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Rapid Optimization of Chemical Parameters Affecting Supported Liquid Membranes

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ABSTRACT

Supported liquid membranes (SLMs) provide a flexible and selective approach to the separation and enrichment of chemical species. Traditional methods used to optimize the chemical and physical parameters of an SLM system have been found to be tedious and cumbersome. An alternative approach is suggested, and the application of the approach is demonstrated. The proposed approach depends on the optimization of principally the chemical components, with an indication of the impact of physical components on a scaled-down membrane arrangement. An in-situ measurement technique is used to monitor the effect of key parameters on important performance criteria.

INTRODUCTION

Supported liquid membranes (SLMs) have received considerable attention from a number of investigators because of their potential for the industrial-scale separation and enrichment of metal species. Their use in environmental applications for the cleanup of effluent streams has also received attention. SLMs have even been suggested as an attractive alternative to solvent extraction. Certain specific applications have been most successful—these are illustrated in the tables in the Appendix, where the potential of SLMs as a selective separation technique in the hydrometallurgical field is documented.

A typical SLM system consists of an organic phase, a support, and two aqueous solutions. The organic phase is immiscible in aqueous streams and contains the extractant, a diluent, and sometimes a modifier. The extractants are those typically used in solvent extraction. They can be present in trace amounts, or more often in significant amounts of up to 30% of the organic phase. The bulk of the organic phase consists of the diluent, which is usually an inert organic solvent, which acts as a solvent medium for the organic extractant. In some cases, however, the diluent 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, which usually favor the extraction of a certain selected species in a synergistic fashion, thus improving the selectivity of the SLM.

The support is typically an inert porous hydrophobic material, and it can be used in one of several geometries. The supports are often membranes commonly used for ultrafiltration. Common geometries available commercially include various flat sheets or hollow fibers. The organic solution permeates into the pores and coats the surface of the support, and the resulting thin film of organic solution forms the SLM. When an SLM is interposed between two aqueous solutions, it acts as a selective semipermeable 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 into the organic phase, and the complex diffuses through the membrane. On the opposite side of the membrane, the reaction between the solute and the extractant is reversed due to different prevailing conditions. In a specific case, the prevailing conditions favor the formation of a stronger complex between a counterion, 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.

Components of a SLM System

Several parameters affect the optimum mass transfer of the solute through the SLM. These are listed in Table 1, and they can be divided into two distinct groups. The physical parameters generally influence the diffusion rate through the SLM while the chemical parameters influence

TABLE 1
Parameters That Influence Permeation

Feed solution	Organic phase	Stripping solution	Physical parameters
Type of solute Concentration of solute pH value Type of buffer Concentration of buffer Ionic strength	Type of extractant Diluent Modifier Concentration of organic reagents Support	Type of counter/co-ion Concentration of counter/co-ion pH value Type of buffer Concentration of buffer Ionic strength	Flow rate of feed Flow rate of strip Contact area of SLM Geometry of SLM

the chemical reactions with their respective kinetic constraints which facilitate selective transport through the SLM (1).

The chemical reactions are associated mainly with the aqueous phases—the feed and stripping solutions and their boundaries with the organic phase. The diffusion process is determined largely by the composition of the organic phase. A convenient approach to the optimization of the various physical and chemical parameters is discussed in the following sections.

Evaluation Criteria

The optimization of specific SLM systems has been the subject of many papers, reviews, and monographs (1–15). In the evaluation of SLMs, various criteria have been proposed. The most common criteria used to evaluate a particular SLM system are flux, selectivity, enrichment, and stability (2, 3).

Flux

Flux, defined as the rate of mass transport of the solute through the SLM, is the criterion used most frequently for the evaluation of SLMs. 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 rate of diffusion (*dn*/*dt*) of a solute across an area (*A*), known as the diffusive flux (*J*), is calculated as follows (4):

$$J = (dn/dt) = -DA(dC/dx) \tag{1}$$

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.

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) (5–7).

$$J = DV \times \frac{dC}{Cdt} \tag{2}$$

where V is the volume of the feed solution and D is the diffusion coefficient. The diffusion 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 (5, 8).

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

$$P = \frac{J}{A} = \frac{dC}{Cdt} \times \frac{DV}{A} \tag{3}$$

This equation can be integrated to

$$\ln\left(\frac{C}{C_0}\right) = -\frac{PAt}{DV} \tag{4}$$

where C_0 is the initial feed concentration. Investigators have illustrated the validity of this equation, particularly for stationary and batch experiments (5, 9–11). 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 two different sets of mathematical equations.

The flux through SLMs is usually between 1.7 and 5 × 10^{-11} $\text{mol}\cdot\text{dm}^{-3}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ for a membrane with a typical thickness of 50 to 200 μm. Cox (12) found that this value is about the same as that observed for Donnan dialysis for the same area and thickness of membrane. Kreevoy (13) states that ". . . even with these best-case estimates it is hard to imagine a flux of more than 10^{-7} $\text{mol}\cdot\text{dm}^{-3}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ for current commercial polymer membranes with a minimum thickness of approximately 2.5 μm. . . ."

Enrichment Factors

The application of SLMs is often aimed at the enrichment of a solute as opposed to 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 have been used by various investigators (12, 14, 15) to study the enrichment obtainable with SLM systems.

The enrichment (Y) of a species is defined by Sato et al. (14) as the ratio of the concentration of the species in the stripping solution $[S_s]$ to its initial concentration in the feed solution $[S_f]$.

$$Y = [S_s]/[S_f] \tag{5}$$

The surface area of the SLM system is identified as one of the stronger deciding factors for enrichment. The feed and strip solutions can be recycled to reuse the membrane area many times and increase the effective enrichment. Cox (12) and Nishiki (15) stated independently that the enrichment factor in SLM systems increases in a logarithmic fashion with contact time. Nishiki (15) 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. From the literature, it is evident that the enrichment achievable with a specific SLM system is, like the flux, dependent on the particular situation and is usually determined empirically.

Selectivity

Extractants used for solvent extraction are seldom completely selective for any one solute. In a solvent extraction separation, a simple comparison of distribution coefficients is often sufficient to predict the success of the 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 thermodynamic equilibria but also on kinetics. These kinetic differences can also be used to good advantage. Differences in the kinetic behavior of compounds can be exploited to achieve an even greater degree of selectivity.

Danesi (5) 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. Because all the data for solving these equations are not always available (or easily determined), and because the equations do not always consider small changes that might be present in the selected system under investigation, most investigators prefer to determine these parameters empirically as well.

Danesi (5) also pointed out that the selectivity of an SLM depends more on kinetic behavior than on thermodynamic considerations. He showed, for example, that a more selective Co–Ni separation can be obtained using SLMs than with solvent extraction. The selectivity of the extraction was enhanced by decreasing the organic extractant 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 (S) of one solute over the next has also been defined as the ratio of the respective enrichments obtained for the species (14). Matsuyama (67) defined selectivity between cobalt and nickel in terms of their respective fluxes as

$$S = \frac{J_{\mathrm{Co}}}{J_{\mathrm{Ni}}} \frac{[\mathrm{Ni_F}]}{[\mathrm{Co_F}]} \tag{6}$$

The respective fluxes are usually determined empirically. 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. He also showed that the simultaneous transport of two metals at low concentrations can be achieved without the flux of one affecting that of the other (12).

Stability

The stability of a given SLM is one of the most difficult parameters to predict from a theoretical basis. This is due to the binary character of the SLM, which is a chemical as well as a physical entity. Most investigators establish the stability of SLMs empirically over a period of months.

Optimization Methodology

Even a cursory investigation of the literature reveals a large diversity in mechanisms, rate laws, and rate constants for similar SLM systems (13). Much of this apparent disagreement arises from small differences in the experimental conditions; for example, the use of a different diluent. Also, optimized experimental designs have been established using univariant optimization procedures. Where parameters are not independent, this is a dangerous approach as it is easy to optimize systems on local optima rather than the more desirable global optimum. Furthermore, in the experimental designs frequently used, swopping from one set of conditions to another is a tedious process—a most undesirable situation during development. These factors make optimization of SLM systems a manual and time-consuming process.

ALTERNATIVE METHOD OF OPTIMIZATION

In this paper a more systematic and convenient approach to the study and optimization of SLM systems is proposed. A key element of this approach is the use of an in-situ measurement technique incorporated into the optimization setup. The technique is called flow-injection analysis (FIA), and it is essentially an automated solution-handling technique.

Flow-Injection Analysis

FIA is widely used as a way to successfully address the automation of classical wet-chemical analytical procedures (16, 17). It is based on the reproducible introduction of a small, but well-defined, sample volume into a continuously flowing reagent stream which carries the sample to a flow-through detector. En route, the sample disperses into the reagent stream and reacts in a reproducible manner to form a detectable species. The chemical environment of the sample can be adjusted by a careful choice of the reagent solution or by merging various reagents with the reagent stream. The detector registers the passage of the sample bolus. The result is a flow-injection peak whose height (and area) indicates the concentration of the sample, and a baseline which is continuously monitored.

The dispersion process, relevant volumes, and the concentration of the various streams can be controlled precisely in space and time by the reproducible stopping, restarting, oscillating, mixing, splitting, and resampling of the flowing stream, or parts of it. Manifold design and repeatable flow patterns ensure reproducible reaction times. Furthermore, FIA permits the detection of a specific stage in the transient formation of complexes, particularly those that are too rapid for detection by normal batch operations.

FIA has led to dramatic improvements in the speed and quality of analysis. As an analytical technique, it has distinguished itself as a fast, precise, accurate, and extremely versatile analytical tool. A further advantage that has emerged in recent years is its proven suitability in both the laboratory and the process environment (18). FIA was found to offer an excellent solution to the requirements for an improved method for optimizing SLM systems. Simply stated, the FIA manifold was incorporated in an SLM test system. The size of the SLM was kept small in this investigation for the sake of convenience. This approach allows both a theoretical and an empirical study of SLMs. Inclusion of the FIA manifold in the test system provides a means of obtaining real-time data (with a frequency of 60 measurements per hour) on the SLM's performance. In addition, the chemical and physical parameters that influence the mass transfer through the SLM can easily be altered, thereby significantly reducing the time to develop a specific SLM system.

EXPERIMENTAL

Reagents

All reagents were of Analytical Reagent grade, and all aqueous solutions were prepared with deionized water. The FIA reagent solution 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 0.4 mol·dm^{-3} ammonia and 0.6 mol·dm^{-3} acetic acid. The organic solution contained 40% di-(2-ethylhexyl)-phosphoric acid (DEHPA) in various diluents. A 1.2 mol·dm^{-3} nitric acid solution was selected for the stripping solution, and the feed solution was buffered at pH 4 using a 1 mol·dm^{-3} ammonium acetate/acetic acid buffer.

Apparatus

SLM Unit

A small-scale SLM unit was constructed from two pieces of clear polyvinyl chloride (PVC) with a milled channel 0.5 mm deep, 1 mm wide, and 240 mm long (19). 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 solution, consisting of a diluent and extractant, was loaded onto the support in situ by injecting 500 μL of the organic mixture into one end of the SLM unit. The lipophilicity of the support caused the organic solution to coat the pores and surface of the support. Excess organic phase was flushed from the unit with distilled water. When required, the organic phase was removed from the support by injecting three 500 μL portions of acetone into the channel and then flushing with water.

FIA Manifold

The FIA manifold was linked to the membrane unit (Fig. 1). 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 the feed or the stripping streams. By passing one of these solutions through an injection valve, a reproducible volume of the stripping solution is introduced into the reagent

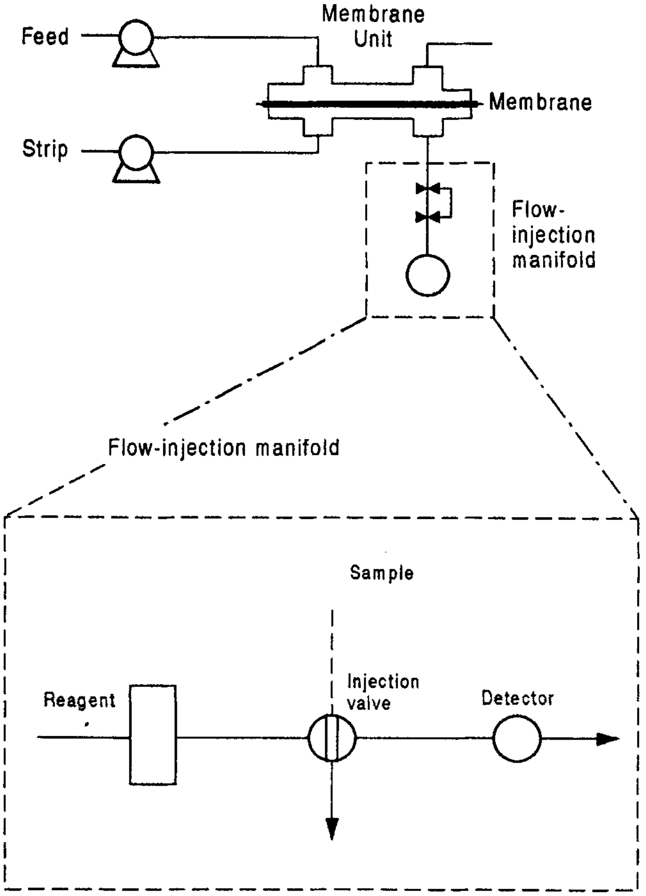

FIG. 1 SLM optimization system incorporating the flow-injection manifold.

solution at specific time intervals using a Valco injection valve (Valco model EC10W). The flowing reagent stream carries the sample to the flow-through detector. Various detectors can be implemented by a simple manifold change. In this particular SLM–FIA system, the concentration of the cation in the stripping solution was detected by its reaction with the PAR in the reagent stream. The resulting color was detected spectrophotometrically at 520 nm with a Jasco Uvidec 100 spectrophotometer.

Procedure

The parameters identified in Table 1 can be optimized according to the specified criteria using this SLM–FIA system. By determining the concentration of the solute in the stripping solution over a period of time, a wealth of information can be obtained on the behavior of the SLM.

When the effect of a particular parameter is to be determined, first the SLM is formed as described above. The selected feed solution and stripping solution are then passed over the SLM. In most experiments a feed solution of known composition is used, and only the stripping solution is monitored. The solute complexes with the extraction reagent on the surface of the membrane and is then transported through the SLM. On the other side of the membrane, the solute is stripped into the stripping solution. The stripping solution is introduced into the FIA manifold where it is analyzed. FIA, being a fast analytical technique, allows rapid analysis of the solution. The concentration of the solute in the stripping solution was determined at regular time intervals (typically every 60 seconds).

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 Fig. 2. The y-axis represents the permeation ratio, and the x-axis represents time elapsed. The time at which the feed solution comes into contact with the SLM is taken as the starting time for the performance profile.

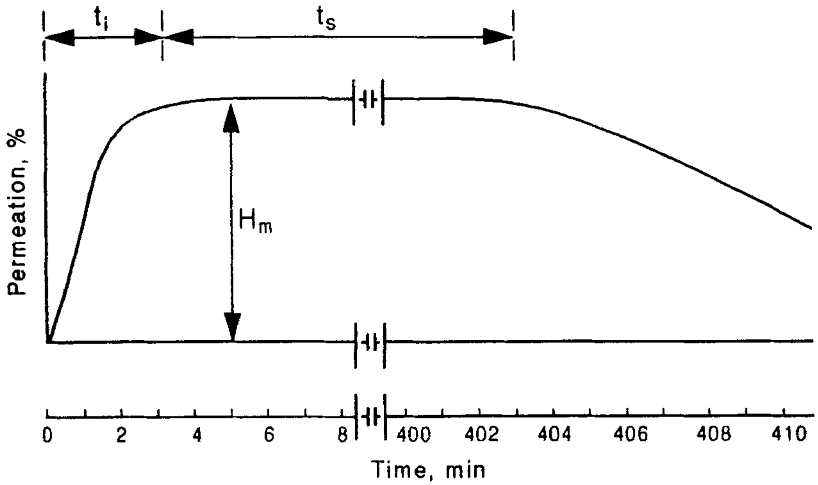

FIG. 2 Typical performance profile of an SLM. H_m = maximum permeation; t_i = initializing period; t_s = stability period (plateau). Note the discontinuity in the x-axis marked by the line breaks.

RESULTS AND DISCUSSION

Discussion of the Performance Profile

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 permissible to refer to permeation rate in terms of percentage permeation. (See Fig. 2.)

Three distinct periods can be identified in a typical performance profile: initial period (t_i) or formation period, the plateau (t_s), 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 backextraction also increases. The concentration of the solute in the stripping solution will increase steadily 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 large extent, on the diffusion rate of the solute through the SLM.

When a dynamic equilibrium is reached, 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 it 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 recognized by Kreevoy (13) 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 it is given by the time, t_s. This is the time that the maximum permeation, H_m, 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 onset of 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. Where a microprocessor-controlled FIA system is used (20), the experiment can proceed totally unattended. The relative stability (t_s) and flux (H_m) through the SLM are conveniently determined. The shape of the profile during the initial period (t_i) reflects on the kinetic behavior of the solute under the conditions prevalent in a specific SLM.

Performance profiles can also aid in the development of more selective systems. Selectivity was defined earlier in terms of the respective fluxes of the species of interest and their respective concentrations. If the total concentration of the competing species is low, the individual curves can be determined for the species of interest, and they will reflect the selectivity of a specific SLM system. At higher concentrations the feed solution will have to contain all the species, and the FIA system can be altered to track the permeation of each individual species.

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 varied include the support material used, the composition of the organic solution, the chemical composition of the feed and stripping solutions, the geometry (shape and size) of the support, the temperature, and the flow rate of the streams. The influence of these parameters on the permeation rate (H_m), stability (t_s), enrichment E, and selectivity can be easily evaluated.

Evaluation of SLMs with Different Diluents

The potential of the proposed method is demonstrated in the evaluation of various diluents for the extraction of copper with DEHPA. In the development of a specific SLM, one would typically begin with a literature survey. A selection of possible cation, anion, and neutral extractants has been compiled from the literature (Appendix). 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 exhaustive. They do, however, serve as a starting point and reference for a study of SLMs.

The extensive literature describing conventional solvent–extraction systems should also be consulted. Extraction curves are available for most commercially available extractants and can aid in the selection of an SLM system. These curves serve as the basis for selecting the pH conditions for both the feed and the stripping solutions. Further optimization for the SLM environment is invariably necessary. Consider the extraction curve for copper with DEHPA (Fig. 3). The region where maximum extraction occurs (pH > 4) specifies the pH conditions under which copper will be extracted from the aqueous solution. A feed solution at this pH value

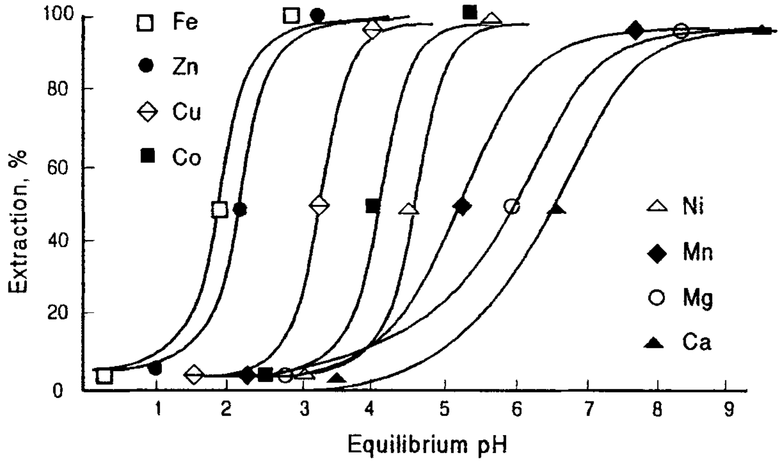

FIG. 3 Extraction curves of various cations with DEHPA.

supports the formation of a copper–extractant complex that will partition into the organic phase. The region of minimal extraction (pH < 2.3) indicates the pH conditions where copper is not extracted to any appreciable extent. Under these conditions the extractant will preferentially combine with a proton, and the solute will partition into the aqueous phase. A solution at this pH value is therefore ideal as a stripping solution.

Various organic solvents are used as diluents in solvent–extraction processes. In industry the choice of organic diluent 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 (22), hydrophobicity, and a low viscosity (23) are also considered. The choice of the organic diluent for an extraction process can be a vital parameter affecting efficient extraction. At present, in solvent extraction, an organic diluent is usually chosen by trial and error or by previous experience. Cussler (24) states that the chief requirement for choosing an SLM diluent is a combination of intuition and good luck. This is also true for SLM systems. To add to the dilemma of choosing an appropriate diluent, most organic diluents produced on an industrial scale vary in their composition (25). Furthermore, 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 coextracting species, is also of the utmost importance. It became clear that the best organic diluent for a particular SLM cannot be easily predicted a priori.

To illustrate the potential of the SLM–FIA system, we evaluated the effect of different diluents on the performance of the SLM. Various organic phases were prepared that all contained the same amount of extractant, diluted using a selection of diluents.

The performance profiles for each organic solution were determined. The results are summarized in Table 2. The SLMs were evaluated by comparing the following factors.

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. This is the period that the permeation could be maintained in a specific environment. It is important to note that 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 degradation of the SLM and allowing a greater number of stability tests to be carried out in a given time.

The time that the system takes to reach equilibrium, t_i, reflects on the resistance of the membrane to mass transfer.

TABLE 2
Physical Properties and Optimization Parameters for Selected Diluents Used in the Organic Phase of SLMs

Diluent	Viscosity (cP)	Solubility in water (g·100 cm^{-3})	Dielectric constant	Density (g·cm^{-3})	t_i	t_s^a	H_m
Ethers and ketones:							
Acetone	0.32	Miscible	21.4	0.79	3	0	2
Methyl-iso-butyl ketone	—	1.700	13.1	0.80	5	10	3
Di-iso-butyl ketone	—	5.000	18.3	0.93	28	15	15
Diethyl ether	0.23	6.040	4.3	0.74	11	15	4
Aromatic diluents:							
Benzene	0.65	0.18	2.3	0.88	5	5	8
Toluene	0.59	0.080	4.8	0.87	3	5	13
Pyridine	0.94	Miscible	12.4	0.98	2	3	3
Diethylbenzene	—	Immiscible	2.5	0.88	12	∞	23
Triethylbenzene	—	Immiscible	—	—	9	∞	18
Aliphatic diluents:							
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
Fatty acid mixture	—	Immiscible	2.7	0.90	30	15	32
Halo-alkanes							
Carbon tetrachloride	0.97	0.008	2.2	1.80	10	∞	18
Dichloroethane	0.79	0.900	10.6	1.25	5	10	5
Dichloromethane	0.43	2.00	9.1	1.32	15	10	4
Chloroform	0.57	1.000	5.0	1.48	4	10	8

[a] ∞ = the SLM was stable for more than 3 hours under conditions of accelerated degradation.

Ethers, ketones, and long-chain alcohols are often used as diluents for solvent extraction. However, SLMs with organic diluents that contain a hetero-atom such as an oxygen or nitrogen tend to be more soluble. These SLMs are relatively more soluble in water than other organic diluents (Table 2), therefore they result in less stable SLMs, as indicated by the short period, t_s. The organic phases of the SLM using these diluents are lost in a short time. With the exception of di-iso-butyl ketone (DIBK), the permeation rate of copper through the SLMs that contained ethers and ketones was very much lower than those with the aliphatic diluents, as indicated by the smaller H_m values. This can be ascribed to the fact that the permeation of the copper will be more torturous through oxygen-containing organic solvents due to electrostatic interactions. A higher permeation rate was observed for the SLM containing DIBK compared to methyl-iso-butyl ketone (MIBK). This can be explained by the relative lack of stability of an MIBK-containing SLM. The time (t_i) needed to establish the maximum permeation rate of the SLM containing DIBK appears to be excessively long; this is attributed to its high viscosity. The high permeation rate was, however, not maintained due to the solubility of DIBK in aqueous solutions (5 g/100 cm^3).

SLMs with toluene and benzene as diluents 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 $mol \cdot dm^{-3}$ nitric acid was used as the stripping solution. At a lower concentration of nitric acid (0.25 $mol \cdot dm^{-3}$), 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 2) explains the incomplete formation of an SLM.

The diluents with low solubilities in water resulted in stable SLMs. Diethylbenzene (DEB) and triethylbenzene (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 3 hours under the severe conditions used.

SLMs incorporating aliphatic diluents such as pentane and petroleum ether rapidly reached their H_m values. Comparison of the respective t_i values indicated that the diffusion of the copper through these two SLMs reach maximum permeation much faster than in the case of SLMs containing other diluents. The maximum permeation, H_m, is also much higher in these membranes, indicating a faster overall transport rate through the SLM. This confirms the general observation that prevailing diffusion rates are faster in diluents with unsubstituted molecules. However, pentane suffers the disadvantage of a high volatility and a low boiling point (36°C), resulting in spurious bubbles in the system due to physical loss of the organic phase. In a plant environment, an SLM containing this diluent would need to be reconditioned often.

The fatty-acid mixture (long-chain unsaturated carboxylic acids) resulted in a 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.

The behavior of SLMs containing halogenated solvents was also evaluated. Carbon tetrachloride forms a very stable SLM with high permeation, suitable to use in macro processes. SLMs containing the other halogenated 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 formation of the SLM and its stability. Of course, the environmental impact of carbon tetrachloride and certain other solvents may preclude their commercial use.

The results of the investigation clearly show that, with regard to their permeation characteristics and stabilities, the different organic solvents tested produce vastly different SLMs. In general, it appears that an increase in the viscosity of the organic phase leads to a lower permeation rate (H_m) with a respective increase in the time it takes to reach this value. Organic solvents used in hydrometallurgical processes are usually of low viscosity in order to improve the permeation rates, and a similar principle holds for SLMs. The stability of the SLM, on the other hand, is determined mainly by the solubility of the diluent in the feed and stripping solutions, and the dielectric constant. An insoluble diluent with a low dielectric constant usually yields a stable SLM.

CONCLUSION

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

An alternative method of optimization is proposed, and it has been tested by means of a specific example. An SLM test unit was designed which incorporates a FIA manifold for system monitoring. FIA, being a fast analytical technique, allows the rapid analysis of the various solutions. 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 is done by way of permeation profiles. The concentration of the solute in the stripping solution can be expressed as a percentage ratio of the concentration present in the feed solution.

The performance profiles for different SLMs are easily obtained. Several parameters can be conveniently changed, and criteria such as the permeation rate, stability, enrichment, and selectivity can easily be evaluated for each individual SLM. 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.

Evaluation of the three zones of a specific permeation profile provide a wealth of information on the mass transport through the SLM. 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 it can be calculated from the height of the plateau. This will be the rate of the slowest stage in the overall permeation. The time period during which 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 can be used to compare their relative stability and flux through the SLM.

The choice of extractant and diluent and their respective concentrations for an SLM is not a trivial task, and their selection still remains an empirical procedure. The effect of the diluent on both the stability and permeation rate through the SLM was found to be substantial, and the different organic diluents tested produce vastly different SLMs. In these empirical studies, the SLM–FIA unit can be extremely useful as a simple and powerful investigative tool.

Furthermore, once a particular SLM system has been selected on the micro-scale, the same FIA manifold can assist in the monitoring of pilot-scale or full-scale processes to further the optimization or control critical process parameters. By substituting the experimental SLM unit with a full-scale SLM process, both the feed and the stripping solution can be monitored. This development promises to be a major step forward in the study of SLM-based extraction processes for both the analyst and the hydrometallurgist.

APPENDIX

Three tables are presented: 1) SLM systems for the extraction of anions, 2) SLM systems using cation extractants, and 3) SLM system using neutral extractants.

APPENDIX TABLE 1
SLM Systems for the Extraction of Anions[a]

Element	Feed	Extractant	Diluent	Modifier	Strip	Geometry	Refs.
Am	HCl	CMPO	DEB	—	HCOOH	Flat sheet	26
Am	HCl	CMPO	DEB	—	HCOOH	—	27
Am	Acid waste	CMPO	Decalin	TBP	0.5 mol·dm^{-3} citrate	Tubular	26, 28
Cd	2 mol·dm^{-3} NaCl/0.1 mol·dm^{-3} HCl	TLACl	TEB	—	NaAc/NaCl	Stirred flat sheet	29
Cd	HCl	Alamine 336	Xylene	—	NaAc	Capillary membranes	7
Cd	HCl	Alamine 336	Xylene	—	NaAc	Flat sheet	7
Cd, Zn	0.5 mol·dm^{-3} HCl	TLACl	TEB	—	NH_4Ac	Flat sheet	10, 30
Cd	1 mol·dm^{-3} NaCl	Alamine 336	*n*-Heptane	—	0.5 mol·dm^{-3} NH_4Ac/NH_4Cl	Flat sheet	31
Co, Ni	8 mol·dm^{-3} LiCl/0.3 mol·dm^{-3} HCl	TLAHCl	Decalin/DIPB	—	pH 6	Composite membranes	32
Cr	—	Alamine 336	Escaid 350	—	—	Tubular	33
Cr	Acidic	Adogen 382	SHELLSOL K	—	NaOH	Hollow fiber	34
Cr	Acidic	TBP	SOLVESSO 150	—	NaOH	Hollow fiber	34
Cr	Acidic	Adogen 283	SHELLSOL K	—	NaOH	Hollow fiber	34
Cr(VI)	H_2SO_4, pH 2	LA-2	*n*-Dodecane	—	0.1 mol·dm^{-3} NaOH	Stirred flat sheet	13, 35
Cr(VI)	Water	Aliquat 336	Kerosene	—	LiCl	Stirred flat sheet	36
Cr(VI)	—	Aliquat 336	Kerosene	—	4 mol·dm^{-3} LiCl	Flat sheet	31
Cr(VI)	H_2SO_4, pH 1.6	PDPP	Nitrobenzene	—	Ammonia	Multi-layer flat sheet	37
Cr(VI)	pH 4.7	TOMAC	*n*-Dodecane	2-Ethylhexyl alcohol	NaOH	Spiral type	2
Cr(VI)	pH 1.0–3.0	TOA	Shellsol AB	2-Ethylhexyl alcohol	NaOH	Spiral type	38
Cu	HCl	Oxime	Toluene	—	HCl	—	27
Cu	pH 1 to 4	Acorga P5300	Kerosene	—	H_2SO_4, pH 0.5	Stirred flat sheet	61
Cu	$CuSO_4$, pH 5.5	LIX 65N	Kerosene	—	0.2 mol·dm^{-3} H_2SO_4	Tubular	28, 62
Cu	pH 1 to 4	Kelex 100	Kerosene	—	H_2SO_4, pH 0.5	Stirred flat sheet	61
Cu	pH 1 to 4	Acorga P5100	Kerosene	—	H_2SO_4, pH 0.5	Stirred flat sheet	61

Cu	pH 3	N 503	PC801	—	H_2SO_4	Flat sheet	63
Cu	HAc/NaAc	DEHPA	Various	—	HNO_3	Flowing flat sheet	19
Cu	pH 2.5	Kelex 100	Kerosene	—	Formic acid	Stirred flat sheet	56
Cu	pH 2.5	Kelex 100	Kermac 470B	—	1 mol·dm^{-3} H_2SO_4	Tubular	45
Cu	HAc/NaAc	β-Hydroxy-oxime	Toluene	—	1 mol·dm^{-3} HCl	Sheet	64
Cu	pH 3.5	LIX 64N	Paraffin	—	NaAc	Stirred flat sheet	65
Cu	—	SME 529	Dispersol	—	2 mol·dm^{-3} H_2SO_4	Tubular	28, 38
Cu	pH 2.5	LIX 63	Kerosene	—	Formic acid	Stirred flat sheet	56
Cu	pH 4 to 6	LIX 54-100	Kerosene	—	2.1 mol·dm^{-3} H_2SO_4	Stirred flat sheet	62
Cu	pH > 7	LIX 64N	Octanol	—	1 mol·dm^{-3} H_2SO_4	Flowing flat sheet	60
Cu, Ni, Co	HAc buffer	PS-Diphenyl thiocarbazon	Chloroform	—	1 mol·dm^{-3} HNO_3	Sheet	66
Cu, Zn	pH 3	LIX 64N	Kerosene	—	pH 1	Hollow fiber	36
Cu, Zn	NaOH	D2EHPA	Kerosene	—	1 mol·dm^{-3} HCl	Stirred flat sheet	36
Cu, Zn	HAc/NaAc	D2EHPA	—	—	HCl	Hollow fiber	14
Er	pH 3	DTMPPA	TMB	—	1 mol·dm^{-3} HCl	Stirred flat sheet	67
Eu	0.1 mol·dm^{-3} HNO_3	DIDPA	1-Octanol	1-Octanol	5 mol·dm^{-3} HNO_3	Flat sheet	68
Eu	HCl	D2EHPA	Xylene	—	1 to 2 mol·dm^{-3} H_2SO_4	Stirred flat sheet	69
Fe	4 mol·dm^{-3} HCl	TBP	Toluene	—	0.05 mol·dm^{-3} HCl	Flat sheet	40
Fe	4 mol·dm^{-3} HCl	Aliquat 336	Kerosene	TBP/decanol	0.05 mol·dm^{-3} HCl	Flat sheet	40
Fe, Ni, Co	LiCl	TLACl	Triethylbenzene	—	0.1 mol·dm^{-3} HCl	Stirred flat sheet	13, 35
D-Glucosamine	—	ODOBA	—	—	—	Stirred flat sheet	39
H	$NaNO_3$	TOPO	DEB	—	NaOH	—	27
H	$NaNO_3$	Primene	DEB	—	NaOH	—	27
H	$NaNO_3$	CMPO	DEB	—	NaOH	—	27
H	$NaNO_3$	CMPO	DEB	—	NaOH	—	27
H	$NaNO_3$	TLA	DEB	—	NaOH	—	27
H	$NaNO_3$	TLA	Dodecane	—	NaOH	—	27
HCl	HCl/NaCl	TLA	iso-Propylbenzene	—	NaOH/NaCl	Stirred flat sheet	41
NO_3	H_2SO_4, pH 2	LA-2	*n*-Dodecane	—	0.1 mol·dm^{-3} NaOH	Stirred flat sheet	42
Nd, Ce	0.2 mol·dm^{-3} HNO_3/3 mol·dm^{-3} $NaNO_3$	OPDIBCMPO	Decalin	—	pH 2	Composite membranes	22
Np	Acid waste	CMPO	Decalin	TBP	0.5 mol·dm^{-3} citrate	Tubular	26, 28

(continued)

APPENDIX TABLE 1 Continued

Element	Feed	Extractant	Diluent	Modifier	Strip	Geometry	Refs.
Pt	HCl	TOA	Xylene	—	$Na_2CO_3/NaOH$	Flat sheet	15
Pt	HCl	TOA	Xylene	—	$Na_2CO_3/NaOH$	Flat sheet	43
Pu	Acid waste	CMPO	Decalin	TBP	0.5 mol·dm^{-3} citrate	Tubular	26, 28
Te(VII)	H_2SO_4, pH 2	TLA	*n*-Dodecane	—	0.1 mol·dm^{-3} NaOH	Stirred flat sheet	42
U	0.1 mol·dm^{-3} H_2SO_4	TOA	Kerosene	—	Na_2CO_3	Stirred flat sheet	44
U(VI)	Various	D2EHPAM2EHE	Kerosene	1-Decanol	0.5 mol·dm^{-3} HNO_3	Sheet	68
U	3 mol·dm^{-3} HNO_3	D2EHPA	Shellsol 2046	—	Na_2CO_3	Sheet	78
U	0.5 mol·dm^{-3} HNO_3	DEHPA	Kerosene	—	5 mol·dm^{-3} H_3PO_4	Stirred sheet	79
U(VI)	HAc buffer, pH 4	Kelex 100	Kerosene	—	0.1 mol·dm^{-3} HNO_3	Stirred sheet	80
U(VI)	HAc buffer, pH 4	Kelex 100	Kerosene	—	0.1 mol·dm^{-3} HNO_3	Stirred sheet	81
Y	pH 3	DTMPPA	Trimethylbenzene	—	1 mol·dm^{-3} HCl	Stirred sheet	10, 73
Zn	HAc buffer, pH 5	Dithiozone	Carbon tetrachloride	—	HCl, pH 2	Stirred sheet	82
Zn	pH 2	DEHPA	Kerosene	—	pH 1	Stirred sheet	11
Zn	pH 4.7 to 6.0	Cyanex 272	Dodecane	—	0.1 mol·dm^{-3} HCl	Stirred sheet	12
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	22
Zn	HAc/NaAc	DEHPA	Chloroform	—	1 mol·dm^{-3} HCl	Flowing sheet	48

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

APPENDIX TABLE 2
SLM Systems Using Cation Extractants[a]

Element	Feed	Extractant	Diluent	Modifier	Strip	Geometry	Refs.
Al	Cu solutions, pH 2 to 3.6	DEHPA	Escaid 200	—	2 to 5 mol·dm^{-3} H_2SO_4	Stirred flat sheet	48, 49
Amines	NaOH	DEHE	*n*-Undecane	—	H_2SO_4	Flowing flat sheet	50
Ag	$HClO_4$/HAc buffer	TTD	*m*-Chlorotoluene	—	0.1 mol·dm^{-3} thiosulfate	Flat sheet	51
Ca	pH 11	D2EHPA	—	—	pH 1	Flat sheet	52
Ce	Acid perchlorate	D2EHPA	Nitrobenzene	—	No strip	Suspended PU-foam	53
Co, Ni	pH 6	DTMPPA	Decalin/DIPB	—	8 mol·dm^{-3} LiCl/0.3 mol·dm^{-3} HCl	Composite membranes	32
Cr(III)	Water	DNNSA	*o*-Xylene	—	pH 4.5	Stirred flat sheet	36
Cr(III)	pH 4.2	DNNSA	*o*-Xylene	—	0.5 mol·dm^{-3} H_2SO_4	Flat sheet	31
Cu	—	LIX 64N	Paraffin	—	H_2SO_4	Flat sheet	52
Cu	0.5 mol·dm^{-3} HAc/NaAc	LIX 64N	Kerosene	—	H_2SO_4	Stirred flat sheet	54
Cu	pH 5.0	LIX 64N	Dispersol	—	H_2SO_4	Flowing flat sheet	55
Cu	pH 2.5	LIX 70	Kerosene	—	Formic acid	Stirred flat sheet	56
Cu	pH 2.5	LIX 64N	Kerosene	—	Formic acid	Stirred flat sheet	56
Cu	NaOH	LIX 84	Decane	—	HCl, pH 2	Hollow fiber	57
Cu	—	LIX 65N	Kerosene	—	H_2SO_4	Flat sheet	58
Cu	NaOH	LIX 84	Kerosene	—	HCl, pH 2	Hollow fiber	57
Cu	pH 2 to 4	LIX 64N	Decalin	—	2 mol·dm^{-3} H_2SO_4	Tubular	13
Cu	0.5 mol·dm^{-3} HAc/NaAc	D2EHPA	Dodecane	—	1 mol·dm^{-3} HNO_3	Hollow fiber	59
Cu	pH > 7	LIX 65N	Octanol	—	1 mol·dm^{-3} H_2SO_4,	Flowing flat sheet	60
Cu	pH 4	Agorga P5100	*n*-Decane	—	—	Tubular	33
Cu	pH 1 to 4	LIX 64N	Kerosene	—	H_2SO_4, pH 0.5	Stirred flat sheet	61
Cu	0.1 mol·dm^{-3} Hac	SME 529	Dispersol	—	2 mol·dm^{-3} H_2SO_4	Tubular	2
Eu	HCl, pH 2	HDEHP	*n*-Dodecane	—	1 mol·dm^{-3} HCl	Stirred flat sheet	70
Eu	1 mol·dm^{-3} $HClO_4$	CMP	Kerosene	1-Decanol	0.1 mol·dm^{-3} HNO_3	Flat sheet	71
Ga	—	IPE	*n*-Dodecane	—	HCl	Stirred flat sheet	55

Ga	—	2-Bromo-decanoic acid	*n*-Dodecane	—	HCl	Flat sheet	72
H	HCl, pH 2	HDEHP	*n*-Dodecane	—	1 mol·dm^{-3} HCl	Stirred flat sheet	70
In	—	TBP	*n*-Dodecane	—	HCl	Stirred flat sheet	55
In	—	DTPPA	*n*-Dodecane	Cyanex 272	HCl	Flat sheet	72
Ni	pH > 7	LIX 65N	Octanol	—	1 mol·dm^{-3} H_2SO_4	Flowing flat sheet	60
Ni	pH > 7	LIX 64N	Octanol	—	1 mol·dm^{-3} H_2SO_4	Flowing flat sheet	60
Ni	0.1 mol·dm^{-3} HAc	2EHPAM2EHE	*n*-Dodecane	—	3 mol·dm^{-3} HCl	Stirred flat sheet	10, 73
Ni, Co	HAc	Cyanex 272	Decalin	—	HCl, pH 3	Hollow fiber	5
Ni-Co	HAc, pH 6	Dialkylphosphonic acid	Decalin	DIPB	HCl, pH 1	Fibers	6, 74
Rare earths	HAc	TBEP	Ethers	—	0.05 mol·dm^{-3} H_2SO_4	Flat sheet	75
U	$NaClO_3$	DEHPA/TOPO	Kerosene	—	6 mol·dm^{-3} H_3PO_4	Flowing flat sheet	76
U	pH 4 to 5	LIX 63	Kerosene	—	0.1 mol·dm^{-3} H_2SO_4	Flat sheet	77
U	3 mol·dm^{-3} HNO_3	D2EHPA	Escaid 100	TOPO	$(NH_4)_2CO_3$	Flat sheet	52
U	pH 1	Alamine 336	Aromatic 150	—	2 mol·dm^{-3} Na_2CO_3	Tubular	45
U	Acid waste	CMPO	Decalin	TBP	0.5 mol·dm^{-3} citrate	Tubular	26, 28
U	pH 1	Alamine 336	Aromatic 150	—	Formate or HAc	Flat sheet	46
UO_2	HCl, pH 1	Alamine 336	Aromatic 150	—	NaAc	Flat sheet	47
Zn	pH 1	TOA	*n*-Dodecane	—	1 mol·dm^{-3} HCl	Tubular	5, 28
Zr	10 mol·dm^{-3} HNO_3	TBP	Xylene	—	—	Flat sheet	42

[a] 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% paraffin.
OMTPP: Oxomolybdenum(V)-tetraphenylporphyrin.
ODOBA: 4-Octyldecyloxybenzalsehyde.
PDDP: 3-(4-Pyridyl)-1,5-diphenyl pentane.
Primene: Alkyl (C_{18}–C_{24}) amine.
TOA: Trioctylamine.
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% paraffin.
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.

APPENDIX TABLE 3
SLM Systems Using Neutral Extractants[a]

Element	Feed	Extractant	Diluent	Modifier	Strip	Geometry	Ref.
Amines	0.1 mol·dm^{-3} NaOH	Aliphatic solvents	—	—	0.05 mol·dm^{-3}	Flowing flat sheet	83
Au, Ag	Potassium solution	Kryptofix 22 DD	Decanol	—	H_2SO_4	Stirred flat sheet	84
CO_2	High pressure	Sodium carbonate buffer	—	—	Distilled water	Stirred flat sheet	85
CPAA	H_2SO_4	Aliphatic solvents	—	—	Low pressure	Flat sheet	86
H_2S	High pressure	Sodium carbonate buffer	—	—	Phosphate buffer	Stirred flat sheet	85
K	$pH > 10$	Crown ethers	NPOE	—	Low pressure $pH < 10$	Flat sheet	87

[a] CPPA: Chlorophenoxyalkanoic acids.
NPEO: 2-Nitrophenyl-*n*-octylether.
Kriptofix 22 DD: Macrocyclic ether.

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