



A Perceptive on Bulk Liquid Membrane: A Brief Review

Jayshree Ramkumar*, S. Chandramouleeswaran

Analytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai - 400 085, Maharashtra, India.

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ABSTRACT

Separation is very important process in which the properties of solutes play an important role. Membrane separation is very important technique that is used extensively in the lab and industrial level. The classification of membranes into solid and liquid have been mentioned. In this article, the various aspects of the bulk liquid membrane including transport mechanism and applications have been discussed in detail.

Key words: Bulk liquid membrane, Mechanism, Theory, Applications

1. GENERAL INTRODUCTION

Separation of various species is very important in the lab and industrial scale, and usually the properties of solutes play an important role in the separation process [1]. In processes like distillation, crystallization, centrifugation, and gas absorption, the difference in the physical properties of the solutes are considered, but such processes are less selective and feasible only when there is a great difference in the physical property of the solute from another component in mixture [2]. In order to overcome these limitations, the difference in the chemical property of the solute is considered. The pertinent solute is selectively converted to a complex, which is then broken down under reversed conditions thus recovering the original component and the complexing agent. Techniques such as precipitation, solvent extraction, ion exchange, chromatography, and membrane separations take advantage of differences in the chemical properties of the solutes [2]. Membrane separation process finds relevance in different industries due to benefits like cost being lucrative, ease of operation, high pre-concentration factor with a high degree of selectivity and can be used for solutes at very low concentration levels [3].

1.1. What is a Membrane?

Membrane, according to International Union of Pure and Applied Chemistry can be defined as a heterogeneous phase, which acts as a barrier to the flow of molecules and ionic species in liquid or vapor phase. If one component of the mixture travels faster in the membrane, a separation can be achieved. Based on their nature, the membranes can be classified into

solid and liquid membranes [4]. Solid membranes are used extensively in different industries in various processes, and processes like reverse osmosis, microfiltration ultrafiltration make use of porous solid membranes. However, the main focus of this review is the liquid membrane and, therefore, further discussion on the solid membranes is out of scope of the present review. Liquid membranes appear as probable separation procedure due to remuneration compared to solid membranes. As the molecular diffusion is faster in liquids compared to solids, the transfer intensity is superior in liquid membranes as compared to solid membranes of micron thickness. Moreover, polymeric solid membranes are less selective than liquid membranes. However, these two advantages of liquid membrane systems cannot make up for the simplicity and operational stability of solid membranes.

1.2. What is Liquid Membrane?

Like most of the developments, this separation technique has various names, e.g. liquid pertraction, carrier-mediated extraction, facilitated transport, two-stage extraction, etc. However, the term liquid pertraction proposed by Schlosser and Kossaczky [5] describes the processes precisely. The name was derived from the liquid-liquid extraction. It reflects the transfer process involved, as well as the multi (three) phase structure of the system. The term liquid membranes also represent the essential feature of the process, but the conventional image of the membrane is not defined. Liquid pertraction explores a very simple idea of two homogeneous, completely miscible aqueous solutions, referred to as donor or feed (F) and acceptor or receiving (R) solutions that are

*Corresponding Author:
E-mail: jrk@barc.gov.in

spatially separated by a third liquid, immiscible and practically insoluble in the two aqueous phases known as the membrane phase (S). Due to the favorable thermodynamics created at the interphase between the feed and membrane phase, some components are extracted from the donor solution and transported into the membrane and favorable conditions at the membrane/receiving phases interphase result in the extraction from the membrane phase.

Thus, it is quite articulate that liquid pertraction is a combination in time and space of two well-known separation processes: Solvent extraction and solvent stripping [6]. This amalgamation is beneficial over conventional extraction as it offers maximum driving force and the extraction capability of organic media is not crucial. Therefore, a great variety of insoluble, inert and harmless organic liquids can be used with small amounts of carriers. These carriers form complexes with the ion of interest and results in the extraction into the organic phase. The selectivity of extraction can be improved using highly selective carriers.

1.3. Mechanism of Liquid Pertraction

The mass transfer in liquid membrane systems is based on the difference in the chemical potentials of the solute in the two aqueous solutions and the intensity of the diffusion of solute is controlled by concentration difference. Mass transfer can be achieved by various mechanisms, which can be divided into two main groups and the role of membrane liquid can be either as a physical solvent or may contain a selective carrier [6].

Figure 1a-d shows the schematic representation of the various mechanisms of transfer through liquid membrane systems. When the membrane liquid acts as a physical solvent for permeate, the removal from the feed occurs due to solubility in membrane liquid (Figure 1a). The concentration gradient plays an important part in the transport. The transport continues till the concentration in both the feed and receiving phases are equal. This is known as a simple transfer process (Figure 1a). However, if the receiving phase contains a reagent that combines with the solute of interest, then there is a continuous transport against the concentration gradient and this is known as “uphill transport” (Figure 1b). When the membrane liquid contains a carrier which will complex with the solute of interest, then there are two different processes at the two phases. At the feed/membrane interphase, the solute carrier complex is formed and at the receiving/membrane, the carrier is broken down. This is known as carrier facilitated transport (Figure 1c). However, if an equivalent amount of some component is co-transferred from receiving to the feed phases during the transport of solute from feed to receiving phase, then it is known as carrier facilitated coupled transfer.

1.4. Classification of Pertraction

There are different techniques of pertraction [6] and these have been schematically represented in Figure 2.

The classification is only conditional since most methods cannot be sharply distinguished. Most of them are close to the classical liquid-liquid extraction. Separation procedures like bulk liquid and supported liquid membranes (SLM) and liquid film pertraction do not involve any phase separation whereas emulsion liquid membrane involves phase separation. Since, the present review deals with the bulk liquid membrane (BLM), the details of the other separation techniques are beyond the scope of the present review.

2. EXPERIMENTAL SETUP OF BLM

There are different setup of BLMs which are normally encountered. A schematic representation of the BLM systems normally encountered in the lab is given in Figure 3.

It is seen that the membrane liquid can have density greater or less than water, and so accordingly the setup will change. In Figure 3a and c, there two aqueous phases are spatially separated but connected by the organic layer. However, in Figure 3b and d, it is seen

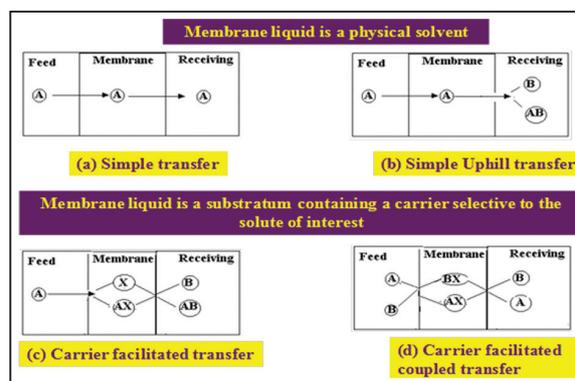


Figure 1: Schematic representation of transport mechanism in liquid membrane.

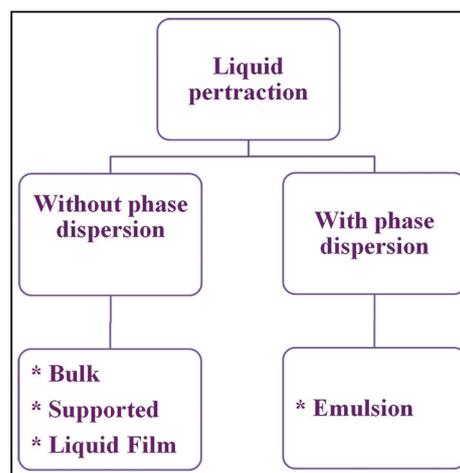


Figure 2: Classification of pertraction techniques.

that the receiving phase is surrounded by the feed phase but the two phases are spatially separated. The most common used setup, known as the Schulman bridge, is the simplest mass transfer cell, which has been used by various authors [7,8] for studying the mechanism of liquid membrane transport (Figure 4). It is seen that the two aqueous feed and receiving phases are spatially separated from each other by the membrane phase S. The constant interface areas, the constant hydrodynamic conditions, the simple design of cell and easy manipulation are the reasons for their broad use in laboratory scale. The cells are convenient for following the kinetics of mass transfer process, for studying the reaction mechanism involved, etc. However, the low specific interface area limits the application of this method to only laboratory use.

3. THEORY OF BLM

The transport of metal ions through liquid membranes can be subjected two modeling using two different approaches. The first very frequently used approach based on the model of Reusch and Cussler developed in 1973 [9] deals with the concentration diffusion layers and treats the interphase between the organic and aqueous phase as the platform wherein the complexation and decomplexation occur [10]. Figure 5 shows the various steps involved in the transport.

The transport from the aqueous source phase through the organic membrane into the aqueous receiving phase can be divided into various steps. There is a diffusion of solute through the diffusion boundary layer (DBL) from the feed bulk to the membrane surface with a linear concentration gradient near the membrane surface. The chemical complexation of the metal ion with the carrier at the aqueous/membrane interphase is a fast reaction in comparison to the diffusion process resulting in an equilibrium and the diffusion of metal carrier complex through DBL on the membrane side occurs. The transport of the metal carrier within the membrane toward the receiving phase is due to convection transport as a result of the continuous stirring of the membrane liquid. Then diffusion similar to that in the feed phase occurs in the receiving phase. The solute of interest (A in Figure 5) is transported to the receiving phase with a simultaneous transfer of other ions of same charge from the receiving to feed phase (B in Figure 5).

In the second approach [11], it is assumed that the carrier moves a bit out of the organic phase and the reactions occur in the portion of the aqueous phase known as “Big Carrousel.” There is one more less popular approach wherein the stagnant diffusion layers on the aqueous/organic phase boundaries are not considered and the diffusion through organic layer is considered [11]. However, this approach is justified only if stirring is efficient.

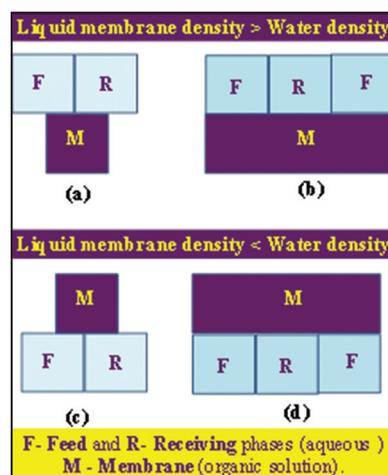


Figure 3: Types of bulk liquid membrane.

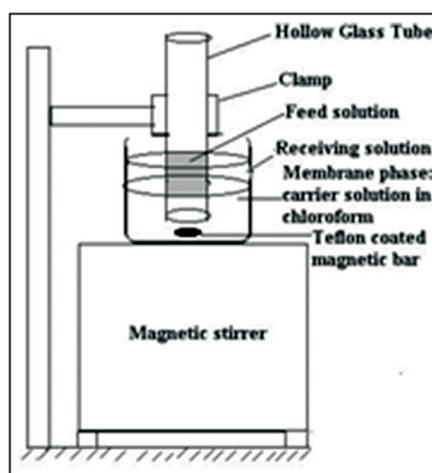


Figure 4: Schulman bridge setup.

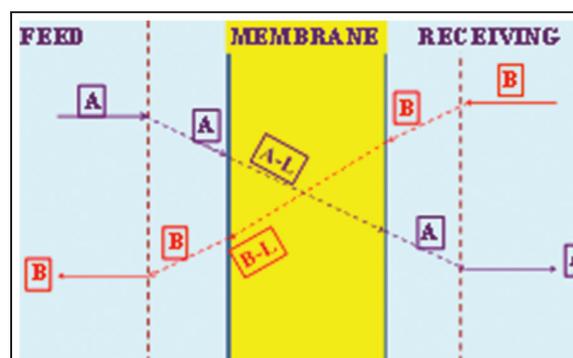


Figure 5: Schematic representation of transport.

3.1. Separation Studies Using BLM

The main use of BLM is to test the laboratory scale performance of various carriers for bringing out the separation of the solute of interest. This can also be used prior to analytical separations. The carriers used in the BLM may be either a well-known gravimetric reagent with complexing property or a newly synthesized organic compound whose complexing ability has to be tested or its use as a carrier for separation is evaluated.

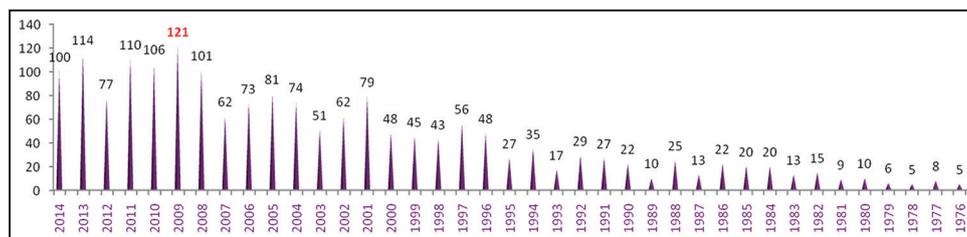


Figure 6: Graphical representation of reports on bulk liquid membranes (data obtained from Scopus).

The literature survey pertaining to BLM shows tremendous amounts of reports that use different kinds of carriers for transport of species such as metal, ions, and organic dyes. A survey of the reports on Scopus with a search term text as “BLMs” and search field type as “Article title, Abstract, Keywords” revealed a total of 1840 publications and 1536 only in the field of physical sciences alone and 125 patents till date. Figure 6 shows a graphical representation of the work carried out using bulk liquid membrane over the years. This goes to show the tremendous amount of work being carried out in the field.

Therefore, it is realistic to discuss some of the work on BLMs to give an idea to the readers. 8-hydroxy quinoline (Oxine) is a well known gravimetric reagent that forms a complex with most of the metal ions. Therefore, it becomes very interesting to use such a well-known non-selective gravimetric reagent to bring about the selective transport of metal ions through BLM. Therefore in such instances, the fine tuning of solution chemistry becomes very important. Studies showed that oxine could be used for the selective transport of metal ions like Cu(II) [12] and molybdenum [13]. The facilitated transport of copper ions was carried out using 0.1M nitric acid (HNO₃) as receiving phase [12]. The synergistic effect of aminopyridine was evident as opposed to negligible changes in the transport by the addition of citric acid or glycine when they were added to the membrane layer along with oxine. It was found that Cu²⁺ transport was not affected even in the presence of 10-fold concentration of ions like Pb²⁺, Zn²⁺, Cd²⁺, Ni²⁺, Fe²⁺ and Fe³⁺ ions. The transport of molybdenum [13] was carried out at pH of 5 with a mixture of nitric acid (0.1 M) and hydrogen peroxide (0.2 M) as the receiving phase. The addition of 1, 10 orthophenanthroline showed an enhancement in the transport due to synergism. The use of masking agents in the feed solution resulted in the selective transport of molybdenum.

The carrier activity of several phenoxy ethers that have been synthesized has been evaluated with respect to transport of alkali metal ions [14]. A brief description of the synthesis of carrier compounds has been given, and the mechanism of transport process has been discussed. The organic carriers are protonated on the receiving side of a permeation cell,

and the protons are exchanged with the metal ions at the membrane interphase of the feed side. Protonation of carriers has been confirmed from electronic spectral studies. A high degree of selectivity for Na⁺ transport has been observed when 1,2-bis-(2-acetyl phenoxy) ethane is used as carrier whereas dibenzo-[a,e]-3,4-dihydroxy-3,4-dimethyl-7,10-dioxocyclodeca-1,5-dione facilitated selective transport of K⁺ [14].

The selective transport of Cu²⁺ ion was achieved from a mixture containing cations like Cd²⁺, Pb²⁺, Zn²⁺, Ni²⁺, and Co²⁺ using 5-nitro-8-quinolinol as a carrier [15]. Under optimum conditions, the extent of Cu²⁺ transport was 33.05% after 24 h. The appositeness of the method was examined for the separation of copper (II) ions from real river samples and the transport efficiency was found to vary between 29% and 32% after 24 h [15]. A new Schiff base containing N, S, O atoms was synthesized and used as a carrier for the transport of Cu²⁺ ions [16]. The various experimental parameters that have an effect on the transport like composition of receiving phase, pH of the feed phase, carrier concentration in the membrane, etc. were studied to get an optimized condition. The use of tetra aza-14-crown-4 (A414C4) and oleic acid as a integrated carrier [17] for transport from a mixture of metal ions containing Cu (II), Cd(II), and Pb(II) and the order of transport was Pb(II) > Cu(II) > Cd(II). Moreover, the influence of Zn(II), Co(II), and Ni(II) ions on the initial fluxes, selectivity coefficient, and removal percentage of Pb(II), Cu(II), and Cd(II) ions in the BLMs was investigated. The sequences of ion initial fluxes and transport selectivity have negligible changes as: Pb(II) > Cu(II) > Zn(II) > Cd(II) > Co(II) > Ni(II). The transport of copper ions using different carriers like D2EHPA, CYANEX 272 and LIX 984N were studied, and a comparison of the kinetics was seen [18]. It was seen that the mechanism of transport was counter carrier facilitated with an equivalent amount of protons being transported in the direction reverse to that of copper ion transport. The transport kinetics were considered by analyzing two consecutive irreversible first order reactions namely that of extraction and stripping and the rate constants of these two reactions were calculated by numerical analysis and there was a relatively good agreement between experimental and theoretically obtained data. It was seen that the LIX984N and D2EHPA

were found to be the most and least efficient carriers respectively [18].

Transport of radionuclides like uranium has also been carried out using BLMs. The uphill transport of uranyl ion of more than 89% using potassium ion selective crown ethers has been reported [19]. The uranyl ion formed anionic thiocyanate complex $[\text{UO}_2(\text{SCN})_4]^{2-}$ in the presence KSCN at pH of 1 and, therefore, could be transported using K^+ ion selective 18 Crown 6 (18C6) and Dibenzo 18C6 as carriers into a receiving phase containing dilute acid (pH=5). Interferences from various metal ions including Th(IV) was removed using suitable masking agents in the feed phase. The main disadvantage of this study was that it could be achieved only at pH 1 in the presence of KSCN [19]. In order to overcome this limitation, uranyl ion selective calixarenes were used as carriers and studies showed that in presence of trioctylphosphine oxide (TOPO) as synergistic reagent, more than 95% transport could be achieved and this was applied to actual seawater sample [20]. The use of bis(2-ethyl hexyl) phosphoric acid (D2EHPA) as carrier in kerosene solvent was reported in both BLM and SLM studies of uranium and it is seen that maximum extraction values obtained were above 95%, and recovery yields were in the range 57-79% for the BLM and 90% for the SLM [21]. The facilitated transport of uranium from the dilute phosphoric acid medium into the more concentrated phosphoric acid medium was studied using D2EHPA as a carrier [22]. The role of different parameters like phosphoric acid concentration in the source and receiving phases, carrier concentration, nature of solvent, stirring speed and temperature and synergistic nature of TOPO was evaluated. The transport study of uranyl ion transport using equimolar amounts of thenoyltrifluoroacetone (HTTA) and dicyclohexyl-18C6 as carrier in chloroform from a feed solution at pH of 2 into receiving phase containing 0.2 M HCl and 4×10^{-3} M sodium dodecyl sulfate showed very no interferences from most of the ions except Th(IV) and Cu^{2+} which were masked using ethylenediaminetetraacetic in the feed phase [23]. 2-HTTA in carbon tetrachloride as a BLM was used to selectively separate thorium from low pH nitrate medium into HCl solution [24] and replicate studies showed a transport of $95.4 \pm 1.2\%$ could be achieved with an initial concentration of 10^{-4} M thorium in the feed phase maintained at pH of 2.4 into a receiving phase containing 10 ml of 0.5 M HCl using 0.02 M HTTA in 20 ml carbon tetrachloride as the BLM phase. Both single ion and competitive transport experiments were carried out to study the selectivity of the system and was applied to spiked water samples.

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***Bibliographical Sketch**



Dr. Jayshree Ramkumar ACD, BARC, is involved in the development of newer procedures for separation and monitoring of different species using membranes and sorbents ranging from bulk to nano materials. Her Ph.D. was on the ion exchange and related studies using Nafion membrane. She has more than 60 publications in international peer reviewed journals and chapters in books to her credit in the field of separation science. She pursued her postdoctoral research on the use of mesoporous materials for remediation, at the NIMS, Japan. She is also an Assistant Professor and guide of HBNI, India and currently guiding students as a co guide for their PhD.