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Liquid Membranes: Basic Concepts and Applications to Nuclear Industry

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ABSTRACT

Liquid membrane is an attractive separation technique which is gaining importance and finding applications in various industries including the nuclear industry. In this mini review, the various aspects of liquid membrane separations have been discussed. Liquid membrane defies the conventional image of a membrane. The separation becomes very interesting due to the presence of only liquid phases which are immiscible with one another. The application to nuclear industry has been illustrated with the studies reported in literature.

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In general, a chemical substance is defined as any material or matter with a definite chemical composition and characteristic properties. However it is not possible to find an absolutely pure substance. Mixtures are quite common. Thus in a mixture, the substance of interest may be present in very low levels. Therefore the matrix refers to all the constituents of the mixture except the solute of interest [1-3]. Hence it becomes essential to carry out separation. Separation maybe understood as a route by which the constituents of the mixture are segregated from one another [4]. The segregation can be achieved by utilizing the differences in either the physical or chemical properties of the solutes. It is seen that in general the processes based on differences in physical property are less selective as compared to those based on differences in chemical property. Separation can be used to purify a substance or to recovery trace level precious elements. There are large number of techniques available. Of these membrane separation is very important technique which can be based on the physical or chemical property of the solute. As per IUPAC, membrane is a heterogeneous barrier to molecular/ ionic flow in a fluid (liquid/gas) resulting in separation due to differences in the travel time of the solutes [5]. The use pressure based membrane filtration in various applications have led to a number of materials being developed [6]. The membrane used in these applications are solid materials which are used [7]. Solid membranes are stable and simple to operate but suffer from slow transport flux and less selectivity [8]. Since molecular diffusion is high in liquids, liquid membranes appear to be an attractive alternate to overcome the limitations of solid membrane [9].

Liquid membrane is a separation process which was originally referred to as liquid pertraction to describe the process very accurately [10]. The system consists of a spatially separated three phases and transport occurs via an extraction mechanism. The three phases are the aqueous feed (F) and receiving (R) phases which are immiscible with the third organic membrane phase (M). Liquid membrane defies the conventional image of a membrane. The extraction of solute into the organic layer occurs at the feed-membrane interphase while stripping into aqueous solution occurs at the membrane-receiving interphase. The main advantage of liquid membrane is that the organic solvent itself need not have complexing ability and so simple organic solvents can be used. In order to achieve selective extraction, carrier (chelating agent) is added to the membrane phase.

Liquid membranes can be classified based on module configuration, transport mechanism, carriers, membrane support and applications which are discussed in brief. Based on the module configuration, liquid membranes can be classified into bulk (BLM), supported / immobilized (SLM / ILM) and emulsion (ELM). Bulk liquid membrane (BLM) consists of a large volumes of aqueous feed and receiving phases separated by a voluminous organic, water-immiscible liquid phase. The different types of bulk liquid membranes have been discussed in detail earlier [11]. Supported Liquid membrane system has a microporous polymeric or inorganic film support with the hydrophobic membrane liquid phase incorporated within it. However in some cases, the pores can be impregnated with aqueous solution [12]. But this arrangement is unstable which can be overcome by using ionic liquids (ILs) as a membrane phase. In order to overcome the stability issues associated with SLMs, different approaches were executed. One such method involved the stabilization of SLM by creating new polymeric layers to the surface of the support [13]. Another approach is the gelation method wherein a homogeneous gel network is applied into the pores of the support which leads to increase in mechanical stability (against liquid displacement) and permeability. However if a thin dense gel layer is applied onto the feed side of membrane the tendency to form droplets is reduced. Thus gelation leads to improved stability. Another method for stabilizing SLM is by combination of dispersed phases and SLM leading to a process known as emulsion-liquid-membrane-extraction in a HF contactor [14]. The emulsion of membrane and receiving phases are made to contact the pores of the support while aqueous feed is allowed to pass through it resulting in no direct contact between the emulsion and feed phase. This reduces the swelling of the membranes to a great extent. SLM with a strip dispersion involves the dispersal of the stripping solution [15]. Another approach is the contained liquid membranes and hybrid liquid membranes in which a large hollow fibre membrane module containing two functional arrays of fibres, one each for feed and other for strip. The organic membrane liquid is situated between the two sets of fibres [16]. In contained liquid membranes, organic system is static and mass transfer is based on pure diffusion. So hybrid liquid membrane was adopted [17]. It was seen that a gel layer was observed covering hydrophilic or cation exchange membrane surfaces at the feed-membrane interface but the mechanism was not explained. In CLM and HLC systems, the loss organic extractant is minimum [18]. SLM can be used in different geometries namely flat sheet SLM and Spiral wound and hollow fibre. Flat sheet is used for basic research as the ratio of surface area to volume is not very high. Spiral-wound and hollow-fiber SLMs have much higher surface areas. Emulsion liquid membranes (ELM) invented in 1968 involves the dispersion of an emulsion (of the receiving phase and liquid membrane phase) in the feed phase. The major drawback of this membrane is the emulsion stability which needs to be taken care of. The membrane transport can be classified based on the transport mechanism which operates. Thus there are six mechanisms which are found to operate [19, 20]. But it is seen that in most of the applications, the carrier facilitated counter mechanism is the most common mode of transport. The method can be classified based on its applications into the following categories of metal separation, biotechnological products recovery, pharmaceutical products recovery, organic pollutants, gas separation, bioreactors, analytical applications and wastewater treatment including biodegradation. Different types of carriers can be used and so the classification based on carrier type may fall into categories of hydrophobic organic carriers, hydrophilic polymers, ion exchange and neutral but polarizable. The membrane supports that are used may be hydrophobic, hydrophilic, charged in nature.

Thus, liquid membrane is a rate process in which separation occurs due to a chemical potential gradient. Primarily the mass transfer phenomenon in liquid membrane is a carrier mediated transport process. In this, the carrier ligand assists the metal ion transport from one side to other side of the membrane. The process involves a cycle of complexation (metal ion-carrier) at feed-membrane interphase, diffusion of complex within the membrane phase and decomplexation at the membrane-receiving interphase. Once the metal ion is released into the aqueous solution, the free ligand diffuses back to the other side of the membrane (feed-membrane interphase) to complex with more metal ion. In order to understand the transport mechanism, two models have been postulated, the first model based on the interphase diffusion is used extensively. It considers the organic- aqueous interphase as a platform for the reactions of complexation (/decomplexation) to occur [21]. In this model, a diffusion boundary layer with a linearly increasing concentration gradient near the membrane surface is postulated. The solute diffuses through this layer prior to the complexation at the feed-membrane interphase. It is understood that complexation has faster kinetics as compared to diffusion resulting in attainment of equilibrium. A similar diffusion boundary layer is hypothesized to be present on the receiving side of membrane through which the metal ion diffuses out. Another approach involves the formation of "Big Carrousel" due to the partial solubility of the carrier in aqueous phase and the complexation tends to occur in this region. A third approach involves the diffusion through the organic layer being the most dominant mechanism. This is possible when stirring is highly efficient [22]. Further studies also show a mechanism of on mobile sites wherein the solute moves by successive migration on several mobile carrier sites. This model clearly explains the high diffusion coefficients obtained in SLM [23]. The fundamental mathematical expressions for the transfer of metal ion in carrier facilitated transport have been obtained [24].

Liquid membranes can be used at lab scale or industrial level. 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 and used prior to analysis. The use of 8-hydroxy quinoline (Oxine) as a carrier for selective separation of copper and molybdenum has been reported. The carrier is a recognized gravimetric reagent that complexes almost all the metal ions. Hence to achieve selective transport, the modifications of the experimental conditions are carried out [25, 26]. In these studies, use of synergistic reagents were also evaluated to improve the efficiency and also selectivity. Another approach to improve selectivity was to use masking agents to inhibit the transport of interfering ions. BLM studies were carried out using newly synthesized phenoxy ethers and it was seen that the structure of the carrier itself rendered a high degree of selectivity [27]. Transport of radionuclides like uranium and thorium have also been studied using BLM setup. The transport of uranium using potassium selective crown ethers [28] involved the conversion of uranyl ion into its thiocyanato complex using KSCN and transported along with potassium ion. The use of calixarene in conjunction with TOPO gave a complete and highly selective of uranyl ion even from seawater samples [28, 29]. The use of bis(2-ethyl hexyl) phosphoric acid (D2EHPA) as carrier could result in excellent separation of uranium even from phosphoric acid medium [30, 31]. The transport study of uranyl ion with equimolar concentrations of thenoyltrifluoroacetone (HTTA) and dicyclohexyl-18C6 as carriers showed that most of the ions did not interfere while the interference from Th (IV) could be reduced by masking [32]. Thorium could be successfully transported using carriers like 2-HTTA and n-benzoyl-n-phenylhydroxylamine (n-BPHA) [33, 34]. Studies were evaluated to obtain high transport efficiency with excellent selectivity.

Supported liquid membranes have also been used for samples with respect to nuclear industry. The transport of tervalent elements in nitrate medium using a flat sheet SLM containing HDEHP in dodecane indicated the effect of acidity on the rate [35]. Study using flat sheet SLM has shown Aliquat 336 to be an efficient carrier for transport of uranyl ion in presence of high concentration of hydrochloric acid [36]. The transport rate was found to be dependent on various factors like pore size, nature of organic carrier and its concentration, the feed acidity etc. It was postulated that an ion pair mechanism was responsible for the transport due to the formation of species like $[R_3R'N^+] \bullet [UO_2HCl_4^-]$, $[R_3R'N^+]$ $2\bullet [UO_2Cl_4^{2-}]$ and $[R_3R'N^+] \bullet [UO_2Cl_3^-]$. This method was applied to separation method for trace level of 233U from thorium matrix making it suitable for processing THOREX feed solutions. The selective separation of Am3+ from its mixture with Eu3+ was achieved using 2, 6-bis (5, 6-dipropyl-1, 2, 4-triazin-3-yl) pyridine (n-Pr-BTP) as the carrier [37]. The transport of uranyl ion from nitric acid medium was carried out using flat-sheet SLM containing a series of mono-amides carriers [38]. Hollow fibre supported liquid membranes also find great applications in nuclear industry.

The various applications in this have been found in an excellent review reported [39]. In this, an encompassing description of methods for separation of various elements in nuclear fuel cycle has been given. Diglycoamide -functionalized ligands show enhanced transport performance as compared to bare ligands [40]. The transport of trivalent actinides/lanthanides from nitric acid medium was achieved using polypropylene HFSLM using a mixture of TODGA (N,N,N′,N′-tetraoctyl diglycolamide) + DHOA (N,N-dihexyl octanamide) as carrier [41]. The transport was nearly complete and could be applied to a simulated sample of reactor waste. The studies using were further extended to the separation of the actinides and the lanthanides using suitable carrier [42].

Conclusions

Liquid membranes separations have several advantages. The selectivity associated with liquid membrane can arise due to use of carriers similar to solvent extraction but the amount needed is much lower. The membrane volume is very low when used in supported and emulsion modules as compared to solvent extraction. The simultaneous extraction and stripping leads to high throughput. The use of supported liquid membranes makes it easy to scale up and easy to sustain. But further research is crucial and there is more scope for use of various ligands as carriers. This gives paramount opportunity for synthesis of new and exotic compounds that may prove to be excellent carrier. The membrane stability is of a concern as there may be a gradual loss of ligands from pores. This has been addressed by various techniques like gelation. However membrane fouling is also another problem that needs to be addressed to. Hence the need to separate the suspended particulate becomes an essential step prior to the liquid membrane separation studies. Another major concern is the radiolytic stability of the membrane support and the module as a whole. This is crucial if membranes need to be used in the nuclear industry for a longer time period.

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