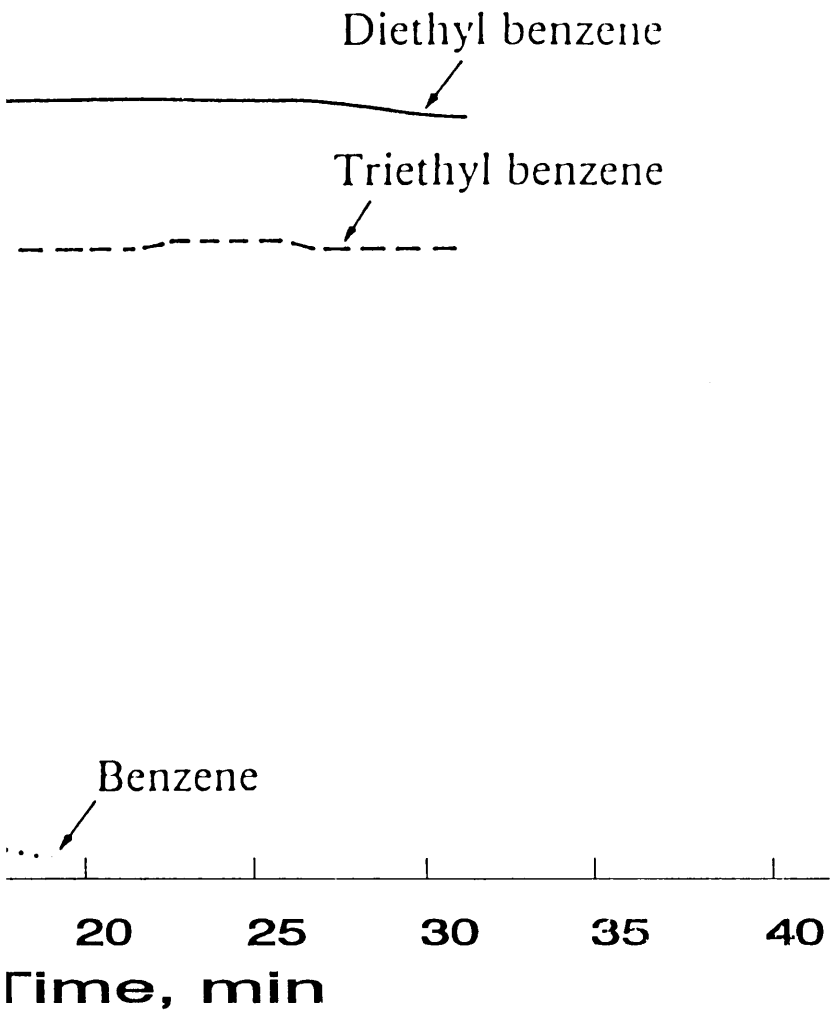

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DEB and TEB both yielded SLMs that reached high H_m values in a relatively short time. They were also stable for extended periods t_s values of more than half an hour under the severe conditions used. This is not surprising, given their poor solubility in water. SLMs with toluene and benzene as solvents reached their H_m values rapidly. However, there was a swift decline in their permeability under the conditions used. Toluene is less soluble in water than benzene. However, an SLM containing toluene degraded faster than one containing benzene when 1,2 mol.dm^{-3} nitric acid was used as the stripping solution. At a lower concentration of nitric acid (0,25 mol.dm^{-3}), the SLM containing toluene was marginally more stable. This indicates a secondary reaction of the nitric acid on the conjugated aromatics. Pyridine, as expected, resulted in a poor SLM. The relatively high solubility of pyridine (*Table 4.2*) explains the incomplete formation of an SLM.

The commercial availability, purity, and low cost of DEB make it an obvious choice for many SLMs in industry [87]. In addition to these properties, the experiments conducted have shown that an SLM containing DEB results in a stable SLM with a reasonably high permeation rate. In the light of these results, DEB is recommended as the prefered solvent for the extraction of copper with DEHPA.

4.5.5 Diluents for anion extraction

The diluent had a less marked effect on extractions using SLMs containing amines. Mooiman *et al* commented on the effect of diluents on the extraction of metal cyanide complexes in solvent extraction by amine extractants [88]. They found that the diluent had an insignificant

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effect on the extraction of gold when primary amines were used. However, the choice of diluent did have an effect on the extraction of gold when secondary, and tertiary amines were used. They also found that organic solutions containing hexane can extract gold from solutions with higher pH values than those containing xylene. This effect was observed only for the extraction of gold, and not for the extraction of the other base-metal cyanide complexes [89, 90].

The effect of the diluent on the permeation of an SLM containing LA-2 as extractant was tested. Four different organic solutions were prepared containing 15 % (v/v) LA-2, 50 % (v/v) TBP, and 40 % (v/v) diluent (DEB), heptane, chloroform, or TBP). SLMs prepared from these solutions were then evaluated, and the results are summarised in *Table 4.3.*

Table 4.3

The effect of different solvents on permeation

Solvent	H_m (%)	
	pH 7	pH 10
Chloroform	14,4	2
Diethyl benzene (DEB)	14,5	7
Heptane	14,4	2
Tributyl phosphate (TBP)	16	9

The effect of the different solvents at pH 10 was more pronounced than at pH 7. Nevertheless, the diluent did have a smaller effect on the performance of SLMs than it had in conventional solvent extraction systems. An SLM that contained the amine dissolved only in TBP gave slightly better extraction kinetics, particularly at pH 10. This can be ascribed to the synergistic effect of TBP and LA-2 described in Section 3.4.2.3.

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The effect of different diluents on the extraction of gold using SLMs containing Aliquat 336 was also tested. Both heptane and DEB were tested, and performed similarly (*Figure 4.13*).

4.5.6 Solubility and stability

Investigators have found that SLMs can be stable for extended periods. Some report stabilities of weeks, and even months [14, 64, 65]. Investigators also remark that the flux of certain SLMs increase as the SLM ages [58]. This is of course dependant on the volume of the organic solution that is immobilised on the support, and also on the solubility of the organic phase, in the respective aqueous phases. A correlation between the solubility and the stability constant (t_s) of the respective SLM is evident from the data in *Table 4.2*. In our SLM test-unit, the volume of organic phase used is extremely small in the order 50 mm^3. Despite this fact, most of the SLMs were stable for a period of hours.

An SLM that contains 40% DEHPA in DEB was found to be stable for a duration of 72 hours at a flowrate of 2 $cm^{-3}.min^{-1}$. At high flowrates (higher than 6 $cm^{-3}.min^{-1}$ the organic phase was physically pushed from the pores of the support over a period of 4 hours. The depletion of the membrane was indicated by a sudden drop (over 2 to 3 minutes) in the permeation rate of the analyte. The performance profiles of the SLMs containing amines is illustrated in *Figure 4.12*. (Only the parts after the initial period (t_s) when H_m has been reached, are shown to simplify comparison of the stabilities).

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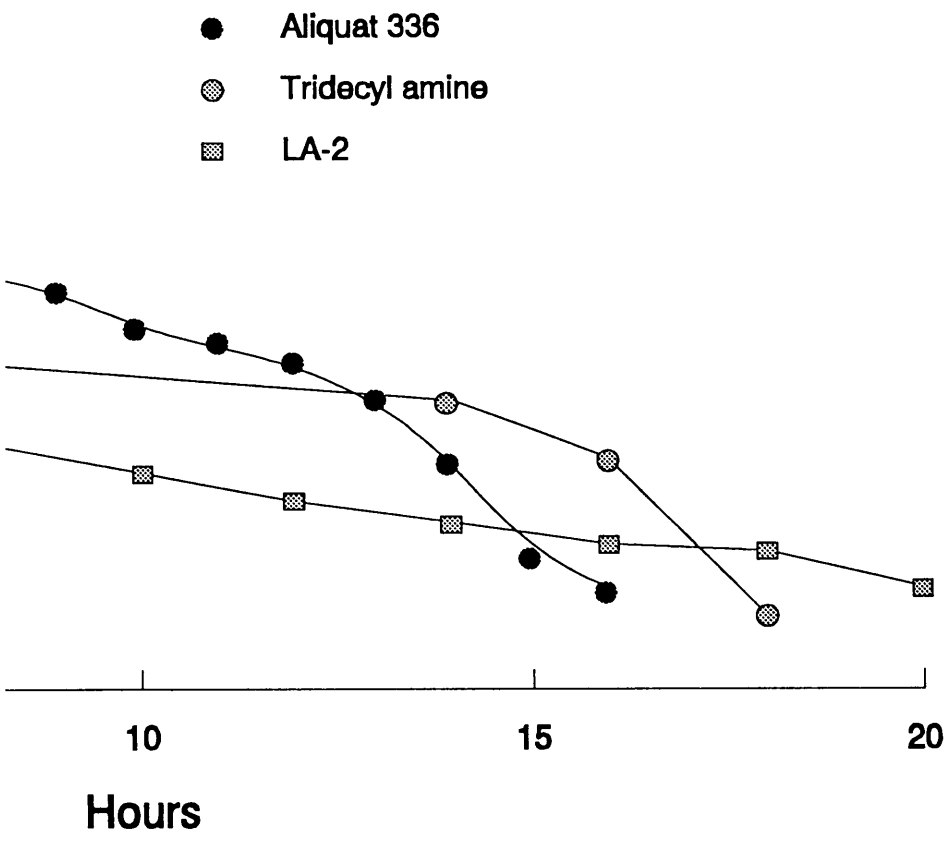

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The permeation of the SLM containing Aliquat 336 remains stable for approximately 4 hours. This is considerably better than the stability of the other two SLMs.

The rapid degradation of the weak-base amines can be attributed to the solubility of TBP, which is used as modifier. A 50 mm^3 aliquot of an organic solution that contains 50% TBP (v/v) contains about 24 μg of TBP (the density of TBP is 0,9727 $g.dm^{-3}$). The solubility of TBP is 6 $mg.dm^{-3}$. This means that the TBP can be dissolved in 3 cm^3 of aqueous solution. At a flowrate of 1 $cm^3.min^{-1}$ the aqueous solutions could wash the TBP from the SLM in 3 minutes under idealized conditions. This is clearly not the case, but explains the instability of the weak-base SLMs in the test unit. All three SLMs demonstrated a similar gradual decrease in permeation rate with time.

Many authors have remarked on the ease with which the SLMs could be rejuvenated. In our experiments the SLMs were easily renewed by flowing a small volume of the required organic phase over the surface of the support and rinsing the membrane to remove the excess. Removal of an SLM was equally simple, and was achieved by flowing a four-times volumetric excess of acetone over the support. This mode of operation was used as the basis for the development of an SLM-based extraction system for process analysis discussed in the next chapter.

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4.5.7 Other parameters

Flowrates. The effect of flowrate of the feed and stripping solution was evaluated using the DEHPA SLM system. The flowrate of one stream was kept constant at 1 $cm^{-3}.min^{-1}$ while changing the other. The concentration of the copper in the stripping solution was recorded.

The flowrate of the feed solution was found to be linearly related to the permeation rate of the solute. A sharp increase in the slope of the line was experienced above a flowrate of 4 $cm^3.min^{-1}$. This is due to the physical movement of the feed solution through the pores of the membrane into the stripping side. This occurs when the pressure on one side of the membrane becomes too high. The feed solution is then physically pushed through the pores in the support.

This was confirmed when the experiment was repeated using a buffer solution as the stripping solution, with the same composition as the feed solution. Because the H^+ concentration on both sides of the SLM was the same under these conditions, no permeation could take place. Under these conditions and at a feed flowrate > 4 $cm^3.min^{-1}$, a leakage of the solute into the stripping solution was again observed. This leakage is also recognised in the field of membrane technology. The phenomenon is known as exceeding the bubble point of the membrane. When the flowrate of the collector stream was increased the permeation rate decreased logarithmically. A similar result has been reported for the observed relationship pertaining to the permeation through dialysis membranes [91]. Experiments showed that the best results were obtained when the flowrates of the feed and stripping solutions were equal but opposite in direction. This is in agreement with Teramato *et al* [31].

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Feed concentration. The influence of the feed solution on the permeation rate was also studied. In *Figure 4.14* the amount of solute that permeated through the membrane is illustrated as a function of its concentration in the feed solution. These graphs show an almost linear relationship for lower concentrations, but eventually reach a plateau at higher concentrations.

In Section 2.3.1 two distinct mechanisms of transport were discussed regarding the flux through an SLM for different concentrations of solute in the feed solution. The one mechanism was for low concentrations, and the permeation rate was mainly controlled by the initial concentration of the feed solution. The second mechanism was controlled mainly by the diffusion of the solute through the membrane. The plateau observed in this SLM system might be a result of the same two mechanisms described for the batch SLM systems. It is interesting to note that the second transport mechanism took place at a much lower concentration in this flowing system than that reported for non-flowing systems. This might be due to the difference in the ratio of aqueous phase to organic phase in the two systems.

4.5.8 Observations

The last two chapters have demonstrated the potential of SLMs as an alternative to solvent extraction processes. The selectivity of the technique has been illustrated. The ease with which existing solvent extraction procedures can be adapted to this mode of operation has been shown. Large amounts of the solute can be transported by an SLM while using a small volume of organic solvent.

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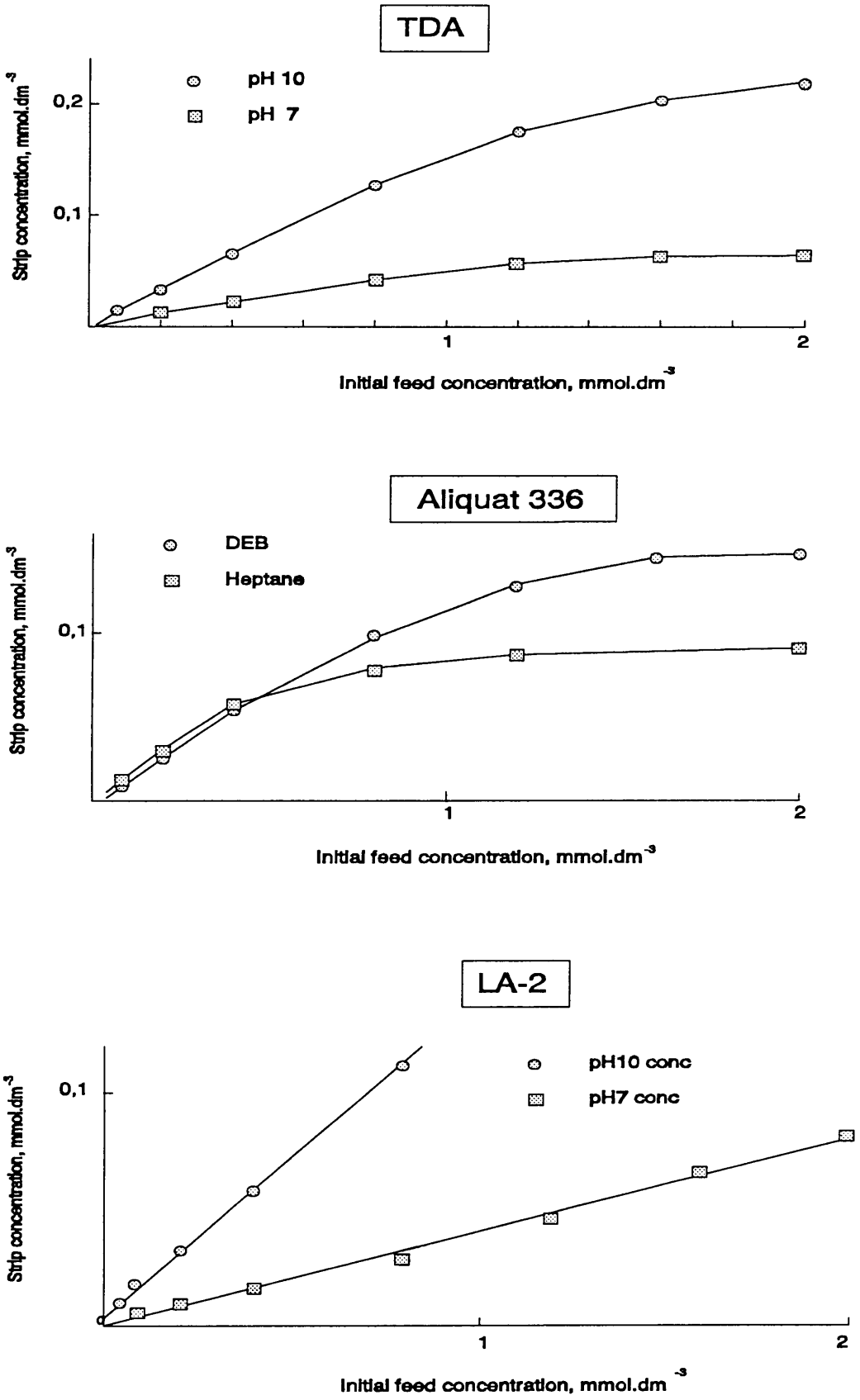

Figure 4.14 : The effect of the concentration of the solute in the feed solution on the permeation of dicyanoaurate through SLMs containing tridecyl amine (TDA), Aliquat 336 and LA-2.

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This part of the investigation also indicated that the solvents usually used in an analytical environment where equal volumes of the aqueous and organic phases are used, are unsuited for SLMs. This can be explained by the ratio of the aqueous to organic phases. When the two phases are in equal volume ratios, the slight solubility of the organic solution in the aqueous phase is not undesirable. However, when the volume of the aqueous phase is considerably larger than that of the organic phase, even a small loss of the organic phase can have a dramatic effect on the stability of the liquid membrane.

The FIA-SLM unit proved to be an excellent tool for the development and selection of the optimum conditions for an SLM system. Furthermore, as an extraction technique, the use of the liquid phase immobilised on a solid support made the organic phases much more manageable. Although the permeation through the membrane was high, it did not lend itself to application in an process environment where rapid enrichment is required. This may be attributed to the unfavourable geometry employed thus far in the investigation of solvent extraction and membrane characteristics. Where enrichment becomes a desirable parameter, an alternative membrane geometry is necessary. This is addressed in the following chapter.

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CHAPTER 5
SLMS AND CHROMATOGRAPHY

The SLM unit that was used in the work described so far, where the SLM separated the feed and stripping solutions, allows the simultaneous extraction and back-extraction of the solute. While this design was useful for studying SLMs, it has limited application in process analytical science. The main limitations are the restricted use of the effective surface area, the large volume of sample required to reach dynamic equilibrium, and the inefficient use of the fast kinetics associated with liquid membranes.

In this chapter a sequential approach is taken. The proposed technique is equivalent to that used in sorbent extraction and will be demonstrated to meet with the requirements that were set out in the initial stages of the investigation. The sequential approach involved using supports in a columnar cartridge on which the liquid membrane could be immobilised to form an SLM. The same extraction principles established for the flat-sheet geometries were used, but in a sequential mode. First the feed solution is passed over the SLM. The solute of interest is captured and concentrated in the SLM. After a set time, the stripping solution is passed over the SLM and the solute is back-extracted or stripped into a small volume. The two aqueous phases (the feed and stripping solutions) are thus not separated in space (as is the case when the flat geometry is used), but rather in time. This use of liquid membranes in this sequential fashion, is considered for use in analytical flow systems.

5.1 BACKGROUND

Solvent extraction and chromatography are two of the most powerful separation techniques available to the analyst. They share certain principles, but differ in technological application and apparatus. Chromatography offers a simple and most effective way of achieving a

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multistage separation process in a flowing system. Solvent extraction, on the other hand, offers higher capacities and a constantly-renewed contact surface between the phases.

The idea of using liquid membranes on spherical supports, in a combination of these two techniques, is not new. This combination has been used before as an organic liquid film on spherical supports remeniscent of chromatographic supports. Various authors, notably Braun, Gersini, Hullet, Cerria and Warshawsky have excellent publications in the field of extraction-, or reverse-phase partition chromatography [1-5]. The rich findings of previous investigators, both from the field of chromatography and the field of solvent extraction, were used in a modified fashion, together with recent advances in analytical technology.

Physical impregnation of supports with organic solvents has fallen out of favour in HPLC techniques. This is partially due to the loss of extractant during separation and the need to supply fresh extractant via the mobile phase. It was also difficult to ensure uniformity of the organic layer on the individual support beads, owing to the column size and geometry used. The unequal distribution of the organic phase on the support had an unacceptable influence on important chromatographic characteristics of the system such as peak shape and plate number.

As a result, extraction chromatography has lost some of its popularity among chromatographers. Instead, the more favourable functionalised supports became readily available and remained the preferred separation media. The functionality is engineered onto

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the support by surface modification and can be achieved by chemical bonding of the reagent, or by attachment of a pellicular bead that contains the active group, to the support.

Alternatively, a more soluble derivative, or equivalent, of the reagent can be used in the mobile phase (ion-interaction chromatography). Ion-interaction chromatography is a technique that Pohlandt [6] applied to the determination of metal cyanide complexes in gold-processing solutions. This method relies on the formation of ion-pairs between metal cyanide anions and a quaternary ammonium ion-pair reagent present in the mobile phase. The different metal cyanide complexes are then separated by a combination of dynamic ion exchange and partitioning of these ion pairs between the mobile phase and a hydrophobic chromatographic surface. Initially, polymeric chromatographic columns were used, but later work has shown the suitability of silica-based C18 reverse-phase columns [7-9].

In the interim, flow-injection analysis (FIA) has developed into an established discipline. It is currently being used for the automation of a host of sample manipulation operations such as multiple sample injection, sample splitting, dilution, and solute focusing. FIA is a technique that lends itself to the miniaturisation and simplification of sample manipulation procedures. There is a trend in FIA to miniaturise manifolds to speed up analysis, diminish the volume of the sample, and improve sensitivity. The use of computers for accurate and reproducible timing of events has added to the popularity of FIA as an analytical tool, and has resulted in the revival of many classical chemical methods in new and imaginative ways. Notably, several workers have attempted to apply separation and enrichment operations to the FIA environment [10-13].

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In particular solvent extraction and sorbent extraction have been applied in FIA in several manifold designs [10-17]. Solvent extraction FIA manifolds involve the extraction of the analyte into segments of organic phase introduced into an aqueous sample stream [18, 19]. The organic phase is then monitored, after phase separation using a suitable phase separator. Although FIA solvent extraction (FIA-SX) is much quicker and less troublesome than manual solvent extraction, it still has some severe limitations pertaining to the manipulation of immiscible phases. Although much attention has been given to the adaptation of solvent extraction processes to the environs of a flow-injection manifold, most have been somewhat cumbersome and certainly not suited to unattended operation [13]. Some of the problems associated with this approach to solvent extraction are:

- the need for a phase separator, which adds to the complexity of the manifold;
- propelling of organic solvents, which needs special consideration;
- lower enrichment factors are obtained due to the difficulties associated with the separation of small volumes of enriched organic solutions from large volumes of aqueous solutions;
- the loss of organic phase due to incomplete separation of the aqueous and organic phases;
- and problems associated with the intimate mixing of two immiscible phases.

Another FIA technique that has become popular in the past five years is sorbent extraction. A water-soluble extractant, or chelating compound is trapped on a suitable chromatographic support. The modified support is then used to extract metal ions from the feed solution, which

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is passed over the support. After enrichment, the complexed metal is flushed from the support to a suitable detector.

In a recent paper on sorbent extraction, Ruzicka and Arndal compared sorbent extraction and chromatography [17]. They state that '...what is ideally needed for any preconcentration in FIA is the ability of the sorbent to provide: (a) rapid and complete separation, (b) rapid and complete elution , and (c) an extensive selection of functional groups to be used off the shelf as required... '. They propose the use of sorbent extraction, as opposed to solvent extraction, to address the difficulties associated with the handling of small volumes of aqueous and organic phases. There has also been considerable development in HPLC support manufacture in the last twenty years, and support materials with excellent homogeneity in particle shape and size are available. Sorbent extraction utilises these commercial and readily available HPLC supports. The columns that are used in FIA are much smaller than those used in conventional HPLC, to allow operation at low pressures.

The extension of sorbent-extraction principles to include the use of immiscible liquid reagents on a chromatographic support formed the basis of this part of the investigation. The thin layer of organic solution on the support is referred to as an SLM. SLMs on HPLC supports can be used in a similar fashion as in sorbent extraction, with the added advantage that the active reagents are those used in conventional solvent extraction. Solutions with different composition are stacked in the FIA manifold, reminiscent of sequential-injection analysis [20]. This technique extends the tool kit of the FIA analyst to include simple but selective separation and enrichment techniques. The approach results in an application that combines

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the selectivity of solvent extraction with the multistage separation characteristics of chromatography. The extensive chemistry of solvent extraction can now be used in a similar way to the complexing reagents of sorbent extraction.

The choice of the term 'supported liquid membrane' in this application needs some qualification. Various terms have been used to describe the techniques that share the following basic concept:

- **delaying** the analyte in a flowing feed solution
- through interaction with an **organic complexing** reagent
- in the presence of a suitable **support**
- to **separate** the analyte, partially or totally, from its matrix.

The current study builds on excellent research that has been done under a variety of names such as extraction chromatography [3] , ion-exchange chromatography, reverse-phase partition chromatography [4], reverse-phase chromatography, reverse-phase extraction chromatography [4], complexation chromatography, chelate-affinity chromatography, and partition chromatography. Although these techniques share a common concept, the different nomenclature indicates the most relevant aspect of the various applications. Although it does not totally conform with the general idea of a 'membrane', the organic film, supported on the various kinds of supports will be the termed SLM in the present investigation.

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The major difference between this study and previous studies in the field becomes clear if one considers the focus of the current investigation.

- SLMs in an FIA manifold aim at the rapid, selective, and complete separation of **one** specific solute from a matrix. Previous studies were aimed at the separation of a **mixture** of chemical species with similar chemical characteristics.
- The use of SLMs in FIA allows for the **renewal** of the extractant between determinations. Previous procedures were directed at **permanent** (or semi-permanent) layers on the support.
- SLMs are aimed at the **selective enrichment** of a solute (all or nothing) while previous methods addressed the **separation** of compounds.

Enrichment and separation of dicyanoaurate(I) from other metal cyanide complexes has been the subject of intensive investigation by the gold-mining industry and several extraction procedures have emerged. These include carbon-in-pulp (CIP) [21], resin-in-pulp (RIP) [22] and solvent-extraction processes [23]. Although CIP and RIP extraction are applicable on a plant scale, their application in analytical methods has been hampered by the slow kinetics of the elution step. Solvent-extraction processes for dicyanoaurate(I) are characterized by much faster kinetics, and have therefore been employed in a number of analytical methods [24, 25]. It was therefore decided to apply the findings of the previous chapters in a study of the sequential SLM approach. The aim of the study is to obtain a quick, simple and selective enrichment technique, based on previous established principles.

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5.2 THEORY

Various SLM geometries has been studied since the first published SLM system in the middle of the 1970s. A spherical geometry is advantageous because of its favourable surface-to-volume ratio. In the late 1960s Li suggested a spherical geometry for unsupported liquid membranes in the form of emulsions [26]. Several developments followed, of which immobilising the organic liquid on a support was significant. Various geometries have been suggested for supports, including flat supports [27], tubular supports [28, 29], and spiral supports [30].

The immobilisation of the liquid membrane in the pores of a flat sheet was one of the first geometries studied. The sheet SLM was used between two stirred tanks in a batch operation [31-33]. Investigators also used these sheets, draped over tubes, suspended in stirred beakers [34]. Later designs supported sheet SLMs between two slabs, not unlike the geometry used in the previous chapters [35, 36]. All of these devices are useful for studying SLMs, but are not really suited to process applications.

The SLM-FIA system used for this investigation took between three and ten minutes to reach a dynamic equilibrium. At equilibrium the maximum permeation rate (H_m) through the SLM was constant. Once this equilibrium was established in a typical system, the concentration of the solute in the stripping solution was a fraction (17%) of that in the feed solution. If we consider that a particular point in the stripping solution is in contact with the membrane for at most 10 seconds the large fractions indicate high permeation rates. The geometry was,

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however, not suited to the application as defined by the initial requirements of this investigation.

Attention was then focused on the evaluation of SLM geometries that would favour enrichment. A closer examination of existing geometries for the liquid membrane in the hydrometallurgical field was undertaken. A tubular crossflow unit has found wide application in the hydrometalurgical field [28, 32].

A preliminary study into the use of a tubular crossflow SLM unit was undertaken. A tubular unit similar to those used by other investigators [28, 32] was then evaluated in a design that allowed simultaneous extraction and back-extraction. The tubular unit was more successful in concentrating the analyte than the sheet SLM. Although the surface-to-volume ratio was much better than that of a flat sheet, the unit still suffered from a large dead volume. A unit with a length of 10 mm, containing 14 porous, hollow polypropylene tubes, was constructed. The feed, stripping and organic solutions were exactly the same as those employed in the FIA test unit. At best a three-fold enrichment could be obtained in a continuous flow and once-through mode of operation. This enrichment did not meet with our expectations. In addition, the unit was also difficult to seal properly, particularly in the aggressive chemical environment used.

Teramato [37] designed a spiral unit with a larger surface-area-to-volume unit aimed at a hydrometallurgical process, and reported on the same difficulties. These geometries were not suited for the environments of interest to the present study.

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The success achieved with immobilising extracting reagents on spherical supports, as used in the FIA-sorbent extraction, stimulated investigation into a sequential mode of operation. Thus, to complete the circle, this investigation returned to the spherical geometry originally suggested by Li [26]. Various materials have been used as supports for organic solvents in extraction-chromatography [1, 5]. The supports include various hydrophobic polymeric materials (Teflon, Styrene/ divinylbenzene, and polypropylene), as well as hydrophilic materials (glass beads, kieselguhr, and cellulose). The support particles varied from being highly heterogeneous to reasonably uniform and homogeneous. With the development of appropriate technology, highly uniform and homogeneous particles became commercially available. These supports are either hydrophobic polymers, which vary from solid spheres to porous (both macro-, and micro-pores), or surface-modified silica particles, which offer a spectrum of hydrophobic properties.

In a recent investigation at Mintek, fibres were suggested as an alternative support for gold enrichment [38]. Qi *et al* recently published an analytical application of fibres in a FIA system for the enrichment of gold from acidic solutions [40]. They reported on the excellent flow dynamics, lower back-pressure and ease of construction. Both authors stated that the functionality could be fabricated into the surface of the fibre. The use of tubular supports in the process application of SLMs prompt us to also consider these supports in a sequential operation.

These supports can be used in an columnar cartridge in flow system. A sequential mode of loading and stripping is suggested, in which the enriched stripping solution can be flowed

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through the flow-through detectors used in process analysis. In the preceding chapters it was shown that the SLM can be formed rapidly, and that the organic solution can also be removed quite easily. Consequently, two approaches can be taken in removing the enriched gold from the SLM:

- the solute can be *back-extracted* from the organic phase (the SLM) into a second aqueous solution, or
- the entire solute-enriched organic solution can be *removed* from the support.

Various stripping solutions can be employed to remove the enriched solute from the organic solution (back-extract) into a second aqueous solution, leaving the organic solution intact on the support. One mechanism is a back-extraction based on a pH change, and another on changing the complexation or oxidation state of the solute.

Alternatively, the entire enriched organic phase can be removed from the support. In the preceding experiments this was achieved quite efficiently with acetone. However, acetone is quite an aggressive solvent and can attack FIA components. It was decided to use a milder solvent such as those commonly used in chromatography, for example acetonitrile or the short-chain alcohols. This total removal of the organic solution implies that no back-extraction reaction is required and different extractants to those considered in the first part the study can be also be considered for the SLM.

These two approaches are not mutually exclusive, and can be combined to various degrees, where a combination of back-extraction and total removal may enhance selectivity.

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5.3 APPLICATION

The results obtained in the previous chapters for the extraction of dicyanoaurate(I) from plant solutions were used in a case study to test the sequential SLM design. The pH-based extraction was used to enrich the organic phase. Both procedures of stripping (total removal and back-extraction) were studied. Three columnar supports were evaluated, *viz.* spheres, fibres, and a tube.

5.3.1 Experimental design

Reagents. In the previous chapters various amines were evaluated for the selective extraction of gold from alkaline cyanide process solutions. TDA was selected as the extracting reagent in most part of the study. A 1% per cent solution of TDA in 1: 1 (v/ v) heptane/ TBP solution was used as the organic solution. The feed solution contained various concentrations of dicyanoaurate(I) buffered to a pH of 7,0 with a ethylenediamine tetra-acetic acid (EDTA)/ triethanolamine buffer. The stripping solution was either acetonitrile or a short-chain alcohol as the stripping solution in the total-removal approach. Alternatively, either sodium hydroxide or acidic thiourea were used when the solute was back-extracted into a second aqueous phase. All solutions were propelled at a flowrate of 1,5 $cm^3.min^{-1}$ unless otherwise indicated.

FIA Manifold. The manifold illustrated in *Figure 5.1* was used in this investigation. An Alitea peristaltic pump (C4-XV) was used to propel the feed and stripping streams

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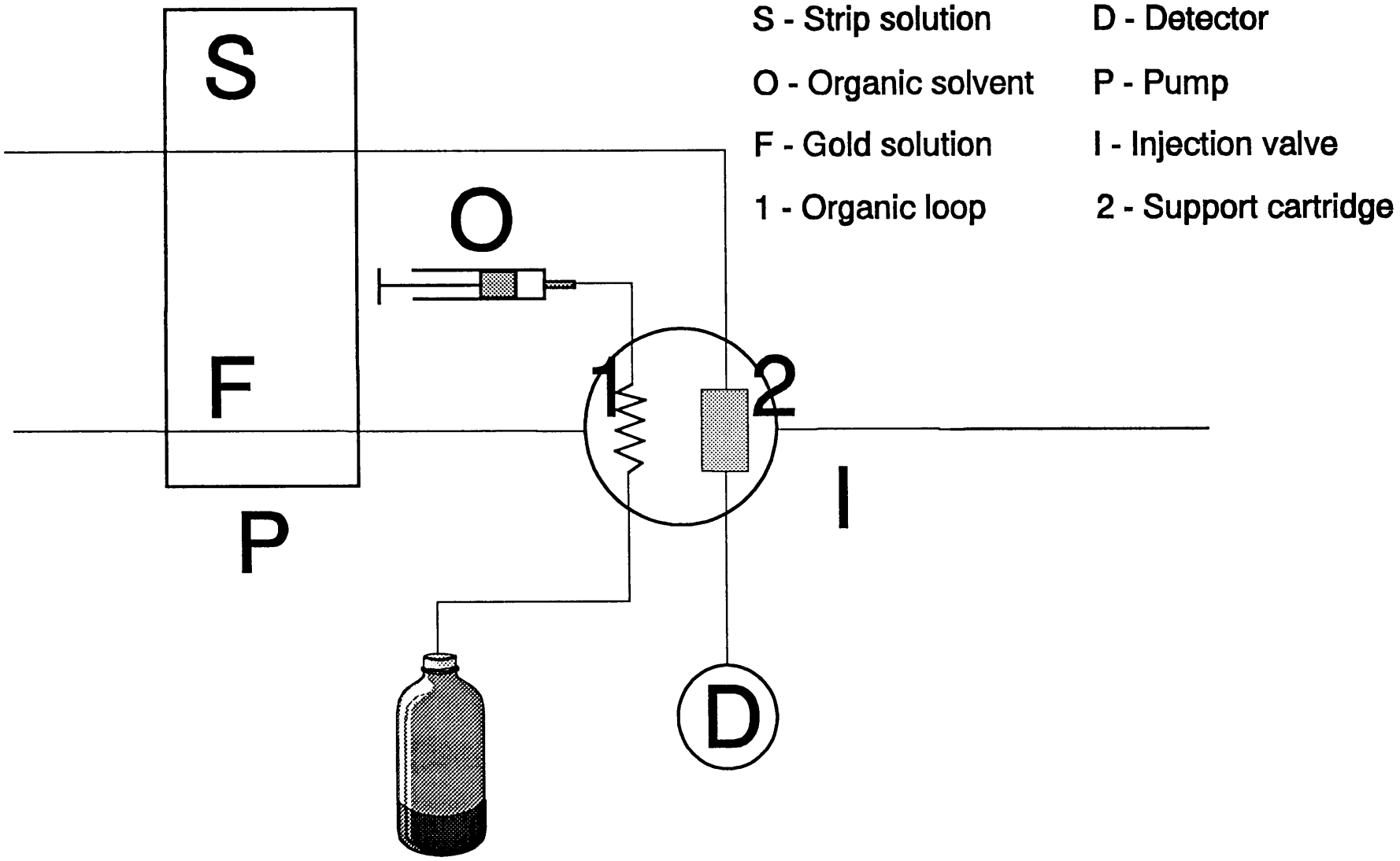

Figure 5.1 : Flow-injection manifold used for the sequential loading and stripping of the SLM.

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through the manifold. The organic stripping solution (acetonitrile, or a short-chain alcohol) was pumped with the same pump equipped with solvent-resistant tubing (Techtron solvaflex).

The organic phase was drawn manually through the sample loop with a syringe. A selection valve (Valco E-CSD 10P) was used to select between various feed solutions, and an injection valve (Valco E-C 10UW) was used to switch the support cartridge between the feed and stripping solutions. The FIA devices were controlled by a PC using the FlowTEK software program [39], which also handled the data acquisition.

Both an atomic-absorption spectrophotometer (AAS) (Varian Spectra 10/20) and a UV-VIS spectrophotometer (Spectra-Physics SP UV2000) were used as detectors for the determination of gold. Measurements with the spectrophotometer provided information on the behaviour of the organic phase and high concentrations of gold, while the AAS was used for the detection of low concentrations of gold.

Supports. Two different column geometries were tested: a packed-column cartridge and a tubular threaded column cartridge. In both cases, the column cartridge was plumbed into a 10-port injection valve.

One cartridge was assembled as depicted in *Figure 5.2*. The cartridge housing was fabricated from a 12 mm diameter Perspex rod in which a 3 mm hole was drilled from the core. Each end of the hole was threaded to take standard flangeless nuts (Upchurch Scientific Inc, Oak Harbor, WA).

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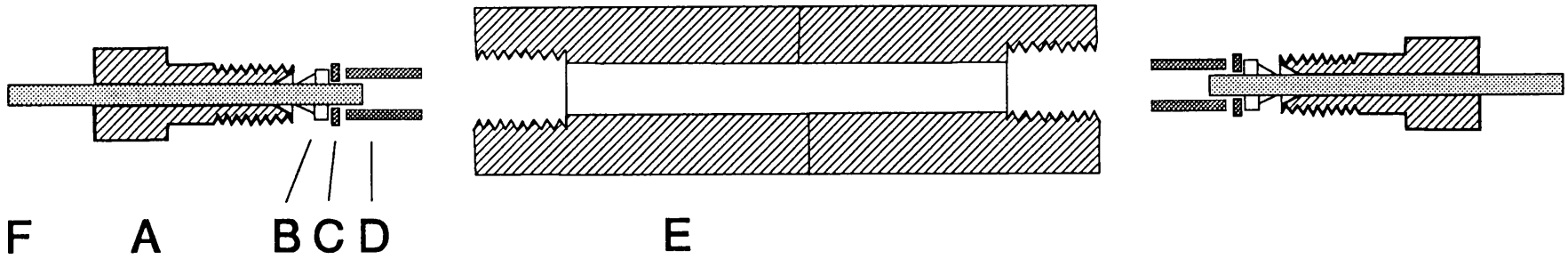

A	Upchurch fitting
B	Ferrule
C	Silicone seal
D	Column
E	Column housing
F	Teflon tubing

Figure 5.2 : Mini-column cartridge for fibrous or spherical support.

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The column consists of a glass tube with an inside diameter of 2 mm and 10 to 15 cm long, placed in the Perspex sleeve. The nuts were tightened to seal the ends of the glass tube against soft silicone washers in front of the ferrules (Upchurch Scientific Inc, Oak Harbor, WA). The glass column was packed with two types of support: spheres or fibres.

Three types of spheres were tested: glass beads (75 - 300 μm), a commercial exchange resin comprising polymeric spheres XAD-8 (200 mesh), and hydrophobic beads (Polysorb MS-1, Interaction Chemicals, California). Polysorb MS-1 is a hydrophobic support, based on highly cross-linked styrene-divinylbenzene, with an average diameter of between 10 and 35 μm. When spheres were used, they were kept in place by a plug of tightly pressed glass wool.

Fibres were also tested using the same column as used for the spherical supports. The two fibrous supports used were glass wool and isotactic polypropylene fibres (Fibremakers, Durban, South Africa) of similar dimensions (25 μm o.d.). A second, threaded tubular cartridge was constructed (*Figure 5.3*) by threading 5 cm lengths of a porous polypropylene capillary tube (0,5 mm o.d. DG2P-320-100, DynaGard, Microgon, California) into a 0,8 mm i.d. Teflon tube. The ends of the tube were fitted with stainless-steel Valco fittings, which were crimped around the outside tube, thus anchoring the inside tube.

Procedure. The injection valve was configured as illustrated in *Figure 5.4*. In the load position, the sample carries the contents of the first injection loop (organic phase) to the

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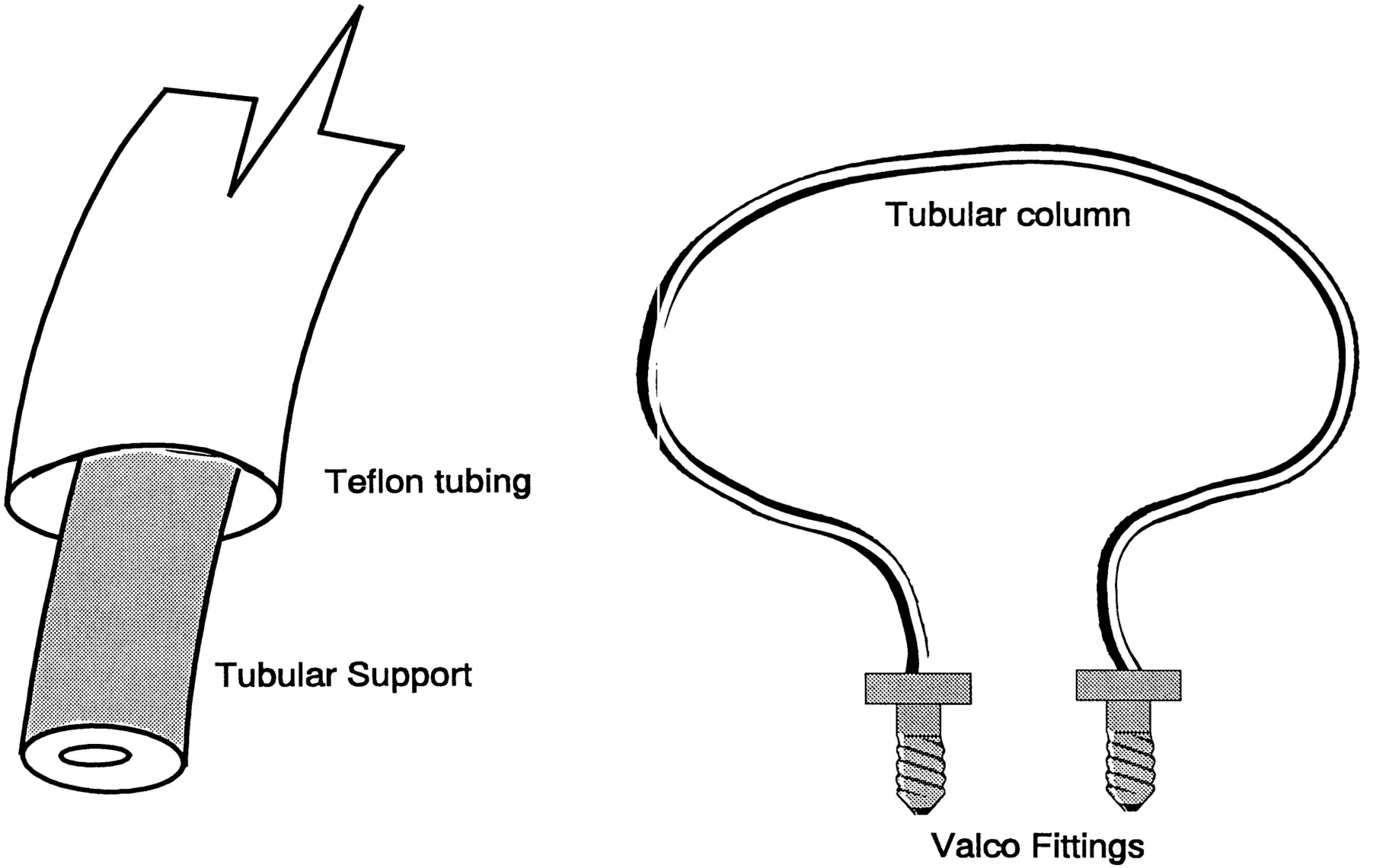

Figure 5.3 : Tubular column cartridge.

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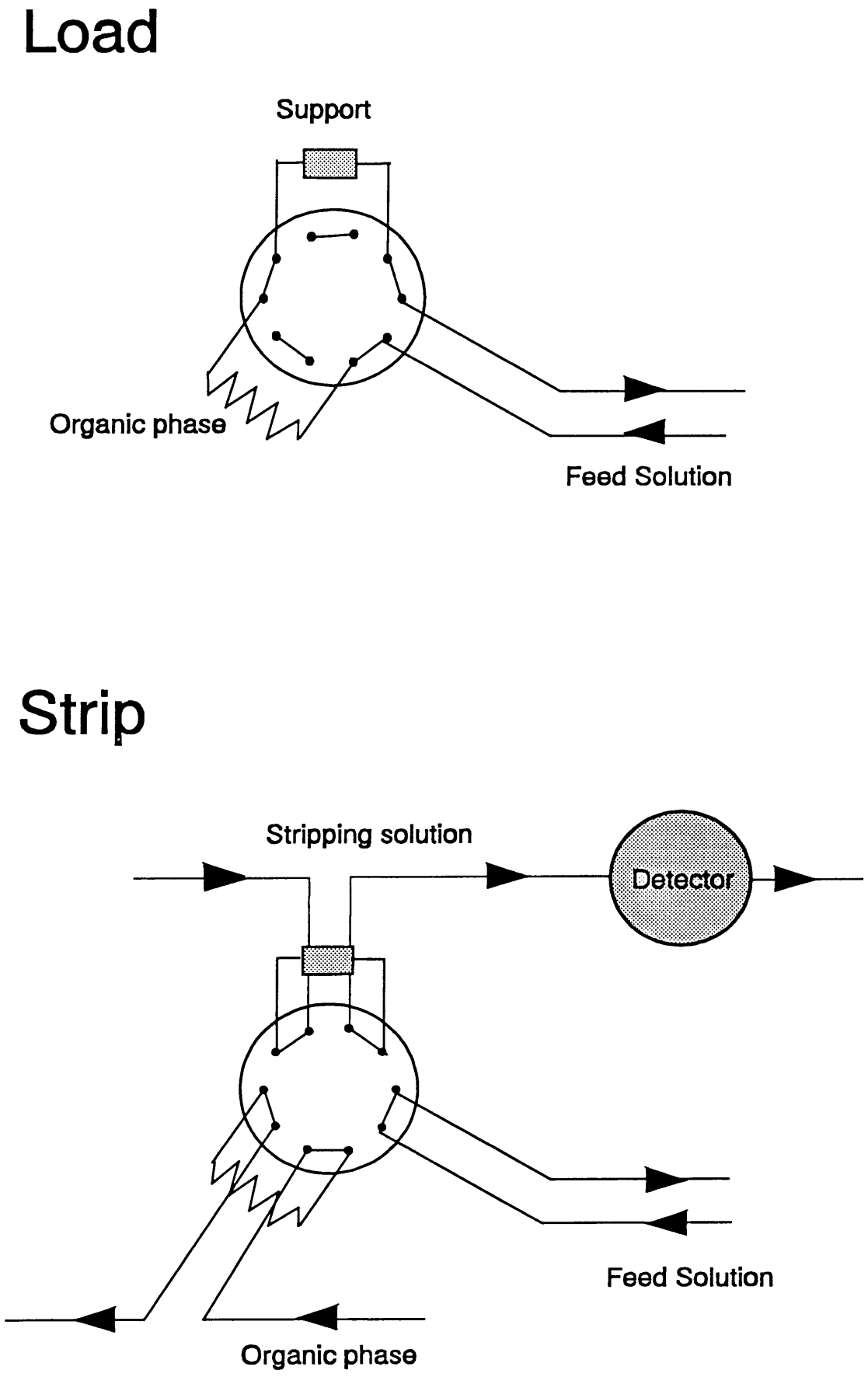

Figure 5.4 : Valve configuration for the sequential loading and stripping of the SLM.

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enrichment cartridge and then flows over the support for a carefully controlled duration (typically 2 minutes). In the strip position, the stripping solution flows over the support, stripping or back-extracting the analyte. During this time the loop for the organic solution is reloaded. In this way, the SLM is formed *in situ* when the organic solution flow over the support. The excess organic solution is flushed to waste by the sample. During the load period the dicyanoaurate(I), in our application, is extracted selectively from the feed solution into the SLM. Also, with the valve still in the load position, the enriched organic phase can be washed with appropriate buffers to eliminate co-extracted species. When the injection valve is switched to the strip position, the gold is stripped from the SLM into a small volume with a suitable stripping solution. Sequential loading and stripping of the SLM results.

5.3.2 Support materials

Three columnar support geometries were investigated:

- spherical support
- fibrous support
- threaded tubular support.

The two approaches were used to study the stripping of the enriched solute from various support materials *viz.* back-extraction and total removal. Also, two ways of evaluating the enrichment was employed, based on either peak height or peak area.

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In order to calibrate the AAS, a single-line FIA manifold with a 100 mm^3 sample loop, (approximately equivalent to the volume of the tubular column) was used. Two calibration curves were constructed, one relating the gold concentration to the height of the FIA peak and another using the total area under the analytical peak. The efficiency of the enrichment is expressed as an enrichment factor, based on either of these parameters. When peak height was used the enrichment factor is the ratio of the peak height obtained when the stripping solution passes through the detector to that obtained when the sample is injected without enrichment. When peak area was used the enrichment factor is the ratio obtained when the stripping solution passes through the detector to that obtained when the sample is injected without enrichment.

Spheres. The enrichment factor obtained with the polymeric support was higher and more reproducible than that attainable with the glass beads, confirming that the hydrophobic character of the support results in a more stable SLM. The smaller the particle size, the higher the surface-to-volume ratio. Therefore, it is preferable to work with small particles. The size of the particles also determines the back-pressure generated in the system. The back-pressure that can be tolerated by a peristaltic pump is low, and this places a limitation on the particle size and the amount of support that can be used. Furthermore, polymeric supports are more suitable supports for SLMs than functionalised silica-based supports, due to their superior pH stability and resistance to organic solvents. A commercial support, Polysorb MS-1, was used as a compromise between maximum surface area and acceptable back-pressure.

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Figure 5.5 shows the comparison between the peaks resulting from the total removal of the organic phase and the back-extraction of the solute for the enrichment cartridge containing the spherical support. The gold was concentrated for 2 minutes from a feed solution that contained 1 mg of gold per litre. Methanol was used to strip the entire organic phase and back-extraction was obtained with a stripping solution contained 0,1 $mol.dm^{-3}$ sodium hydroxide. Sodium hydroxide concentrations below this value gave inefficient and irregular back-extraction, and higher concentrations did not improve the back-extraction.

The smooth shape of both peaks indicates an even removal of the gold from the support. The analyte is more dispersed when back-extracted than when the entire organic phase is removed. The total enriched volume that resulted with a back-extraction approach was calculated to be 270 mm^3, versus 150 mm^3 for the total-removal approach.

Fibres. Fibres performed in a similar fashion to the spherical support. In general, the peaks were more dispersed and the peak heights lower. The polymeric fibres performed better than the glass wool. The cartridge packed with fibres offered no advantages over the spherical supports, and this approach was abandoned.

Tubular support. The threaded tubular design (as shown in *Figure 5.3*) was also tested. *Figure 5.6* shows the comparison between the peaks resulting from a total removal of the organic phase and the back-extraction of the analyte for a column containing the threaded tubular cartridge. The peaks that resulted from this approach are in general more diffused.

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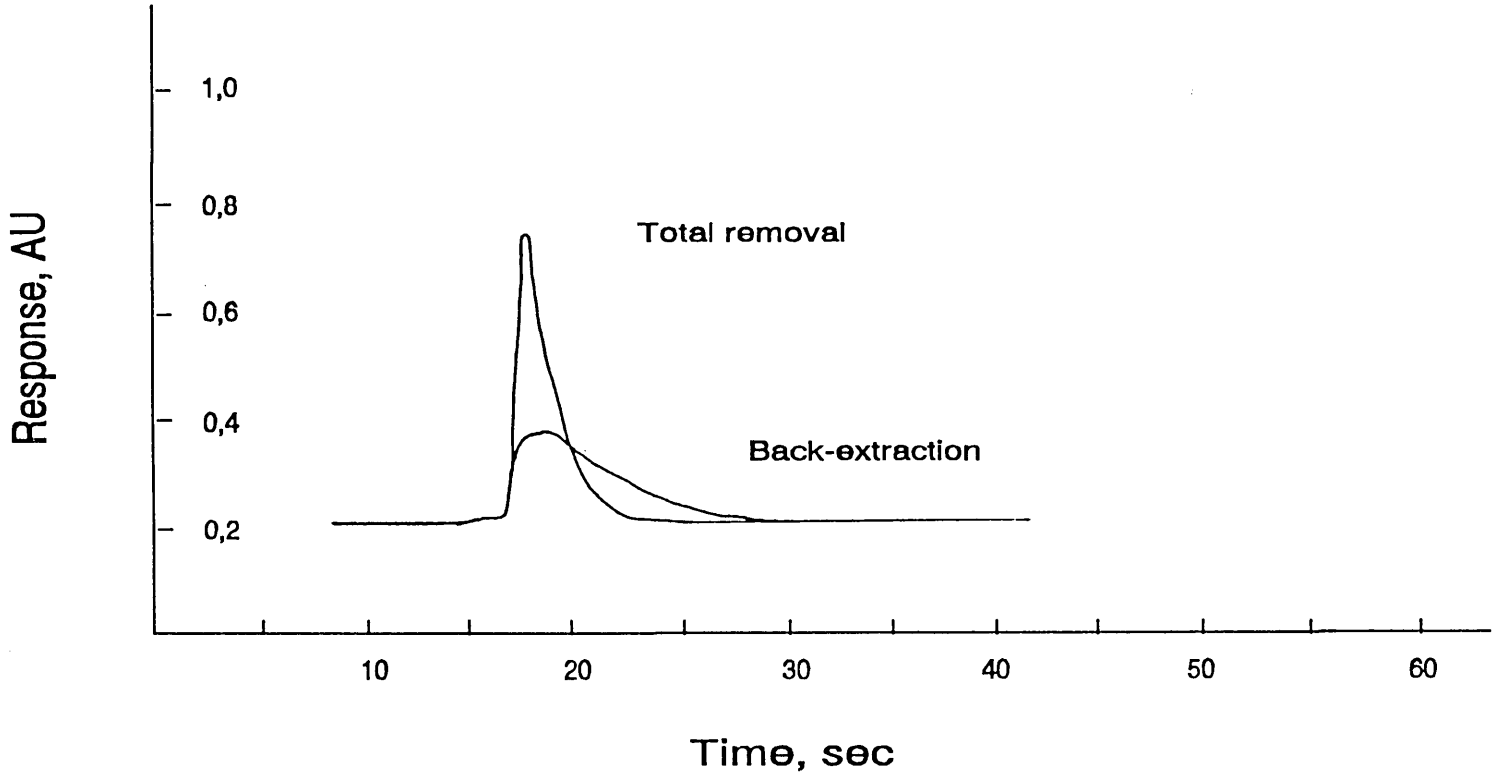

Figure 5.5 : Comparison of stripping peaks using hydrophobic spheres as the support medium.

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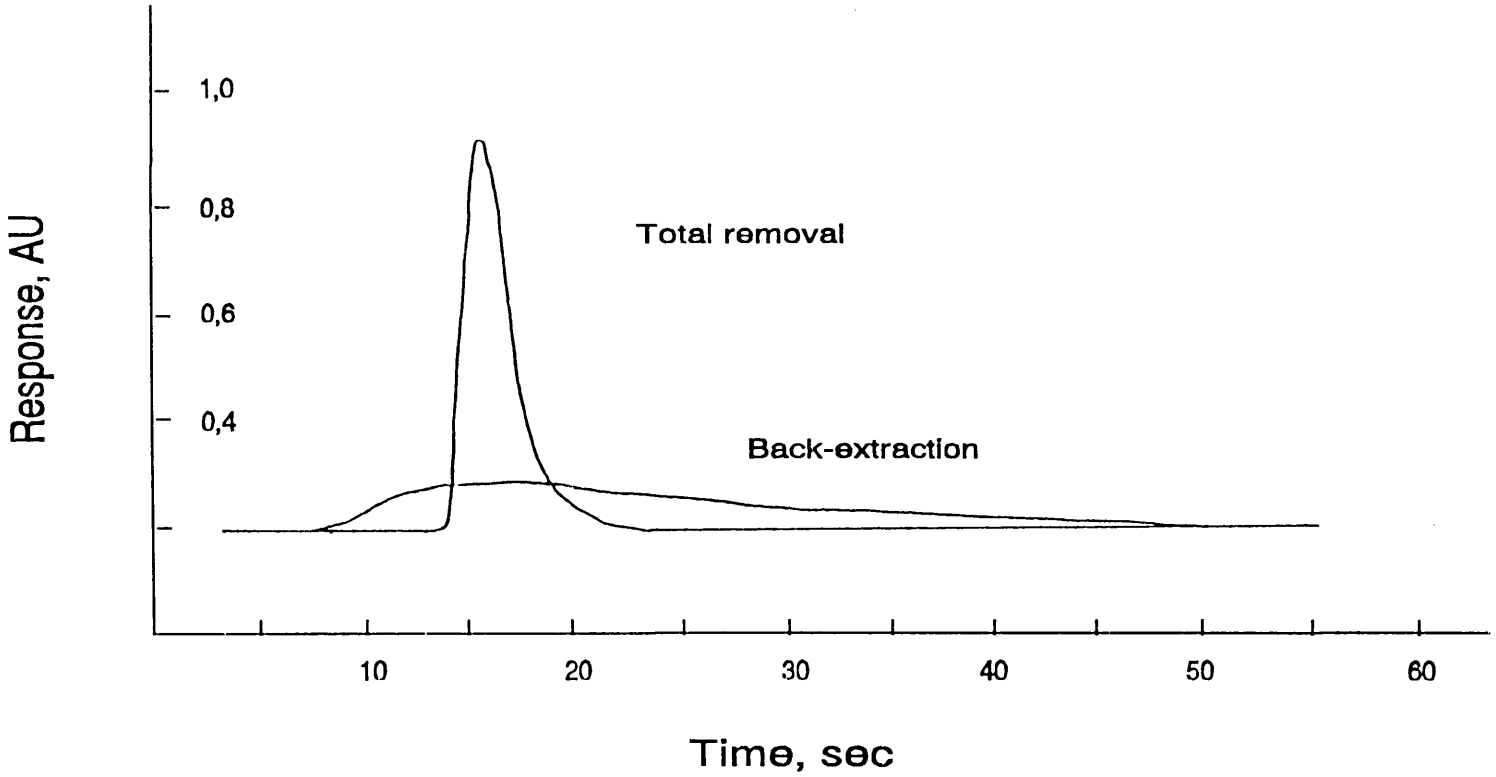

Figure 5.6 : Comparison of stripping peaks using a threaded tubular column as support.

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As for the spherical support, this phenomenon was aggravated in the back-extraction experiment. Also, if the areas of the two peaks are compared, the total amount of gold determined after using back-extraction is approximately one-fifth less than that determined after total removal of the organic phase. This indicates that methanol has a conditioning effect on the support.

The results obtained from this part of the study are summarised in *Table 5.1*

Table 5.1

Enrichment factors obtained for different geometries in a sequential mode of operation

Operation	Enrichment factor (E)		Dispersion volume
	Area	Height	(mm^3)
Total removal			
Resin	8,9	22,1	150
Fibres	5,4	7,6	300
Tubular	17,3	30,7	200
Back-extraction			
Resin	7,0	7,5	270
Fibres	4,3	4,7	500
Tubular	13,8	4,6	1 200

The enrichment factors (E) were calculated as follows:

$$E = \frac{\text{Peak parameter after enrichment}}{\text{Peak parameter before enrichment}} \qquad (5.1)$$

Peak areas were determined from the mass of the cut-out peaks.

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The enrichment obtained using fibres, were lower than those obtained when equivalent volumes of spherical supports (*Table 5.1*) were used. This may be partially due to inefficienct column packing. Another reason may be the physical volume of organic phase retained by the two supports. The beads are porous, and can therefore absorb larger amounts of organic solution, whereas the fibres are solid.

The performance of the tubular threaded column *(Figure 5.6)* was compared to that of the packed column *(Figure 5.5)*. The experimental conditions were identical for the two column cartridges.

First the profiles obtained when the organic phase was removed, were evaluated (*Table 5.1*). If the enrichment is calculated on the peak area, the tubular column resulted in almost twice the enrichment of the resin-based column. If the peak height is used for comparison the enrichment is only one-quarter higher using the threaded column. This is due to the more efficient removal of the enriched phase when the spherical support is used, which results in a sharp well-defined peak. The dispersion volume that resulted from the resin-packed column was 150 mm^3 as compared to the 200 mm^3 for the threaded tubular column.

If a back-extraction approach is used, the enrichment based on peak area that is obtained from the threaded tubular column is also almost twice that from the spherical support column. However, using the peak height, the threaded tubular column resulted in a signal that is two-thirds of that obtained with the resin-based column. This can be explained by comparing the dispersed volumes of the analyte for two geometries. The threaded tubular column

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resulted in an enriched volume that is 4,5 times greater than that obtained with the resin-based column.

The extent to which the SLM could be re-used with a back-extraction approach was tested. An SLM was prepared in the usual way and was repeatedly loaded for two minutes with a 1 $mg.dm^{-3}$ gold feed solution and stripped with 0,1 $mol.dm^{-3}$ sodium hydroxide solution. The profiles obtained for each experiment were compared. With the spherical support, the subsequent back-extractions were not reproducible, and a gradual decrease in enrichment was obtained for each consecutive cycle. However, freshly formed SLM in the tubular cartridge could be used for the enrichment of gold for seven consecutive experiments before the SLM was depleted. The resulting profiles were extremely reproducible for each of the first seven cycles. The SLM enrichment failed completely the eighth time, indicating a loss of reagent (possibly the more soluble TBP as explained earlier).

Both spherical support cartridges or threaded tubular cartridges are suitable for analytical applications in flow-based measurement procedures, and warrant further investigation. The spherical support cartridge gave more efficient stripping profiles and is well suited for automated laboratory application. The threaded tubular support cartridge is more suited to unattended use because it does not suffer from large back-pressures and it is less prone to blockages.

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5.3.3 Application using spherical support

It is envisaged that the spherical support will be used in a laboratory environment, for enrichment prior to detection by any of the many instrumental techniques. Where the organic components associated with the total removal of the organic phase does not pose a problem, this approach would be the procedure to strip the enriched phase from the support.

Composition of the organic phase. If the stripping technique is based on the total removal of the organic phase, the requirement for a suitable back-extraction technique becomes obsolete. Other extractants from those initially studied could also be considered.

In the search for an extraction system that would give rapid yet selective extraction, three amine-based extractants were identified namely: weak-base amine - tridecylamine (TDA); strong-base amine - Aliquat 336; and a modifier - TBP. Their composition were as follows:

- 1% (m/v) tridecylamine (TDA) in a diluent consisting of 50% TBP in heptane.
- 1% (v/v) Aliquat 336 in heptane.
- 50% (v/v) TBP in octanol or iso-decanol.

Amberlite LA-2, also a weak-base amine that performed well in the previous geometries was not included in this part of the study to avoid duplication.

The volume of organic required in the manifold was considered first. When a minimum volume of 10 mm^3 of organic extractant was injected onto the polymeric support, only a portion of this volume loaded onto the column. Droplets of organic phase could be seen

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eluting from the column and flowing to waste at the beginning of the load cycle. It was therefore unnecessary to inject a volume of organic phase greater than 10 mm^3.

During the initial stages of this study, a 15% solution of Aliquat 336 in di-isobutylketone (DIBK) was used as the organic phase. Heptane was later used in place of DIBK, since its lower solubility in the aqueous phase resulted in a more stable SLM and higher absorbance values in the AAS detection. During the interference studies, it was found that Aliquat 336 was not sufficiently selective (coinciding with the results found in Section 3.4.2.4.), and gave poor gold recoveries in the presence of other metal-cyanide complexes. The search for a more selective extractant system led to an investigation of the TBP and TDA extraction systems.

TBP has been shown to be a selective extractant for the dicyanoaurate(I) anion [41]. Batch experiments carried out by shaking 10 cm^3 TBP with 100 cm^3 cyanide process solution revealed the formation of a milky white emulsion which separated only after an extended period. Several different diluents, namely butanol, octanol and iso-decanol, were investigated in an attempt to increase the efficiency of phase separation. Of these, decanol proved to be the most successful in preventing emulsification but problems were still experienced with the emulsion blocking the column when actual plant solutions were analysed. Attempts to use TBP as an extractant were therefore abandoned.

Due to its superior selectivity, the TDA system was selected for the remaining investigation.

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Selectivity. The effect of high concentrations of base-metal cyanides on the capacity of the organic extractant was examined to determine whether these anions would retard the loading of dicyanoaurate(I) by the SLM. (This was particularly important in view of the poor selectivity exhibited by Aliquat 336 [42].)

Solutions were therefore prepared containing a known concentration of gold and up to 1000 mg.dm^{-3} of the following metal cyanide complexes: $Fe(CN)_6^{4-}$, $Cu(CN)_4^{3-}$, $Co(CN)_6^{3-}$, $Ni(CN)_4^{2-}$ and $Ag(CN)_2^-$. These solutions (pH 10) were used as a synthetic sample solutions. Actual plant solutions from several different mines were also analysed and the results compared with those obtained by graphite-furnace AAS *(Table 5.2).*

Table 5.2
Interference of some typical constituents of a plant solution

Ion	Concentration mg.dm^{-3}	Gold added mg.dm^{-3}	Gold found mg.dm^{-3}	% Recovery*
Ca^{2+}	1000	0,03	0,031	103
$Fe(CN)_6^{4-}$	1000	0,03	0,032	107
$Co(CN)_6^{3-}$	1000	0,03	0,032	107
$Cu(CN)_4^{3-}$	50	0,05	0,047	94
$Ni(CN)_4^{2-}$	50	0,04	0,036	90
$Ag(CN)_2^-$	1	0,05	0,047	94

* $\frac{\text{Gold found}}{\text{Gold added}} \times 100$

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The effect of varying levels of other metal cyanide complexes on the determination of low levels of dicyanoaurate(I) was also examined. It was found that significant interference was encountered from the argentocyanide anion ($Ag(CN)_2^-$) at levels above 1 $mg.dm^{-3}$.

This can be attributed to the fact that $Au(CN)_2^-$ and $Ag(CN)_2^-$ are both singly charged and have similar effective ionic radii (2,33 and 2,28 Å respectively) [43]. This means that they both behave as large, weakly-hydrated anions which are preferentially extracted into the organic phase by bulky, singly-charged cations such as TDA. The dicyanoaurate(I) and dicyanoargentate anions therefore compete for charged amine groups in the organic phase. However, the method was capable of tolerating a 20-fold excess of silver, a situation that would rarely arise. In real samples, an average gold-to-silver ratio of 9:1 is found in most South African gold ores.

The other metal cyanides investigated are all multi-charged and behave as hard anions which are not readily extracted by TDA. The technique can tolerate the presence of up to 1000 mg/dm^3 of iron, calcium or cobalt and up to 50 $mg.dm^{-3}$ of copper or nickel (*Table 5.3*).

Typical tailings solutions contain trace levels of gold, and cobalt, nickel, copper, iron and silver present as complexed cyanides. They also contain free cyanide at the 100 to 200 $mg.dm^{-3}$ level, and sulphur compounds such as sulphate and thiocyanate. Although the base-metal concentrations are generally far below those tested in the interference studies, it was necessary to assess the applicability of the method to typical plant solutions. Tailings solutions were obtained from several sources and analysed using the proposed technique.

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Table 5.3
Comparison of results obtained by tubular SLM enrichment and by graphite furnace-AAS.

Sample solution	Concentration in $mg.dm^{-3}$		
	By SLM trace enrichment	Graphite-furnace AAS - Standard additions	Graphite-furnace AAS - Direct calibration
Sample 1	0,052	0,052	0,061
Sample 2	0,088	0,091	0,066
Sample 3	0,071	0,084	0,078
Sample 4*	0,034	0,040	0,039
Sample 5†	0,049	0,058	0,058
Dump leach SL14	0,070	0,067	0,068
Dump leach SL27	0,047	0,051	0,051
Dump leach CIND	0,071	0,080	0,074

* *Leach solution containing humates.*
† *Tailings solution from a sand/ slimes retreatment plant.*

Table 5.3 illustrates the good agreement between the results obtained by enrichment prior to flame AAS and those obtained by graphite-furnace AAS using the standard-additions method of analysis. Samples 1, 2 and 3 represent typical tailings solutions obtained from various Witwatersrand gold extraction plants.

Enrichment. The parameters that determine enrichment were studied next. Previous work has shown that an aqueous-to-organic ratio of 400: 1 can be used to lower the detection limit when solvent extraction is used as a means of enrichment [42]. In this study, a high aqueous-to-organic ratio was achieved by using high sample flowrates, extended load times, and a

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minimum volume of organic phase. The enrichment and the selectivity results obtained in this part of the study were based on peak height measurement.

Due to the rapid kinetics of the liquid-based extraction it was possible to use a high sample flowrate when loading the SLM. *Figure 5.7* illustrates an increase in the peak height absorbance with increasing flowrate up to 5 $cm^3.min^{-1}$. The precision (s_r) displays a marked deterioration at flowrates higher than 5 $cm^3.min^{-1}$. A sample flowrate of 5 $cm^3.min^{-1}$ was chosen for the next phase of the study.

A high aqueous-to-organic phase ratio can also be achieved with the use of extended load times.

A linear relationship between the enrichment factor and the load time was obtained for a load time of less than three minutes (*Figure 5.8*). Thereafter, a deviation from linearity was observed. This was probably due to the solubility of TBP in the aqueous phase (0,04% m/v) [43] which resulted in TBP being washed out of the SLM. Using a load time of 120 seconds at a flowrate of 5 $cm^3.min^{-1}$, a 53-fold enrichment was achieved for solutions that contains 50 $\mu g.dm^{-3}$ of gold. Under these conditions, it was possible to analyse 24 samples per hour.

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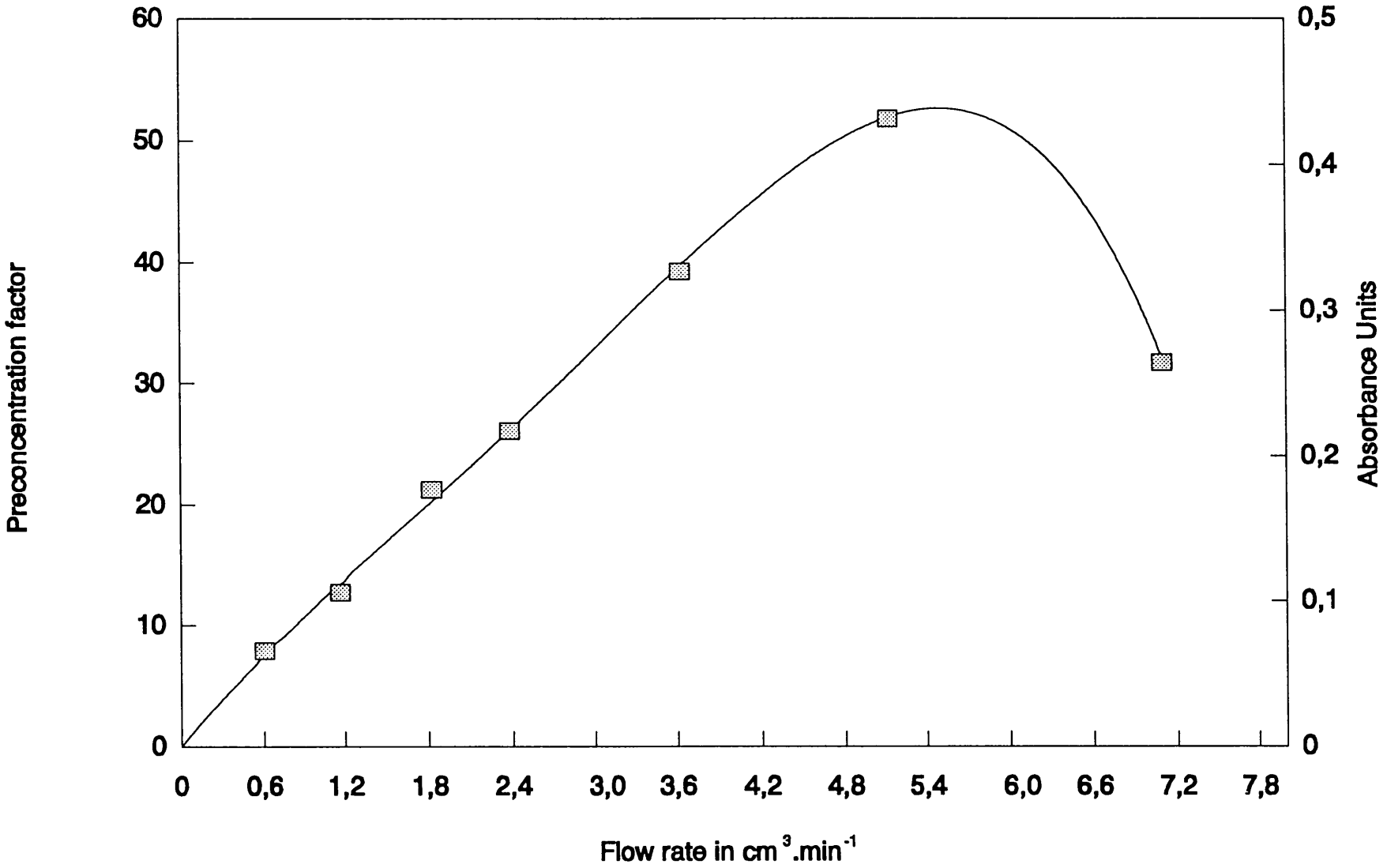

Figure 5.7 : Enrichment factor versus sample flowrate for a 0,1 mg.dm^{-3} gold solution.

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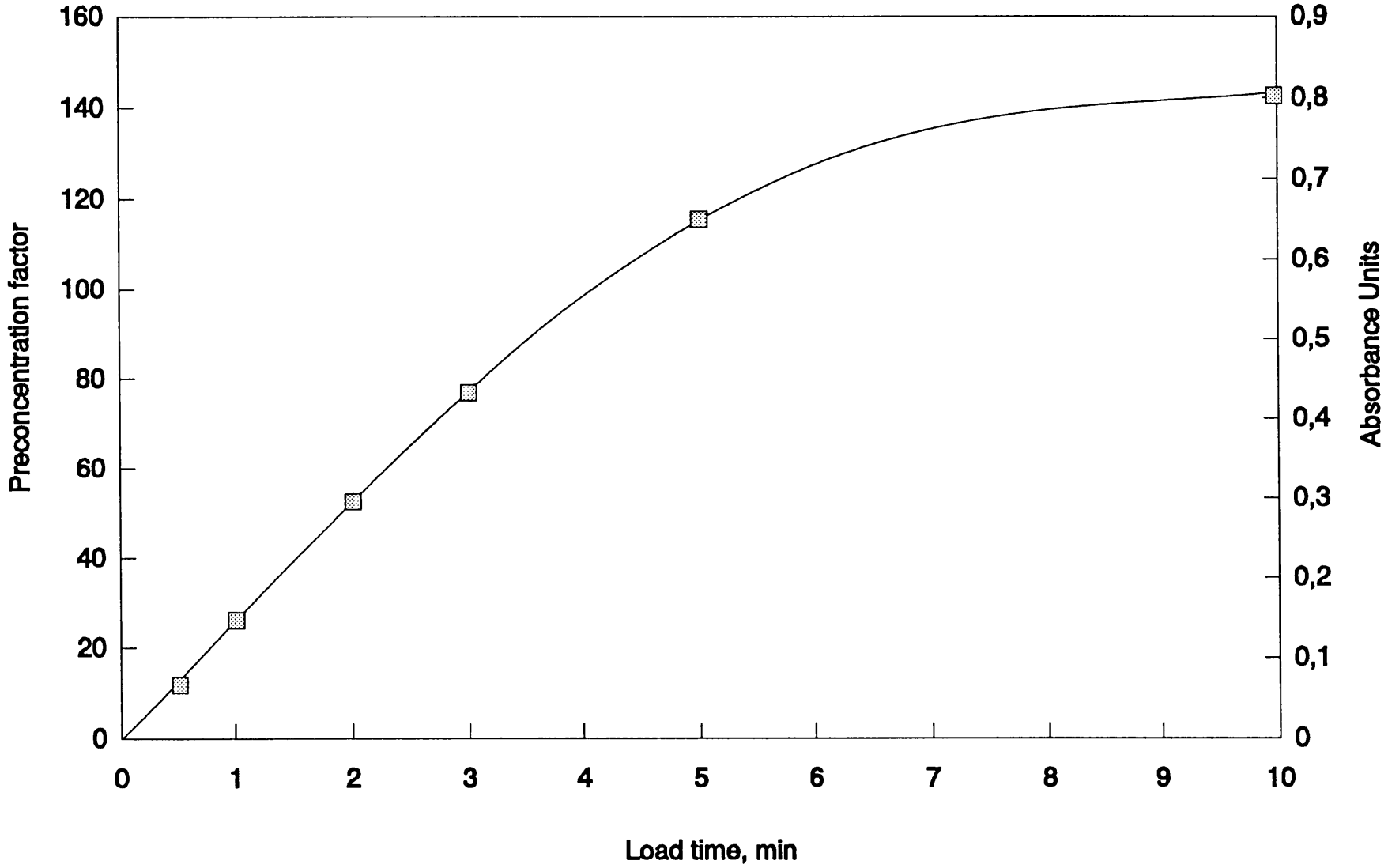

Figure 5.8 : Enrichment factor versus sample load time for a 0,1 mg.dm^{-3} gold solution.

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5.3.4 Application using a tubular column.

This unit was much easier to assemble and had lower back-pressure than the column cartridge, and was therefore less prone to blockage. Although the contact of the sample and the SLM is not as intimate for the tubular support, the tube has the advantage of a longer contact time with the sample. A threaded tubular column of 3 m could easily be used without having an adverse effect on the back-pressure. As a compromise between enrichment and experiment time, a length of 200 mm was arbitrarily chosen, and the amount of organic solution absorbed onto this length of threaded support, corresponded to four times the amount loaded onto the resin-packed support [44].

Analyte Detection. The SLM enrichment/ separation technology can be used in combination with different detectors. These include atomic-absorption spectrophotometers (AAS), UV-VIS spectrophotometers, and electrochemical detectors such as anodic stripping voltameters [45]. The AAS is a selective detector and was used for most of this study. However, it is strictly a laboratory instrument and unsuited to unattended operation. For process analysis, more robust detectors are required.

If detectors such as the UV-VIS spectrophotometer and AAS instrument are used, it is important to minimise the dispersion of the enriched analyte. Low dispersion results in a sharp peak with a large peak height. The total-removal approach results in such a peak, but the enriched volume is a heterogeneous organic solution comprising a mixture of the stripping solution, the organic reagent, and the extracted species. The high organic content of this enriched volume makes detection of low dicyanoaurate(I) concentrations with a UV-VIS spectrophotometer difficult. This problem is worse in electrochemical detectors, where fouling of the electrode surface occurs.

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Although the back-extraction approach results in a more dispersed analyte, it is an aqueous solution free from organic contaminants. This approach is therefore, more advantageous for UV-VIS spectrophotometers and electrochemical detectors. In certain detectors an integrating approach may be taken. In these detectors the total amount of analyte (peak area) is more important than the stripping rate (peak height). The tubular cartridge was therefore evaluated using a back-extraction approach. The enrichment values obtained in this section are based on both peak area and peak height measurements.

Alternative stripping techniques. Due to its robust nature the tubular cartridge lend itself ideally for testing the effect of various stripping solutions. Alternative stripping techniques were evaluated. Various organic stripping solutions will achieve the removal of the organic phase, *viz.* acetonitrile and the short-chain alcohols. These were tested first.

Methanol resulted in marginally higher degree of enrichment than acetonitrile. However, the enriched analyte was more dispersed after stripping with methanol than with acetonitrile. This apparent discrepancy was attributed to the higher hydrophilic character of methanol ($\varepsilon^{o}_{(Al_2O_3)}$ = 0,95) compared to that of acetonitrile ($\varepsilon^{o}_{(Al_2O_3)}$ = 0,65). Small amounts of the residing organic stripping solution may have a conditioning effect on the next loading or extraction cycle, leading to differences in the over-all enrichment. This may effect either the formation of the next SLM or impact on the initialy interaction of the SLM and the feed solution. Ethanol or propanol ($\varepsilon^{o}_{(Al_2O_3)}$ = 0,88 and 0,82 respectively) also resulted in lower enrichment levels.

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Methanol is more economical, more available, and less toxic than acetonitrile, and is therefore likely to become the preffered stripping solvent in process analysis.

In reverse-phase ion-interaction chromatography, elution is usually achieved with a miscible mixture of a polar organic solvent and an aqueous solution. Acetonitrile and methanol were compared as stripping solutions at different concentrations. The resulting stripping peaks for acetonitrile are displayed in *Figure 5.9*. When decreasing amounts of the organic solution were used, the rate of extraction decreased as is evident by the increased dispersion of the enriched volume.

An alternative back-extraction technique based on acidic thiourea was tested next. Different inorganic acids (nitric, sulphuric, and hydrochloric acids) that contained thiourea were used as stripping solutions. The reactions associated with thiourea extraction are slower than those associated with the pH-related extractions, and very irregular and much smaller stripping profiles resulted that were spread over four minutes. Sulphuric acid resulted in a flat irregular peak profile, while a slightly higher profile was obtained with nitric acid. With hydrochloric acid, a small peak resulted which increased with successive loading and stripping cycles. This suggests that the thiourea/ hydrochloric acid stripping solution does not remove all the gold from the organic phase. The consecutive higher peaks might be due to entrapped chloride ions that facilitates successive stripping cycles.

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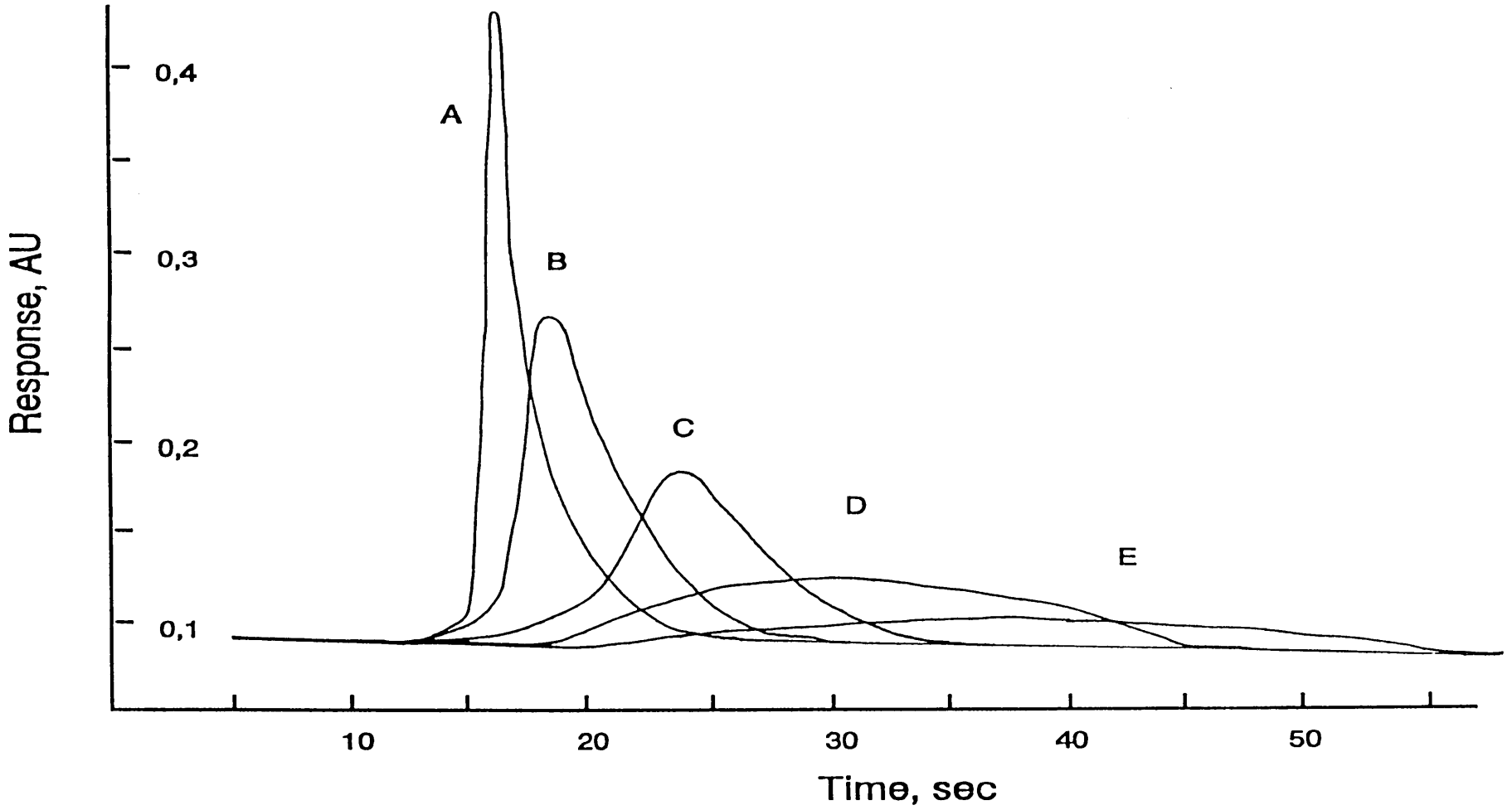

Figure 5.9 : Comparison of stripping peaks resulting from various concentrations of acetonitrile in water. (A) - 100% (B) - 80% (C) - 60% (D) - 40% (E) - 20% (v/ v in water)

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These results did not offer any advantage over the back-extraction procedure based on sodium hydroxide, and 0,1 mol.dm^{-3} sodium hydroxide was used as the stripping solution for subsequent experiments.

Enrichment. As expected, enrichment increased linearly with the length of the tubular column used. However, longer columns resulted in longer stripping times. A 200 mm length of coil was chosen in order to limit the experimental time. The back-extraction was completed in 60 seconds.

The 200 mm threaded tubular column was loaded for two minutes using a 1 mg gold per litre feed solution at various flowrates, and was stripped with a 0,1 mol.dm^{-3} sodium hydroxide solution. The results are shown in *Figure 5.10.* The enrichment factors, calculated both from peak height and peak area, are plotted against the flow-rate. A plateau is reached in both the peak height and the peak area at a flowrate of 4 cm^3.min^{-1}. The plateau could be the result of the limited capacity of the column, or it may reflect the fact that some kind of dynamic equilibrium that has been reached. The study by Mooiman *et al* indicated that the capacity of the organic phase is at least one gram of gold per litre of organic solution [18]. The amount of gold trapped by the SLM at the plateau conditions is calculated to be roughly 5 μg. This amount represents a fraction of the 40 μg expected from the work of Mooiman *et al*, thus suggesting a limitation from a dynamic equilibrium such as the dissolving of the slightly soluble TBP from the organic phase.

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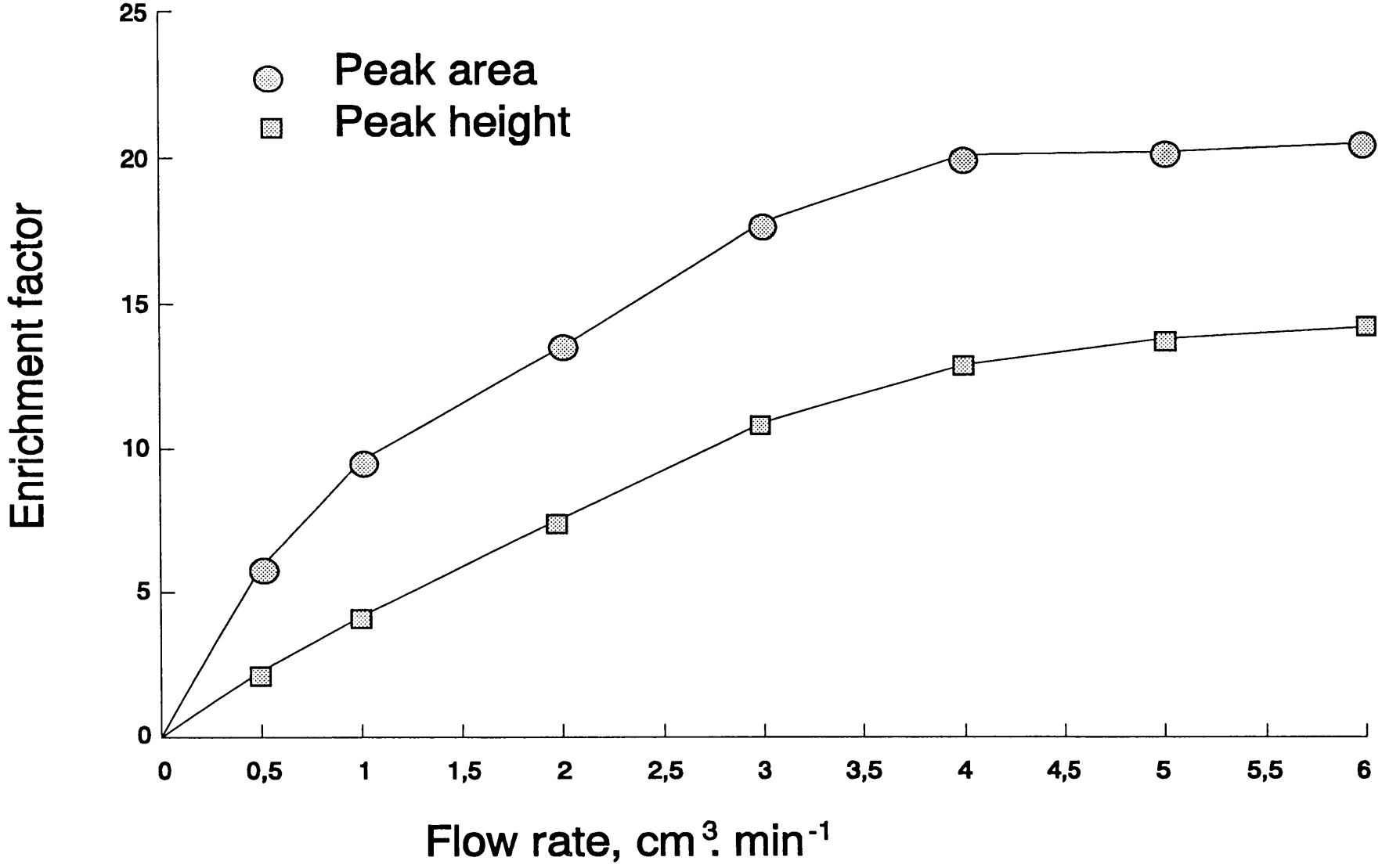

Figure 5.10 : The effect of sample flowrate on the enrichment obtained with the threaded tubular column, using back-extraction.

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The efficiency of the SLM in trapping the dicyanoaurate(I) was also calculated. The amount of gold that is recovered, compared to the amount available for recovery at 4 $cm^3.min^{-1}$, is of the order of 63%. At a flowrate of 1 $cm^3.min^{-1}$, it is as high as 90%. The injection valve could be plumbed so that the stripping stream flowed through the column in either the same direction as the feed solution or in the opposite direction. In the studies using the spherical support, a reversed flow reduces compaction of the column packing and dispersion of the gold, and reversal of the flow is therefore advantageous. Using the tubular support, the direction of flow had no noticeable effects on the stripping efficiency.

The volume of the organic solution required to cover a 200 mm length of tubular support was found to be 40 mm^3. It is also interesting that this is the volume that can be immobilised in the pores of the tube by soaking it in the organic solution. Any excess organic reagent foul the manifold.

5.4 OBSERVATIONS

The chromatographic approach proved to be advantageous for trace enrichment, particularly for analytical applications. Two designs were considered; a resin, or fibre-packed mini-column cartridge and a threaded tubular cartridge. The mini-columns gave the efficient separation (sharpest peaks). This approach is envisaged for laboratory use where selective automated enrichment is required before an instrumental technique such as AAS or ICP-AES or MS.

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The tubular design resulted in more dispersed enriched volumes, but it was easier to construct and maintain. Its favourable flow-dynamics makes it more suited to long periods of unattended use, and is suggested for use in process analysis.

Two analyte recovery approaches were evaluated for each system, *viz.* a total removal of the liquid membrane, and a back-extraction. The enriched sample obtained when the organic layer is removed results in an undiffused plug. This is desirable for certain detectors, provided that the complex organic phase can be tolerated as for instance when a flame AAS is used. A back-extraction approach results in a cleaner aqueous phase, but the enriched analyte is contained in a larger volume. The absence of organic solution makes it more suited to a variety of detectors used in process analysis, e.g. spectrophotometers or electrochemical detectors.

A sequential mode of operation provides an ideal application of SLMs in flow systems for automated use both in the analytical laboratory and in the process environment. Selective separation, as well as the required trace-enrichment, was achieved. High enrichment factors - 50 times for a tubular threaded column and as high as 140 times for a resin-packed column could be obtained in relatively short times (5 minutes). The renewable organic surface has definite potential in sample pretreatment. As the organic phase can be immobilised on the support before each determination, fouling of the active surface is eliminated. This sequential approach also allowed the incorporation of a washing step between extraction and back-extraction to strip the organic phase of unwanted co-extracted compounds. This addresses one of the criticisms against the use of SLMs as an alternative to solvent extraction in existing systems.

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CHAPTER 6
CONCLUSION

6.1 SIGNIFICANCE OF THE STUDY

This investigation has evaluated the application of SLMs, in a flowing system, for automated wet chemical analysis environment. The aim was to obtain selective separation and enrichment of inorganic solutes in order to improve the quality of analysis, reduce manual sample manipulations, and shorten analysis time, both in the laboratory and in the process environment.

SLMs have been used successfully on process scale as an alternative to solvent extraction, and their use simplified the extraction system. However, their application in analytical science has been limited. In order to achieve the aim stated above, SLMs were studied as an interdisciplinary technique that is based on principles associated with solvent extraction, membrane separation and chromatography. The study concentrated on the application of SLMs, and by placing SLMs alongside related established separation techniques, new insights into this powerful tool have emerged. The use of these organic-impregnated supports has several important benefits, such as selective separation, potential enrichment, efficient use of the fast kinetics associated with liquids, and the elimination of phase separation. The improved understanding of SLMs subsequently led to their useful application.

In the course of this study:

- An FIA-SLM test unit was developed.

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- The test unit was used to develop and optimise SLM systems. The usefulness of this approach was demonstrated for the selective extraction of dicyanoaurate from alkaline process solutions.
- A hybrid technique was designed, using SLM and FIA technology, for selective extraction in an automated fashion.

6.1.1 SLM-FIA test unit

A survey of the literature indicated that existing methods of optimisation of SLM systems are a manual and time-consuming process. The selection of a small component of the SLM system, such as the choice of an appropriate diluent for the extractant, was normally a laborious trial-and-error procedure. It was clear from a literature survey that a simple and rapid method of optimisation of SLMs and their behaviour in a flowing system was required for the current investigation.

An FIA-SLM unit was designed. A flow-through SLM unit was linked to an FIA manifold which monitored the solute concentration in the stripping solution. The initial concentration of the solute in the feed solution is known. FIA, being a fast analytical technique, allows the rapid analysis of the stripping solution. The concentration of the solute in the stripping solution is determined at regular time intervals (typically every 60 seconds) by injecting portions into the FIA manifold for analysis. The amount of solute in the stripping solution at a given time is an indication of its permeation rate through the SLM at that moment.

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The concentration of the solute in the stripping solution was expressed as a percentage ratio of that present in the feed solution. These percentages (permeation ratios) were plotted against time to give a performance profile of a specific SLM. Three distinct zones were identified in a typical performance profile:

- initial period
- the plateau (with the associated maximum permeation rate), and
- decay period.

The initial period reflects the diffusion rate of the solute through the SLM. The maximum permeation rate of the solute through a specific SLM is attained when the plateau is reached, and can be calculated from the height of the plateau. This will be rate of the slowest stage in the overall permeation. The time period that the plateau is maintained provides information on the stability of a particular SLM. The suitability of the SLM for process applications can be determined from this parameter, which reflects on both the chemical and the physical stability of the SLM.

The performance profiles for different SLMs are easily obtained and can be used to compare the relative stability, and flux through the SLM. The ease with which SLMs are formed and stripped in this system allows the investigator to compare different SLMs containing a variety of extractants or organic diluents. An important consideration in the evaluation of this approach to the study of SLMs is the flexibility afforded by the FIA monitoring system. Parameters that can be conveniently changed or varied include among others:

- the membrane used
- the composition of the organic solution

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- the chemical composition of the feed and stripping solutions
- the geometry of the support
- temperature
- flowrates of the streams

The influence of these parameters on the permeation rate, stability, enrichment and selectivity can easily be evaluated.

The use of the SLM-FIA unit was demonstrated by studying broad concepts in a commonly used DEHPA-SLM system for the extraction of copper. The effect of the diluent on both the stability and permeation rate through the SLM was found to be substantial and the apparent conflicting results of previous investigators could thus be explained.

The effect of change in the composition of either the feed and stripping solution, on the performance of the selected SLM, was also investigated. The choice of extractant and diluent for a SLM and their respective concentrations is not a trivial task, and their selection still remains an empirical procedure. The results of this investigation clearly show that, with regard to their permeation characteristics and stabilities, the different organic solvents tested produce vastly different SLMs. In these empirical studies the SLM-FIA unit proved itself as a simple and powerful investigative tool.

Furthermore, once a particular SLM system has been selected on this micro-scale, the same FIA manifold can assist in the monitoring of pilot-scale or full-scale processes to further the optimisation. By substituting the experimental SLM-unit with a full-scale SLM process, both

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the feed and the stripping solution can be monitored and the data used to control the processes. This development represents a major step forward in the study of SLM-based extraction processes for both the analyst and the hydrometallurgist.

6.1.2 Extraction system for dicyanoaurate

Solvent extraction is a powerful analytical technique that has proved itself in batch-type operation for sample pretreatment. Various attempts have been made in flow-injection analysis to capture the power of this technique in an automated and continuous flow fashion However, the separation of the two phases has always posed a problem. SLMs were evaluated as an alternative approach. The extraction principles established by previous investigators for a batch type solvent-extraction were used to design an SLM based extraction system. The application dealt with the selective extraction of dicyanoaurate(I) from alkaline process solutions.

The most obvious advantages of SLM technology over conventional solvent extraction in flowing systems are as follows:

- SLMs are easily incorporated in flowing systems, thus favouring automation.
- Supporting the organic phase on a solid phase eliminates, the problems associated with the intricate manipulation of two immiscible solutions.
- More exotic organic extractants can be employed because of the enclosed environment of the organic phase and the small volumes required.

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- High permeation rates can be achieved by combining the high diffusion coefficients of solutes in liquids, enhanced by facilitated transport using an extractant.

The SLM-extraction method developed, used a weak-base amine modified with a Lewis base in an appropriate diluent for the selective extraction of dicyanoaurate(I) in the presence of other base metals and interferents from alkaline cyanide process solutions. The ease with which existing solvent extraction procedures can be adapted to this mode of operation with the aid of the FIA-SLM unit has been shown. In the developed system, the gold-bearing solution was contacted with a thin coating of the organic phase on a polymeric support. The dicyanoaurate was extracted from a buffered feed solution into the SLM. The concurrent stripping of the enriched gold on the opposite side of the SLM was achieved by back-extraction. The developed principles are also applicable to larger-scale systems as well.

6.1.3 SLM-FIA in process analysis

The SLM-FIA unit which incorporated a sheet-like SLM, was well suited to the development and study of various SLM systems. However, it has limited use as an enrichment procedure in FIA-based analytical techniques, specifically those for process analysis.

In the search for an appropriate design to be used in process analysis, various geometries were considered. The goal was to find a system which maximised parameters such as surface area, dead volume, enrichment factors, and analysis time. A sequential mode of operation, similar to that used for FIA sorbent-extraction was found to offer several advantages. A hybrid

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technique, based on existing SLM, FIA and chromatographic principles, was therefore developed.

The support was confined to a micro-column, which formed part of an FIA manifold. The organic phase was coated onto a porous support to form a supported organic phase that contained the extraction reagent, similar to the stationary phase used in sorbent extraction. When the sample solution passed over this supported membrane, the solute was extracted into the organic phase. In the proposed sequential mode of operation, a washing step can easily be carried out before retrieving the solute into a small volume of stripping solution.

Two geometries were proposed: A column containing spherical support beads resulted in high enrichment factors in a short time. This geometry is envisaged for selective enrichments in an automated fashion for laboratory use. The second geometry uses a robust tubular design which can be used for extended periods of unattended use, as required in process analysis.

Two stripping techniques was used: The entire organic coating was removed (total-removal) or the gold was leached from the SLM (back-extraction). Total removal is well suited to laboratory application, where the stripping solution can be analysed by various instrumental techniques. With back-extraction, the enriched gold is slightly more dispersed in the stripping media; however, the solution is free of organic contaminants. This solution is well suited to the spectrophotometric and electrochemical detectors envisaged for unattended use in the process environment.

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The potential of this technique was illustrated for future use in a process analyser. In the SLM system developed for the extraction of dicyanoaurate from process solutions, a precision (s_r) of 0,027 at the 0,04 mg/ dm^3 level was achieved. With an analysis time of less than 150 seconds per sample, a selective enrichment of more than 50 times was achieved with process solutions.

The use of SLMs in a sequential mode has several advantages over previous automated solvent-extraction methods.

- The support surface is used to effect phase separation **before** extraction of the analyte into the organic phase. This differs from the *modus operandi* of the FIA solvent extraction manifolds, and overcomes the problem of separating small volumes of organic phase from large volumes of aqueous phase.
- Micro-volumes of organic phase can be used, which reduces the cost of expensive organic extractants. Existing solvent-extraction technology can be applied on a micro-scale using the SLM approach. This opens up a vast range of selective, readily available extraction reagents.
- The organic phase forms a thin coating on the column surface and pores, exposing a high contact area to the aqueous phase. This results in preconcentration factors of more than 150-fold in less than 10 minutes, and ensures the efficient utilisation of the organic phase.

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- The solute-enriched organic phase can be removed entirely from the support (allowing only an extraction), or the selectivity can be enhanced by performing both an extraction and a back-extraction on the solute using a second aqueous phase.

6.2 FUTURE PROSPECTS

The study has illustrated the viability of SLMs in a flow-injection manifold for sample pretreatment in combination with various detection methods, by examining a specific and notably difficult selective enrichment problem. The process analyst can now include the developed technology in his toolkit of analytical techniques and use it in a variety of other applications. Also, the use of the FIA-SLM system can aid process chemists in developing SLM systems.

Sensors command much attention in the scientific literature for obvious reasons. Recent research has addressed the use of immobilised membranes in sensors. For the most part, these membranes have been solidified polymeric materials. The diffusion coefficients of solutes are typically an order of magnitude higher in liquids than in polymers. The present study illustrates the potential of SLMs as a stable and workable selective surface. Both optical and electrochemical sensors could benefit from this result.

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APPENDIX A

COMMUNICATIONS THAT RESULTED FROM THIS STUDY:

1. Barnes D.E. and J.F. van Staden **(1991)** 'Flow-injection as a diagnostic tool in the evaluation of solvent extraction processes based on supported liquid membranes' presentation at: The 31st South African Chemical Institute Conference, Grahamstown, South Africa,
2. Barnes D.E. and van Staden J.F. **(1991)** 'The use of Flow-injection analysis (FIA) in the evaluation of Supported Liquid membranes (SLMs)' presentation at FLOW ANALYSIS V, Kumamoto, Japan.
3. Barnes D.E. and van Staden J.F. **(1991)** 'Flow-injection analysis as a diagnostic tool in the evaluation of solvent extraction based on supported liquid membranes' presentation at the University of Pretoria, South Africa.
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5. Barnes D.E., Taylor M.J.C. and van Staden J.F. **(1992)** 'The extraction of gold using supported liquid membranes, 3rd International Symposium of IUPAC, Sandton, South Africa.
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