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## Analytical Applications of Transport Through Bulk Liquid Membranes

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### ABSTRACT

This review discusses the results of research in the use of bulk liquid membranes in separation processes and preconcentration for analytical purposes. It includes some theoretical aspects, definitions, types of liquid membranes, and transport mechanism, as well as advantages of using liquid membranes in laboratory studies. These concepts are necessary to understand fundamental principles of liquid membrane transport. Due to the multiple advantages of liquid membranes several studies present analytical applications of the transport through liquid membranes in separation or preconcentration processes of metallic cations and some organic compounds, such as phenol and phenolic derivatives, organic acids, amino acids, carbohydrates, and drugs. This review presents coupled techniques such as separation through the liquid membrane coupled with flow injection analysis.

### KEYWORDS

Anions and organic compounds; bulk liquid membranes; flow injection analysis; separation or preconcentration of metallic cations

## Introduction

### General principles

The term of *liquid membrane* has appeared since 1902 when a system consisting in an oily phase that separates two electrolyte solutions was studied (Nernst and Riesenfeld, 1902). This concept became widely known in 1968 when Li patented hydrocarbon separation through a liquid membrane (Li, 1968). The membrane is a semipermeable barrier that separates two phases (Kislik, 2009). In particular, for liquid membranes these consist of two aqueous phases separated by an organic phase. The two aqueous phases are known as source phase, feed phase, or donor phase and receiving phase, stripping phase, or acceptor phase; they are separated by an immiscible with water organic phase called a liquid membrane. The transport of a solute through a liquid membrane, known also as pertraction, represents an alternative to classical liquid-liquid extraction. In practice membrane extraction represents a variant of liquid-liquid extraction in which the extraction and re-extraction take place in a single step (Stanisław and Szczepański, 2011; Szczepański and Wódzki, 2013; Szczepański et al., 2014).

Recognized advantages of liquid membrane separations such as simplicity in concept and operation, low energy consumption, and selectivity led to intense research for the use of liquid membranes in various fields. Among these areas we can include organic, inorganic, and analytical chemistry, biomedical engineering, and wastewater treatment. Thus, separation or recovery of organic compounds (Branco et al., 2008; Fathi et al., 2011; Kubisova et al., 2002), toxic metals (Dalali et al., 2012; León and Guzman, 2008; Zhang et al., 2009), and fermentation products (Cascaval et al., 2003, 2004a, 2004b) were realized.

### Types of liquid membranes

These liquid membrane applications are carried out using different types of liquid membranes. Depending on the possible configurations that liquid membranes can adopt these can be classified as bulk liquid membranes (BLM), emulsion liquid membranes (ELM), and supported liquid membranes (SLM) (Belova et al., 2014; Ghoshal and Saha, 2014; Kamiński and Kwapiński, 2000; Kislik, 2009; Moyo and Tandlich, 2014; San Roman et al., 2010). The most well-known type of liquid membrane is the bulk liquid membrane. A bulk liquid membrane (BLM) consists of a bulk aqueous feed and receiving phases separated by a bulk organic, water-immiscible liquid phase (Kislik, 2009). A graphical representation of this type of liquid membrane is presented in Figure 1. There are many classification criteria for liquid membranes, depending on the configuration of the experimental device and on the density of the feed and stripping phase and of the membrane. Based on the design of the experimental device, there are several types: membrane wall in wall (Figure 1(a), showing a dilution of the stripping phase, and Figure 1(b), showing a concentration of the stripping phase), U-type membrane (Figure 1(c)), and H-type membrane (Figure 1(d)). Depending on the density of the aqueous phases and of the membrane they can be classified as liquid membranes with density higher than water (Figure 1(a)–1(c)) and with density lower than water (Figure 1(d)). This type of membrane, BLM, will be further detailed in this review.

Another type of membrane is emulsion liquid membranes. This is a particular type of configuration because the membrane consists of a surfactant-stabilized emulsion in which the receiving phase is found. This is dispersed in an aqueous feed phase

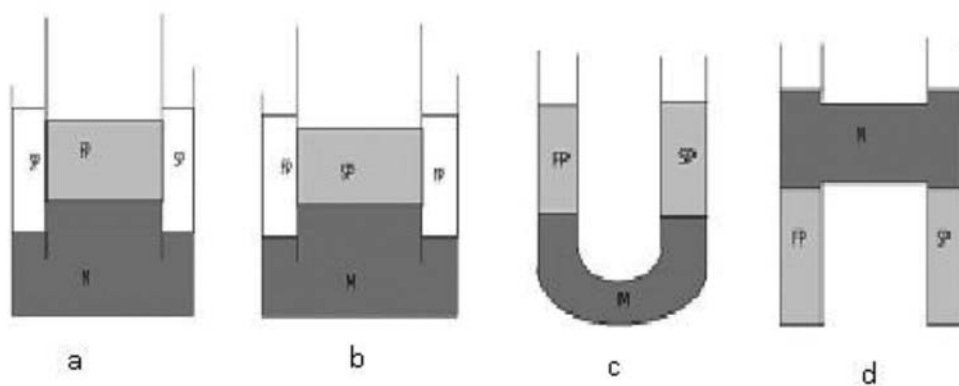


Figure 1. Experimental devices for BLM: (a) and (b) wall in wall, (c) U-type, and (d) H-type.

called the external phase (Ahmad et al., 2011; Berrios et al., 2010; Fathi et al., 2012; Ho and Li, 1992). For this type of membrane the extraction and re-extraction take place simultaneously. The typical process for emulsion liquid membranes consists in three steps: (1) the preparation and dispersion of fine droplets in oil, (2) the permeation of the solute through the membrane, and (3) the stabilization of the solution and of the external phases followed by the breakage of the emulsion in order to recover the membrane phase (Ahmad et al., 2011; Mokhtari and Pourabdollah, 2015).

The disadvantages of emulsion liquid membranes are: the forming of the emulsion; the stability of the emulsion, which depends on a large number of factors; and the breakage of the emulsion in order to recover the membrane phase and also recover the separated substances (Kamiński and Kwapiński, 2000; Kislik, 2009; Teng and Talebi, 2012).

Another type of membrane is supported liquid membrane. In this case a thin organic film is immobilized on an adequately inert micropore polymeric support forming a liquid immobilized membrane, or, as it is generally known, a supported liquid membrane (Jönsson and Mathiasson, 2001; Kislik, 2009; Parhi, 2013). This membrane system also consists of three phases; the supported liquid membrane is interposed between the aqueous feed and stripping phase. The configurations of the supported liquid membranes are flat sheet supported liquid membranes and hollow fiber supported liquid membranes. Detailed descriptions of these configurations are found in various reviews and studies (Jönsson and Mathiasson, 2001; Kislik,

2009; Kocherginsky et al., 2007; Parhi, 2013; San Roman et al., 2010; Trtić-Petrović and Jönsson, 2005). The main disadvantage of supported the liquid membrane is its stability, which can be affected by a series of factors such as the elution of the liquid membrane, the stability of the polymeric support, and the possibility of forming of an emulsion in the liquid phase, among others (Jönsson and Mathiasson, 2001; Kamiński and Kwapiński, 2000; San Roman et al., 2010;).

#### Transport mechanisms for bulk liquid membranes

In order to discuss the analytical applications of liquid membranes it is necessary to explain the transport mechanisms that govern the transport through liquid membranes. The main types of mechanisms of transport through liquid membranes are: simple transport, facilitated transport, and active transport (Kislik, 2009; López-López et al., 2010; Noble and Stern, 1995).

The simple transport of a solute takes place when it crosses the liquid membrane due to its solubility in the membrane and due to a concentration gradient between the aqueous phases of the membrane system. The efficiency of transport with this mechanism is low (Figure 2(a)). Uphill transport and selectivity were improved by introducing a compound in the stripping phase that irreversibly transforms the solute into an inactive compound for membrane transport (Figure 2(b)). Using this mechanism the transport and concentration of organic compounds such as phenolic and phenolic derivatives and carboxylic acids (Cichy et al., 2005; Galaction et al., 2007) were realized.

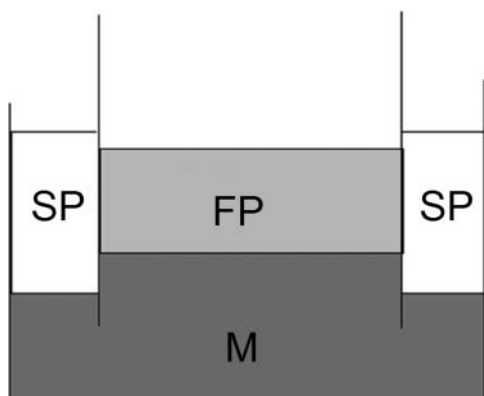


Figure 1(a).

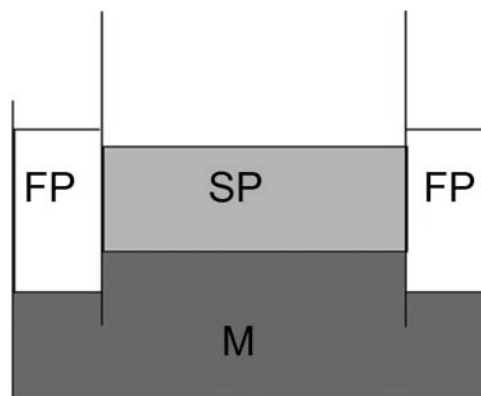


Figure 1(b).

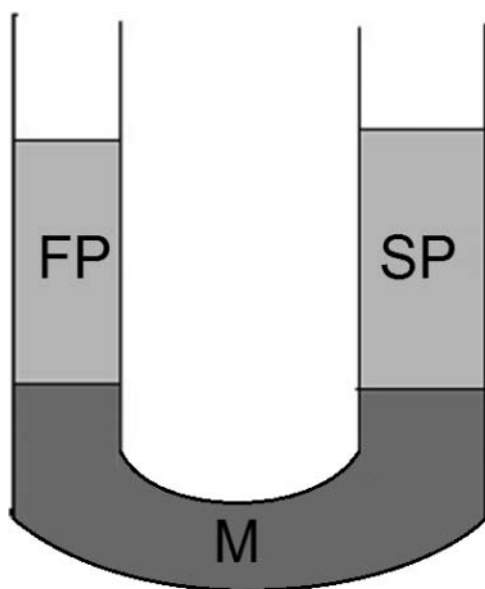


Figure 1(c).

Assisted or facilitated transport (assisted by carriers) takes place when a compound, called a carrier, is dissolved in the membrane. This compound is able to react with the solute at the interface of the feed phase and membrane. At the interface of

the membrane and stripping phase the decomplexation takes place, and the regeneration of the carrier and the accumulation of the solute in the stripping phase as a compound inactive for transport (Figure 2(c)). For example, in the transport of  $\text{Hg}^{2+}$  through a BLM containing calix [4] arene thioalkyl derivative as a carrier (Minhas et al., 2010), in parallel with facilitated transport, simple transport can also take place (Caşcaval et al., 2009).

Another version of facilitated transport is assisted transport accompanied by a co-transport or counter-transport of protons or anions in an equivalent flux in the same way or in the opposite way, respectively (Figures 2(d) and 2(e)) (Ma et al., 2004).

Found under the name of active transport in the literature are transport processes where complex processes (redox, complexing) take place in the feed and stripping phase. These processes are very selective.

#### **Advantages of bulk liquid membranes in laboratory studies**

The advantages of liquid membranes are represented in a large number of studies that approach this technique for both analytical and industrial applications. Among the multiple advantages we can include: simplicity in operation (Domínguez-Lledó et al., 2007; Govindaraju and Ibrahim, 2013; Schlosser and Sabolová, 2000), use of small volumes in the membrane due to

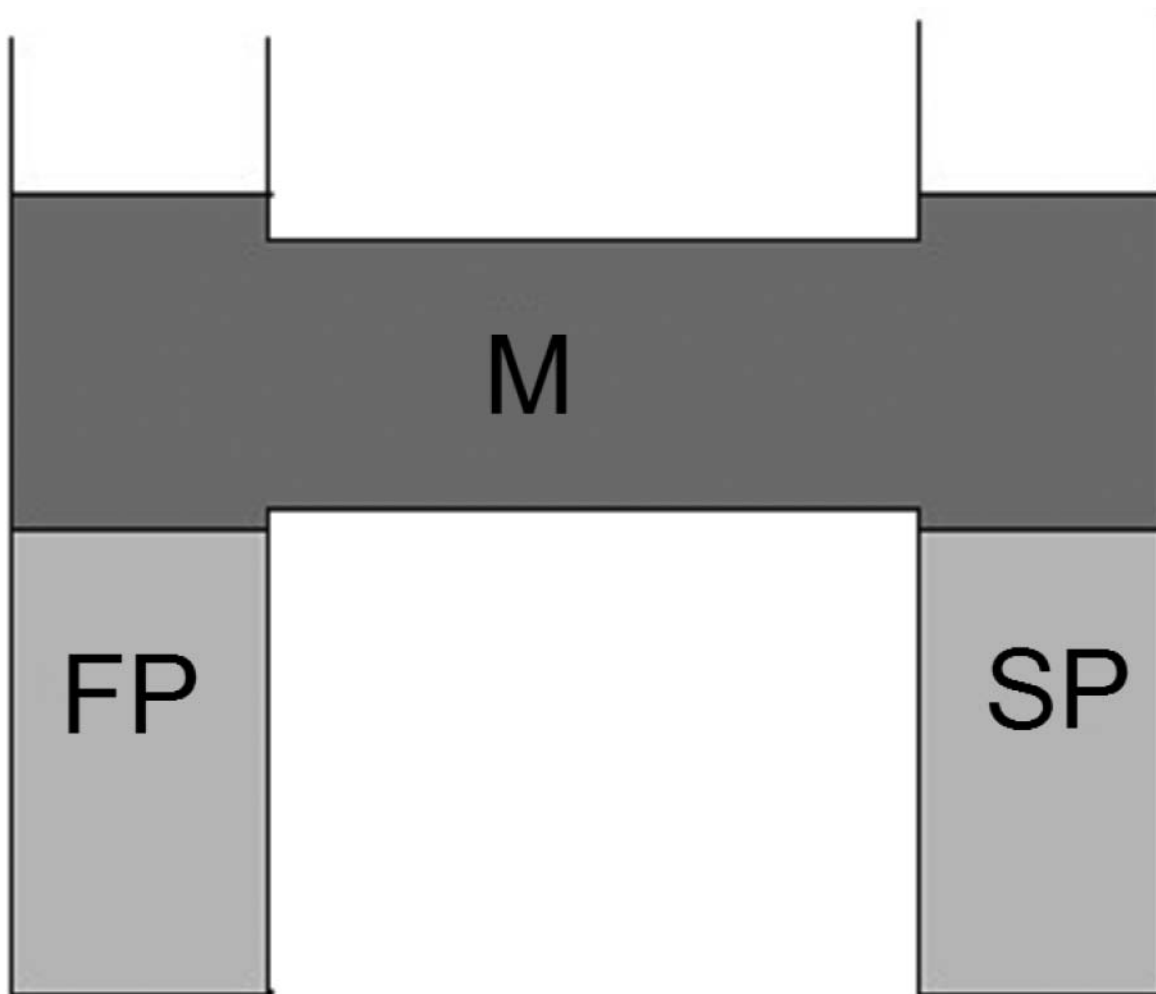
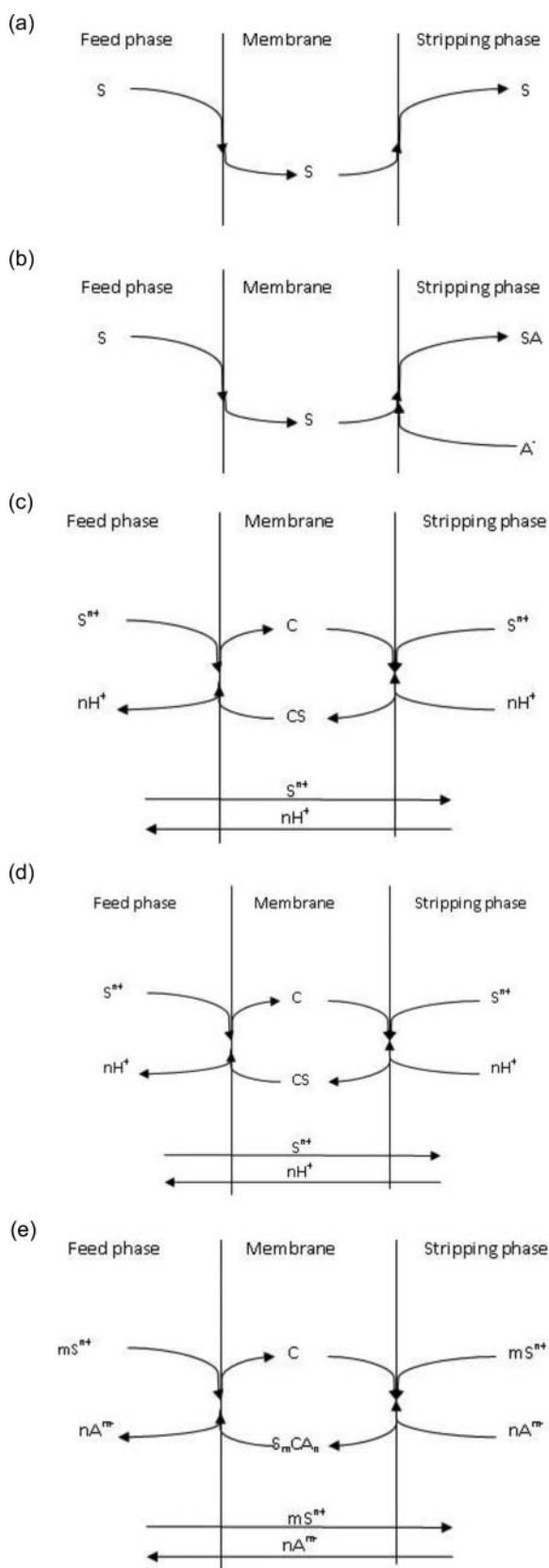


Figure 1(d).



**Figure 2.** Schematic mechanisms of transport: a) simple transport; b) simple transport with reaction in the stripping phase; c) facilitated transport; d) coupled transport with counter-transport; e) coupled transport with co-transport; S - solute, C - carrier, A - counter-ion.

the fact that they are not lost and can be regenerated, reducing operation costs (Blaga et al., 2006; Galaction et al., 2008; Lakshmi et al., 2013; López-López et al., 2013), and energy economy (Govindaraju and Ibrahim, 2013). Due to high selectivity of this technique it was taken into consideration in a large number of studies that a great advantage lies in the fact that separation and preconcentration operations can take place simultaneously (Aouarram et al., 2007; Reddy et al., 2010; Shahriar et al., 2013).

## Analytical applications of bulk liquid membranes

### Preconcentration and separation of metallic cations through bulk liquid membranes

In recent years the technique of liquid membranes has become more and more used in preconcentration and separation (Sastre et al., 1998). For example, for using macrocyclic compounds in metal membrane extraction the BLM technique was developed intensively from the period 1985–1990 up to the period 2006–2011, becoming a basic technique in such studies (Singh et al., 2013) (preferable to other types of liquid membranes: supported liquid membranes, emulsion liquid membranes, polymeric inclusion membranes).

Membranes have been intensively used in analytical applications and there are a large number of reviews in this field (Jönsson and Mathiasson, 1999a, 1999b, 2001; Moskvina and Nikitina, 2004; Sastre et al., 1998, Singh et al., 2013).

The permeation of BLM was applied, in particular, as a method of sample preparation for the determination of hard metals in marine and natural waters (Granado-Castro et al., 2004a, 2004b; Safavi and Shams, 1999; Slaveykova et al., 2004). In these matrices the heavy metal concentration is at a microgram or nanogram level, but not all laboratories have high-performance equipment that permits the detection of heavy metals at this level of concentration, and preconcentration of the analyte becomes necessary. The well known separation and concentration methods are: liquid-liquid extraction, solid phase extraction, ionic exchange, and selective precipitation. These methods present a series of disadvantages; for example, liquid-liquid extraction cannot be combined with atomic absorption due to difficulties of introducing the organic solvent into a flame, plasma, or furnace. That is why the technique of pertraction through liquid membranes represents an alternative to the conventional methods mentioned above (Domínguez-Lledó et al., 2007).

The transport through BLM of metallic cations is a facilitated transport. In the organic solvent, which is the membrane, there is a complexing agent (the carrier) for the metallic cation. At the interface of feed phase and membrane the carrier complexes the metallic cation and so transports it through the membrane, while at the interface of the membrane and stripping phase, where the decomplexing takes place, the metallic cation is released in the stripping phase and the regeneration of the carrier is realized. There is a large list of carriers used for this purpose, classified into a few main groups: acid carriers such as bis-2-ethylhexyl phosphoric acid (DEHPA), bis (2,4,4-trimethylpentyl)phosphinic acid (CYANEX 272), base carriers (Aliquat 336, trioctyl methyl ammonium chloride

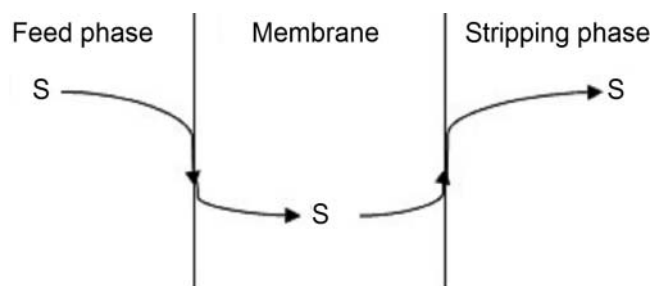


Figure 2(a).

(TOA), and neutral carriers (tributyl phosphate (TBP), and trioctyl phosphine oxide (TOPO)).

The BLM technique has been applied for the separation and preconcentration of some heavy metals such as nickel, lead, cadmium, chromium, cobalt, and many others.

For the preconcentration and separation of nickel for analytical purposes several BLM permeation systems have been studied. One of these permeation systems contains pyridine-2-acetaldehyde benzoylhydrazone (2-APBH) dissolved in chloroform and is used for the separation and preconcentration of nickel from natural waters (Domínguez-Lledó et al., 2007). The operational parameters of the membrane system were: pH of the feed and stripping phase, salinity of the feed phase, and influence of the nickel concentration in the feed phase. Using optimum transport conditions an efficiency of 99–101% and a preconcentration factor of 18 were obtained. The stripping phase that contains the separated and concentrated nickel was analyzed through atomic absorption spectrometry (AAS).

A similar study of separation and preconcentration of nickel cation was carried out (Aouarram et al., 2007). The separation and preconcentration of nickel was accomplished using a BLM system in which 2-hydroxybenzaldehyde *N*-ethylthiosemi-carbazone (2-HBET) was used as carrier. With this compound nickel forms a chelate type complex—neutral from the electrical point of view—that solubilizes nickel in a toluene membrane. The study determined the optimum transport conditions, namely feed phase pH = 9.4, a stripping phase solution of  $\text{HNO}_3$  0.3 mol/L, and carrier concentration in the toluene membrane of 1.66 mmol/L. The transport time was 4–7 h depending on the salinity of the samples (expressed through the content of NaCl). The NaCl presence determined a decrease of transport efficiency. This negative effect was reduced by increasing the transport time from 4 to 6–7 h. The transport efficiency was 100% and the preconcentration factor was 20.83. The nickel samples obtained after separation and concentration were analyzed by AAS.

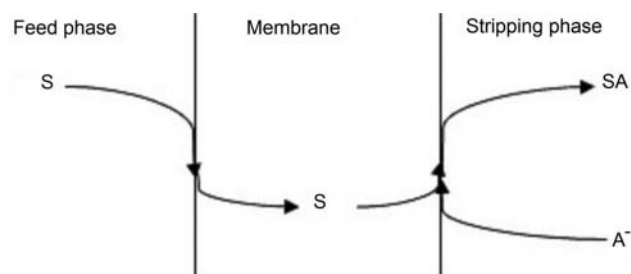


Figure 2(b).

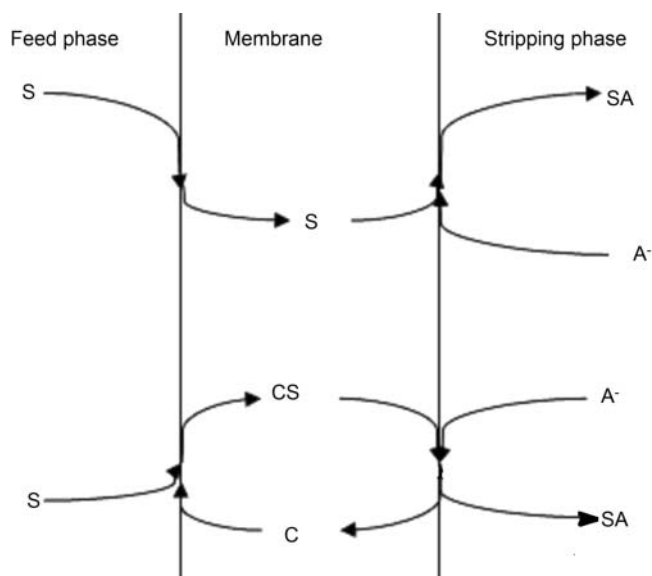


Figure 2(c).

The preconcentration procedure was correlated with the method's performance parameters. Assessed were parameters such as reproducibility, preconcentration transport efficiency, and method precision, which was 4.7% for a significance level of 95%, the recovery of nickel being  $99 \pm 3\%$ . Accuracy of the method was evaluated using fortified samples. The efficiency of the preconcentration had errors of 5.9% and respectively 2.2% for the two studied samples. The method was applied for the determination of nickel from marine water samples; the results were correlated with the results obtained using other methods.

Lead, like nickel, is found everywhere, accumulating in water and soil as a trace element. This makes detection difficult and requires methods of separation and preconcentration. Knowing the high selectivity of the ligand benzo-18-Crown-6 (B18C6), it was used as carrier for the separation of lead through BLM in order to determine it spectrophotometrically (Fahmideh-Rad et al., 2010). In order to obtain efficient transport of the cation  $\text{Pb}^{2+}$  parameters specific to the transport process were studied such as: membrane solvent, carrier concentration, effect of the

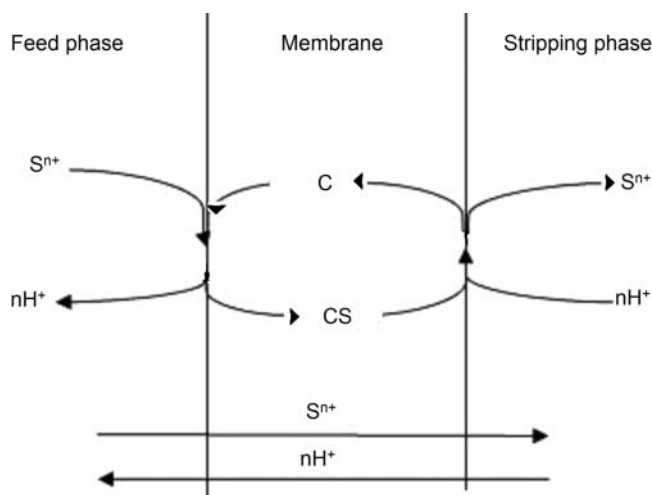


Figure 2(d).

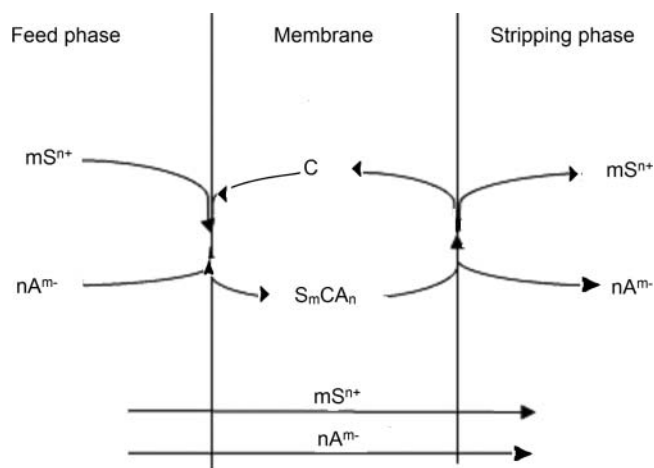


Figure 2(e).

counter-ion from the feed phase (in this case picric acid was realized), the feed and stripping pH influence, and transport time. In this case performance parameters such as reproducibility and selectivity were studied. This method can be used for the determination of lead, showing advantages such as high precision, selectivity, and efficiency.

Another method of preconcentration of lead from saline waters uses D2EHPA as carrier (Mostapha et al., 2011). The transport was carried out in an experimental device using wall in wall and a kerosene membrane. The membrane system was optimized by the simplex method (Bayne and Rubin, 1986) using the software Multisimplex 2.0. Thus the optimum working conditions for the highest value of the permeability coefficient were: acidified feed phase at pH = 4.7 with a buffer solution of 0.08 mol/L acetate, a stripping phase formed from 0.23 mol/L solution of HNO<sub>3</sub>, and a concentration of D2EHPA, used as carrier, of 0.07 mol/L in kerosene. Using a rotation speed of 700 rpm a transport efficiency of  $93.8 \pm 0.1\%$  was obtained. This method was applied on real samples and proved to be successful for the preconcentration of lead at the ppb level for its determination through inductively coupled plasma-mass spectrometry (ICP-MS).

The BLM membrane system was used as a preconcentration instrument in order to determine cadmium spectrophotometrically (Irigoyen et al., 2006) from marine waters. The toluene organic membrane contained dissolved D2EHPA as carrier. The preconcentration efficiency is 100% if the working procedures are: feed phase pH 4.7, receiving phase of 0.3 mol/L solution of HNO<sub>3</sub>, and a carrier concentration of 0.17 mol/L. The presence of calcium and magnesium ions decreases the preconcentration efficiency by their participation at the transport. That is why in order to obtain high efficiency it is necessary to mask these ions with, for example, citric acid. After preconcentration, cadmium was quantified by AAS, and results obtained were with comparable with those of reference methods such as anodic stripping voltammetry (ASV).

A selective system for the concentration of copper was obtained using piroxicam as carrier in an organic chloroform membrane (Sadeghi et al., 2005). A few important parameters in the uphill transport of copper were investigated, such as carrier concentration, feed phase pH, composition of the stripping

phase, and transport time. The transport efficiency was  $98 \pm 2\%$  when the transport parameters had the following values: concentration of Cu<sup>2+</sup> ions in the feed phase of  $5 \times 10^{-4}$  mol/L (the other cations were in equal concentrations in various mixtures) at pH = 5, stripping phase of a 0.01 mol/L H<sub>2</sub>SO<sub>4</sub> solution, a chloroform membrane with  $10^{-3}$  mol/L piroxicam, and a transport time of 4 h. The system is selective in relation to a series of cations, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, and ZrO<sub>2</sub><sup>2+</sup>, when masking some of these ions in the feed phase. The results demonstrate the applicability of liquid membranes in preconcentration and selective separation processes of copper ions from real samples. A preconcentration efficiency of over 76% for the copper ion was obtained using D2EHPA as carrier in kerosene in a BLM system (Mendiguchía et al., 2002). The preconcentration factor was 4.3. The copper ions from the preconcentration sample were quantified using flame atomic absorption spectrometry. The validity of the method was confirmed on real marine water samples. The average relative error was over 9.96%, while the average relative standard deviation was 0.33%.

Another heavy metal, silver, when found in trace levels in water samples is still toxic and thus needs to be monitored. Since it appears in very low concentrations, preconcentration is required, and BLM is a versatile alternative to the classical separation methods. Using an organic toluene membrane that contains tri-isobutylphosphine sulfide, the assessment of free silver and its chlorinated complexes was possible (López-López et al., 2013). By quantifying the saline effect and the effect of organic matter concentration, the content of total silver was successfully estimated.

Additional research has had as an objective preconcentration and separation studies of metallic cations from complex samples that contain more target cations.

A separation and preconcentration method for seven heavy metals present in marine water samples was developed (Mendiguchía et al., 2008). For this purpose the authors used the BLM technique with a toluene membrane that contains D2EHPA as carrier, considered a good complexing agent for metallic cations (Irigoyen et al., 2006). The samples prepared using this technique were quantified using ICP-MS. The membrane system was optimized for copper cations. The efficiency varied from 44% Cd<sup>2+</sup> to 77% Cu<sup>2+</sup> after 9 h of transport in the following order: Cu<sup>2+</sup> > Zn<sup>2+</sup> > Pb<sup>2+</sup> > Mn<sup>2+</sup> > Ni<sup>2+</sup> > Al<sup>2+</sup> > Cd<sup>2+</sup>. The preconcentration efficiency for each ion was studied as a function of the working parameters of the membrane: concentration of the metallic cation in the feed phase, feed phase pH, concentration of nitric acid from the stripping phase, and transport time. The real sample matrix affected the reproducibility of the preconcentration and the method accuracy for the determination of some metals from real samples. The results obtained by ICP-MS were comparable with those obtained with other standard methods, like anodic stripping voltammetry. Although some disadvantages were reported when using BLM, this method is preferred due to the low risk of contamination, low reagent consumption, and formation of small amounts of residues. In aqueous solutions the Cu<sup>2+</sup> and Zn<sup>2+</sup> ions are found as chlorides, namely MCl<sub>3</sub><sup>-</sup> and MCl<sub>4</sub><sup>2-</sup> (Dalali et al., 2012). This can lead to the possibility of forming a membrane system with a BLM of kerosene and Aliquat 336 as

carrier. This membrane system will allow a preconcentration and after that a separation of these metallic ions from real samples. Aliquat 336 can form ionic pairs with the chlorides of these metallic ions, and they can be transported through the membrane system. The efficiency of the membrane system was optimized by studying the effect of the NaCl from the feed phase, the effect of feed phase pH, the carrier concentration in the membrane, and the effect of transport time and also by choosing the optimum stripping solution from the receiving phase.

Studying the selectivity of this preconcentration method of these metals in the presence of  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  ions, it was found that the cadmium and zinc ions were successfully separated using Aliquat 336 in benzene. This method was applied successfully on real samples, and the separation of cadmium and nickel ions and their preconcentration were successfully realized, accomplishing their determination at low concentration.

### **Preconcentration and separation of anions through bulk liquid membranes**

In general, the transport of anions through liquid membranes has been much less studied than that of metallic ions, which have been intensively studied. The studies of anions involved their transport as they are or in complex combinations. In the case of the study of anionic complex structures the aim is actually the transport of a metal in a complex anionic structure. Such an example is the transport of  $\text{Ag}^+$  ions as  $\text{Ag}(\text{CN})_2^-$  through a BLM system that contains a solution of Victoria Blue as carrier (Safavi and Shams, 1999). The membrane system was optimized by studying parameters such as the effect of the feed phase pH, the cyanide concentration from the stripping phase, and the NaOH concentration from the feed phase as well as the carrier concentration in the membrane. In such an optimized system the transport of  $\text{Ag}^+$  takes place selectively and efficiently in the presence of cations such as those of alkali metals, alkaline earth metals,  $\text{Zn}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Al}^{3+}$ .

A special study was carried out (Aydinler et al., 2005) on the transport of cyanide ions. The membrane system was chosen using extraction studies. The optimum membrane solvent was  $\text{CHCl}_3$ . The carrier was selected by studying a series of quaternary ammonium salts, namely hexadecyl trimethyl ammonium bromide (HDTMABr), tetrabutyl ammonium bromide (TBABr), tetraoctyl ammonium bromide (TOABr), tetrabutyl ammonium chloride (TBACl), and tetraoctyl ammonium chloride (TOACl). Another parameter studied for the optimization of the system was rotation speed. The optimized system uses a chloroform membrane solvent in which TOACl is dissolved, and a rotation speed of 200 rpm permits obtaining a transport efficiency for the cyanide ions of 82%.

A selective and efficient method for the separation of iodide ion was developed using a chloroform BLM. The iodide anion from the feed phase was oxidized at  $\text{I}_2$  with sodium nitrite in acid medium ( $\text{H}_2\text{SO}_4$ ). The molecular iodine resulting from the reaction was transferred through the chloroform membrane in an alkaline stripping phase (NaOH 0.3M) with an efficiency of 90–91% after a transport time of 50 min. In these conditions

the iodide anion was separated from the  $\text{Br}^-$ ,  $\text{Cl}^-$  anions and a few metallic cations:  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ , and  $\text{Cd}^{2+}$  (Ensafi and Eskandari, 2001a). A preconcentration study of iodide assumed the oxidation of iodide in an acid medium with potassium dichromate (Craciun et al., 2006). The neutral molecule of iodine crosses the chloroform membrane and is recovered in the stripping phase with sodium thiosulfate. By choosing the optimum concentration of potassium dichromate and sulfuric acid the iodide can be preconcentrated in the stripping phase in a proportion of over 90%.

A similar study was carried out in order to preconcentrate bromide (Ensafi and Eskandari, 2001b). The difference was that the stripping phase used for the recovery of bromide was formed from  $\text{NO}_2^-$  anion. The preconcentration accomplished in the stripping phase in this case was over 90%.

### **Preconcentration and separation of organic compounds**

Transport through BLM has been applied to organic compounds, but not to such a great extent as the case of inorganic substances, especially metals. Although for the majority of organic compounds separation was accomplished with high efficiency, the aim of the studies was not an analytical application, and the membrane separation processes and transport processes were not coupled/hyphenated with an analysis method. In the majority of the cases the purpose was an industrial one, namely the recovery or selective recovery of some target compounds or the mathematical modeling of the membrane system. High efficiencies of over 90% and the separation of certain compounds can determine potential analytical applications of organic transport through BLM.

### **Preconcentration and separation of phenol and phenolic derivatives**

Due to their antioxidant capacity, essential phenols have gained increased attention in various industries such as cosmetics and pharmaceuticals, and thus there is a necessity to recover, separate, and monitor these compounds. The liquid membrane is an efficient alternative to the classical separation methods of liquid-liquid extraction coupled with high-performance liquid chromatography (HPLC). Separation through a BLM of a mixture of essential phenols, caffeic acid, hydroxytyrosol, and tyrosol, has been proposed (Shadabi et al., 2013). The membrane system proposed a feed phase composed of the compounds to be separated, a membrane formed from a chlorinated solvent, and a solution of  $\text{Na}_2\text{HPO}_4$  that acts as a stripping phase using a wall-in-wall type of experimental device. In optimum conditions for the membrane system (pH = 2 for the prepared feed phase, stripping phase solution with pH = 9, membrane phase formed from  $\text{CH}_2\text{Cl}_2$ , time of 570 min, and a rotation speed of 350 rpm) specific parameters were determined for the BLM-HPLC-UV system such as correlation coefficient, limit of detection, and repeatability. This method was applied for real samples and proved to be an efficient alternative compared to the classical separation methods for essential phenols.

Unfortunately not all phenols have a beneficial effect; there are also phenols that frequently encountered in wastewater that are extremely toxic such as phenols and nitrophenols (Diaconu et al., 2009a, 2009b, 2010a, 2010b; Szczepański and

Diaconu, 2012). Nitrophenols can successfully be concentrated when the membrane system is optimized by studying the effect of the feed and stripping phase pH (Diaconu et al., 2011). With an acid pH in the feed phase, the nitrophenols exist in a neutral form, and thus they can be transported through a BLM. Having a strong alkaline pH > pKa permits the concentration of the nitrophenols in the stripping phase. Depending on the volume of the stripping phase the phenolic derivative is concentrated, and maybe even in a higher concentration than in the feed phase. Thus with pH = 2 for the feed phase that contains the nitrophenols and a stripping phase formed from a NaOH solution with pH = 12 nitrophenols can be preconcentrated through a chloroform BLM system with efficiencies that range between 95.3 and 97.7%.

#### Preconcentration and separation of organic acids

BLM systems have shown potential applications in processes of separation and preconcentration of organic acids (Cascaval et al., 2004a, 2004b; Yang et al., 2009). In this case the feed phase contains, besides the organic substrate, a mineral acid that assures a mainly undissociated form, increasing its solubility in the membrane. The stripping phase is an alkaline phase that transforms the acid into a salt inactive for transport. The transfer of the organic acid from the feed phase takes place in this case through a simple transport mechanism. Obviously, the efficiency and the selectivity can be improved by introducing a carrier so that besides simple transport we also have facilitated transport. Research conducted by the Cascaval team (Cascaval et al., 2004a, 2004b) revealed selective transport of a mixture of citric acid, maleic acid, and succinic acid in the presence of Amberlite LA-2 carrier dissolved in 1,2 dichloroethane as the organic membrane. The efficiency of the pertraction is influenced by the pH gradient and the carrier concentration.

A BLM system was used for the separation of a racemic mixture of mandelic acid. The BLM system contains as a carrier a chiral binary mixture formed from D2EHPA and O,O'-dibenzoyl-(2R, 3R)-tartaric acid (L-(-)-DBTA) dissolved in octanol. Experimentally, a separation factor of 2.74 and a value of enantiomeric excess of 46.7% were obtained.

#### Preconcentration and separation of aliphatic and aromatic amines

Amines are used in the chemical, pharmaceutical, and dye industries as intermediary and synthesis products. They also have a huge biological importance, as they appear in different decomposing processes of living matter. The analysis of these compounds may raise great difficulties due to the complexity of the matrixes in which they are found in low concentrations, under the detection limit of the methods used in laboratories. Thus, the concentration and separation of these amines from different samples represent a priority in chemical analysis. BLM can in this case be an optimal option for preconcentration and separation for analytical purposes. The method of preconcentration with the help of BLM followed by gas chromatography detection can be applied to a series of aliphatic and aromatic amines (Ruse et al., 1999). The best results were obtained for the transport of cyclohexylamine through a chloroform liquid membrane with dicyclohexyl-18-crown-6 as

carrier. The transport was carried out with an efficiency of 98%, corresponding to a preconcentration factor of 2.86.

The selectivity of the carrier dicyclohexyl-18-crown-6 as well as the optimum transport conditions of feed phase pH (pH = 7) and stripping phase pH (pH = 2) allow the use of BLM in separation processes of some amines. Thus, aniline was separated from *N,N*-dimethylaniline with an efficiency of 89.5%. The presence of *N,N*-dimethylaniline in the stripping phase was under the detection limit of the gas chromatographic method, thus separation was carried out (Josceanu et al., 2001).

#### Analytical bio-separations

The transport of amino acids through BLM has been the subject of many studies. Recent research has turned towards enantioselective transport to separate optical isomers. Thus, Canepari et al. (2009) studied enantioselective transport of D,L-phenylalanine and D,L-phenylglycine through a bulk liquid membrane containing cinchona alkaloid derivatives as chiral selectors. Parameters that influence the efficiency of the transport and the enantioselectivity of the process were identified.

In recent years there has been increased interest in the recovery of drugs from different natural or synthetic mixtures using the BLM technique. Galaction et al. (2008) selectively recovered gentamicin C<sub>1</sub> from a mixture of bio-synthetic compounds with similar structures. The separation was carried out through facilitated pertraction with D2EHPA as carrier dissolved in dichloroethane as liquid membrane. The efficiency and selectivity of the separation depend on the aqueous phase's pH, the carrier concentration, and the rotation speed. Maximum selectivity was obtained for: pH<sub>feed phase</sub> = 8, pH<sub>stripping phase</sub> = 3, carrier concentration = 10g/L, and rotation speed = 100 rpm. Cephalixin was recovered from diluted solutions using Aliquat 336 as carrier, dissolved in *n*-butylacetate as BLM (Sahoo et al., 1997). The transport efficiency was higher than 90%.

#### Coupled systems: liquid membranes-flow analysis

The analysis of different chemical species of an element is very difficult because even the best performing analysis techniques cannot differentiate between chemical species. In this case researchers use a separation technique followed by a quantification technique. A solution to these problems is tandem techniques based on the coupling of separation techniques with online detection methods. Such an analytic system permits a high degree of automation, high efficiency, good reproducibility, short analysis time, and reduction of sample contamination due to the use of a closed system.

A coupled system, BLM-flow analysis, was used for the spectrophotometric determination of vanadium in marine water (Pinto et al., 2013). The BLM, used for preconcentration of the sample to be analyzed, contains Aliquat 336 dissolved in a mixture of dodecane and dodecanol. For optimization of the membrane system the following factors were studied: the saline matrix, the feed and stripping phase pH, rotation speed, and transport time. The optimum values established were pH gradients of the aqueous phases of the membrane system of pH<sub>feed phase</sub> = 3.2 and pH<sub>stripping phase</sub> = 9.8 at a carrier concentration of 0.57 mol/L Aliquat 336, a transport time of 3 h, and a rotation

speed of 900 rpm, yielding a transport efficiency of 100%. The concentrated samples of vanadium were quantified as vanadium pentavalent using the flow injection system. The flow analysis consisted in the spectrophotometric detection of vanadium based on the reaction of di-2-pyridyl ketone benzoyl hydrazone (dPKBH) in acid medium. The quantification system through flow injection allowed a detection limit of  $4.7\mu\text{g/L}$  and a relative standard deviation (RSD) of 2.72% for the determination of vanadium in saline water.

## Conclusions

This article presents the results of research studies on the use of bulk liquid membranes in preparing samples for analytical purposes. Studies carried out in this direction have highlighted the benefits of bulk liquid membranes, such as simplicity in operation, simultaneous separation and preconcentration, elimination of matrix, and low operating cost, in comparison to other analytical sample preparation methods. These advantages of bulk liquid membranes make them a viable alternative to conventional methods of sample preparation such as solvent extraction, ion exchange, and precipitation.

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