Liquid membranes and their technological applications: A brief review

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***Abstract*- A membrane is a thin barrier that allows preferential passage of certain substances. Whenever this barrier is in liquid state the membrane is called a liquid membrane. Liquid membranes are formed at every interface encountered by a surfactant solution. As permeation through liquid is orders of magnitude faster than those though solid polymers of comparable thickness. This rate advantage is exploited for some separations by using an immiscible liquid film as the membrane tomediate the transport of selected substances. Various types of liquid membranes have been used in variety of technological applications, a short review is presented herein.**

INTRODUCTION

Transport phenomena occurring across membranes are of considerable interest in chemistry, chemical engineering and biology(1-13). Membranology has emerged as a multidisciplinary field and is growing by leaps and bounds due to the role of membranes in separation process and other applications such as electrodes for quantitative analysis of ions, neutral species etc. some important applications of liquid membranes are in reverse osmosis and desalination, waste water treatment, in gas, petrol and separation of organics. Liquid membrane have proved to be of immense use in the above noted technological areas. A Liquid membrane usually consists of a water immiscible (organic) layer separating a source aqueous phase consisting of a mixture of metal ions (feed) and receiving aqueous phase where the metal ion of interest gets concentrated (receiver) preferentially.

The first most widely used liquid membrane was by Martin. Finally Markley, Cross and Bixler accepted the liqid membrane theory of Kesting. Different solutes will have different solubilities and diffusion coefficients in a liquid. The product of these two terms is a measure of the permeability. A liquid can yield selective permeabilities and therefore a separation.

Because the diffusion coefficients in liquids are typically orders of magnitude higher than in polymers, a large flux can be obtained. Hence it was thought desirable to discuss the various types of liquid membranes and their technological applications.

Broadly speaking there are three different types of liquid membranes.

(i) **Bulk Liquid Membrane (BLM)** : Bulk Liquid Membrane (BLM) is a stirred organic phase of lower density than the aqueous phase positioned under it or vice-versa. In case of bulk liquid membranes, the two aqueous phases viz. the feed and the receiver, are separated by an immiscible organic carrier phase. As the driving force in the transport is through the bulk organic phase, it often provides the resistance to the transport of the metal ion of interest. Tri-n-butyl phosphate (TBP) and di-2-ethylhexyl phosphoric acid (HDEHP) have been used as extractants in several hydrometallurgical operations. Selective transport of Pu^{4+} over other long lived fission product contaminants was accomplished from aqueous acidic solutions through an organic BLM containing TBP as the mobile carrier dodecane as the membrane solvent and 0.5M ascorbic acid as the strppant. With increase in carrier concertation in the organic membrane , the amount of Plutonium that could be extacted into the membrane as well as the viscosity of the organic solution increased. These opposing effects resulted in maximum plutonium permeation with about 30% TBP in dodecane.

(ii) **Liquid Surfactant Membranes or Emulsion Liquid Membranes (ELM) :** Emulsion liquid membranes are also known as double emulsion. Two immiscible phases are mixed with a surfactant to produce an emulsion. This emulsion is then dispersed in a continuous phase , mass transfer takes place between the continuous phase and the inner phase through the immiscible (membrane) phase. These emulsion type membranes are usually stabilized by use of a surfactant. Since the membrane are thin and present a large surface area, they offer the potential of moving large amount of materials in a short time for concentrating and /or separating chemical species.

(iii) **Supported Liquid Membranes (SLM)** : Supported liquid membranes are also known as immobilized liquid membranes (ILM). It is prepared by impregnating the poe structure of a microporous polymer film with the liquid membrane, which may contain a complexation agent. Depending upon the support, immobilized liquid membranes are fabricated in thin sheet or hallow fibre configurations. Fig 1. Shows BLM and Fig2. Shows ELM and SLM. The principle involved in supported liquid membrane transport is as follows : two homogeneous, completely miscible liquids, which may be referred to as feed or source phase (F) and receiver phase (R) solution are spatially separated by a third liquid (M) which is practically insoluble in F and R and is immobilized in a porous hydrophobic polymeric support. Due to the favourable thermodynamic conditions created at the F/M interface, some components are selectively extracted from the feed and transported into the membrane liquid. Simultaneously, at the M/R interface, conditions are such that the reverse transport is favoured.

Liquid membranes are formed spontaneously because of the surfactant capacity of certain feed additives. As the concentratuion of the surfactant increases, the interface gets progressively covered with the surface liquid membrane. At the critical micelle concentration (CMC) the interface is completely covered. Use of liquid membrane results in significantly higher permeability for a solute retention than is possible with conventional membranes by themselves.

Applicatios of Liquid Membranes in the field of Technology

The application of liquid membrane in technology and separation success has increased heavily during the last 40 years. The introduction of liquid membrane technology includes configurations, transport mechanisms experimental techniques. Besides, it also involves the concept of reactive liquid membrane which combine traditional unit operations such as extraction or absorption with stripping.

Liquid membrane based separation methods are more effective than solvent extraction method because the two major drawbacks of the solvent extraction method viz thid phase formation and prolonged phase disengagement time which can be overcome with the liquid membrane based separation methods as they involve non-dispersive mass transfer. Hallow Fibre Supported Liquid Membrane (HFSLM) separations are particularly attractive due to large surface to volume ratio, faster mass transfer rates and continuous flow.

Commercial and laboratory applications of liquid membrane technology include gas transport, sensor development, metal ion recovery, Waste water treatment, biotechnology and biomedical engineering. within these disciplines, the technology has been applied to a range of diverse applications such as hydrocarbon separation organic removal, development of selective sensing devices, enzyme reactor, reverse osmosis and recovery of fermentation products.

Amongst the various separation techniques, liquid membrane based separation methods are getting increasingly popular due to factors such as high efficiency, low power consumption easy scale up due to a compact design etc.

(a) **Liquid Membranes in Reverse Osmosis and Desalination** : Osmosis is a natural phenomenon in which a liquid-water, in this case passes through a semi-permeable membrane from a relatively dilute solution towards a more concentrated solution. This flow produces a measurable pressure, called osmotic pressure. If pressure is applied to the more concentrated solution and if that pressure exceeds the osmotic pressure water flows through the membrane from the more concentrated solution towards the dilute solution. This process called reverse osmosis or RO removes upto 98% dissolved minerals, and virtually 100% of colloidal and suspended matter.

The tremendous impetus given to reverse osmosis by the invention of a highly asymmetric cellulose acetate membrane by Loeb and Sourirajan has moved it to the forefront of interest in membrane separation processes. Reverse-osmosis can also be defined as the retention of solutes of molecular weight below 500. Solvent transport through reverse-osmosis membranes is substantially diffusive in nature (Fig.3)

Martin first utilized poly (vinyl methyl) ether liquid membrane for reverse osmosis desalination. Reverse osmosis occurs when a solution is pressurized against a membrane preferentially permeable to solvent and the applied pressure exceeds the osmotic pressure difference across the membrane. The selectivity of the membrane originates from its much higher permeability to water than to the solute the barrier layer of a reverse osmosis is typically a moderately hydrophilic polymer.

The future of the reverse osmosis process in the separation of aqueous solutions is one of the brightest portions of the membrane separation spectrum. It is already being utilized on the modest scale to improve the quality of tap-water for industrial and home use.

(b) **Liquid Membrane in Waste-Water Treatment** : Various chemical, petrochemical, textile and metal finishing industries typically produce many different types of waste waters which contain various concentrations of toxic organic and inorganic substances. In most cases these pollutants are still present in trace quantities even after being treated by conventional means such as biological oxidation or alum coagulation. Further treatment is usually required to remove these contaminants before the streams are discharged into the environment.

Many different technologies have been applied for treating waste-water streams. Stream stripping, packed tower aeration (PTA) and granular activated carbon, GAC. Adsorptions are just a few of the techniques that have been successful in selectively removing trace organic pollutants from aqueous stream.

The first work performed by Li dealt with the separation of a binary mixture of aromatic and paraffinic hydrocarbons. Cahn and Li described a liquid membrane formulation for phenol removal in which sodium hydroxide is encapsulated by an organic liquid membrane and also solved a number of waste disposal problems. Halwachs et al reported the removal of phenol and other organic solutes. Terry et. al. presented further work on removing phenol and organic acids including mixtures using ELM technology.

Boyadhiev and Benzenshek reported mercury removal from waste-water. They also discussed the removal of phenol from waste-water by using combined ELM and creeping film pertraction. Fuller and LI reported on chromium and Zinc extraction from cooling water blowdown. Extraction of Uranium extraction has also been reported. Teremoto et al studied phenol and cresol extraction with ELM.

In recent years emphasis has been shifted to hollow fibre contactors as well as hollow fibre non-dispersive solvent exraction techniques its major advantage over other membrane separation techniques , independently variable flow rates without flooding limits, no phase density difference / phase separation requirement and large surface area to volume ratio (10^4 m^2 / m^3). Polymer inclusion membranes also deserve particular attention in view of their durability and ability to incorporate varying degree of selective extractants.

(c) Liquid Membranes in Gas, Petroleum and Separation of Organics

Amongst the various separation techniques, liquid membrane based separation methods are getting increasingly popular due to factors such as high efficiency, low power consumption and easy scale-up due to in a compact design etc. Membrane separation of a mixture has gained considerable importance in recent times. A mixture is simply fed to a suitably packaged membrane from which separated components flow, no relegation or replacement of any constituent is required.

In recent years, much has been done to improve the quality of membrane materials and to vary their properties with respect to a specific need or use. On the other hand, the development of technical processes using gas separation with membranes has not developed any further since the publication of works by Weller and Steiner in the fifties.

Membrane separations almost always use one single kind of membrane and as such only a binary separation can be achieved. The fundamentals of membranes permeation and the engineering considerations relevant to the specification of membrane gas separations have been presented by Michaels and Bixler and Stern. Kammermeyer in 1957 was the first to determine that for common gases such as O_2, N_2, H_2 and CO_2. Silicon rubber was the most permeable polymeric material known. In 1967 Robb reported the permeation properties of silicon rubber for a wide variety of gasses and vapour.

Synthetic polymeric membranes are often used in industrial practice for the separation of gas mixture. For instance recovery of hydrogen from purge gas streams containing CO_2, CO, CH_4 etc, recovery of $CO_2$from mixed well head gases in enhanced oil recovery applications, separation of atmospheric air etc. are now carried out in permeation using synthetic polymeric membranes.

In view of the increased demand for energy by the entire world, the application of liquid membrane for increasing the yield of petroleum wells has become important. A yield of about 30% of all the petroleum in a reservoir is obtained by the extraction due to the pressure of the natural gases forcing it out of the well and extraction by pumping in water after the gas pressure drops. The extraction of part of the remaining petroleum can be achieved by pouring in micellar solutions, resulting in lowering of the surface tension and viscosity of the petroleum micellar solution interface so that the remaining fuel will be immobilized and will combine with the total mass of the liquid.

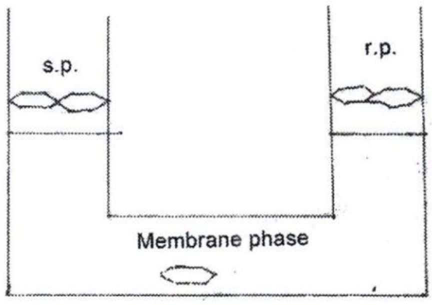

Fig. 1 Bulk-liquid membrane

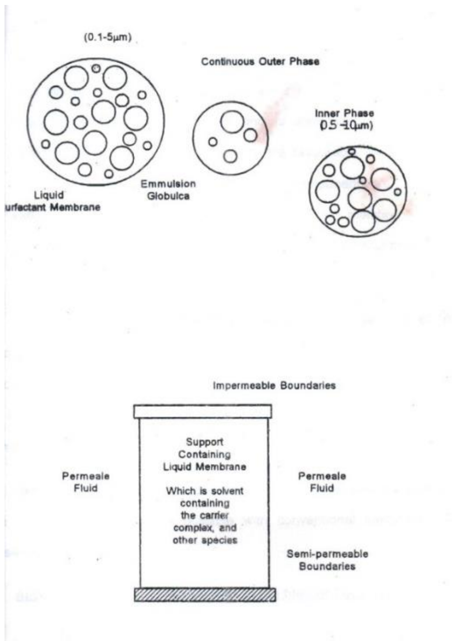

Fig. 2 Emulsion & immobilized Liquid Membranes.

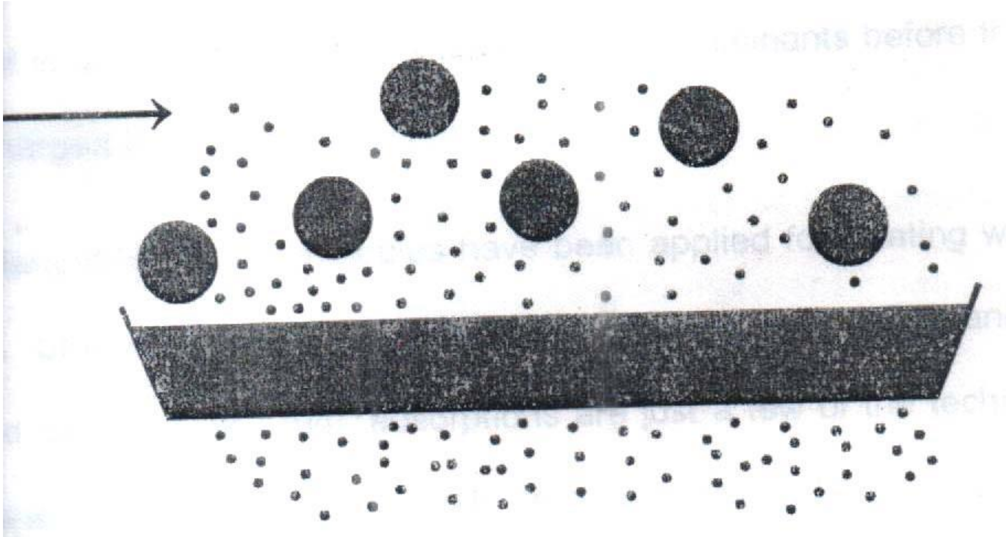

Fig. 3 Reverse Osmosis Process

REFERENCES:

1. N. Lakshminarayanaiah, " Transport Phenomenon in membranes", Academic Press, New York (1969) P.1.
2. J. W. Lorimer, "Applied fiber Sci. (F. Happy ed.), Vol.2", Academic Press, New York (1979) p.71.
3. C. P. Bean, "The Physics of porous membranes-natural pores" in G. Eiseman ed. "Membranes-Vol.I",Marcel Dekker Inc., New York (1972) P.1.
4. H. K. Lonsdale, J. Memb.Sci., 34 (1987) 125.
5. S. T.Hwang and K. Kammermeyer, "Membranes in separation vol.3", in A. Weiss berger ed. "Techniques of Chemistry" John Wiley and Sons, New York (1975).
6. P. Mears Ed., "Membrane Separation Processes"' Elsevier Publishing Co. Amsterdam (1976).
7. R. L. Blokhra et. al., J. Memb. Sci, 21 (1984) 123-135.
8. M. S. Suwardi and S. A. Stern, J. Polymer Sci. Polym. Phys., 11 (1973) 663-681.
9. M. L. Srivastava and S. N. Lal, J. Memb. Sci., 7 (1980) 21-37.
10. Opden Kamp JAF, Annu. Rev. Biochem., 48 (1979) 47.
11. W. Wickner, Science, 210 (1980) 861.
12. H. T-Tien, J. Phys. Chem., 72 (1968) 4512.
13. H. T-Tien and N. Nobamoto 'Nature' 224 (1969) 1107.
14. F. Martin, Aerojet-General Corp., Private Communications March (1963).
15. R. Markley, R. Cross and H. Bixler, OSW. Res. Develop, Rept. 281, December 1967.
16. R. Kesting, A. Vincent and J. Eberlin, DSWR and D report 117, August, 1964.
17. R. Kesting, "Reverse Osmosis process using surfactant feed additives" OSW Patent application SAL 830, Nov. 3,1965.
18. R. Kesting, "W. J. Subcasky and J. D. paton, J. Colloid, Interface Sci. 28, 156 (1968).
19. P. K. Mohapatra and V. K. Manchanda, Indian Journal of Chemistry, Vol. 42A, Dec. 2003, pp. 2925-2938.
20. Cusseler. E. L. and Evans, D. F. Sep. purify. Methods, 3, 399 (1974).
21. Maugh, T. H. Science, 193, 134 (1976).
22. N. N. Li, U. S. Patent 3, 410, 794, (1968). Chem. Abster, (1969), 70, 39550.
23. Gabelman, A and Hwang St, J. Memb. Sci., 159 (1999) 61.
24. Ortiz I., Galan B and Irabien A, J. memb. Sci. 118 (1996) 213.
25. Yang ZF, Guha A. K and Sirkar K. K., Ind Eng. Chem Res., 35 (1996) 1383.
26. A. M. Hochhauser and E. L. Cussler, Concentrating Chromium with liquid Surfactant Membranes, AICHE, Symp. Ser., 71 (152) (1975) 136.
27. T. P. Martin and G. A. Davies, The extraction of Copper from dilute aqueous solution using a liquid membrane process, Hydro Metallurgy, 2 (1976) (1977) 315.
28. K. Kondo, K. Kida, I. Koida, J. Iric and E. Nakashio, Extraction of Copper with liquid Surfactant membranes containing benzoylacetone, J. Chem. Eng. Jpn., 12(1979) 203.
29. W. Volkel, W. Halwachs and K. Schugeri, Copper extraction by means of liquid Surfactant Membrane Process, J. Membrane Sci., 6 (1980) 19.
30. J. Strzelbickil and W. Charewicz, The liquid Surfactant membrane Separation of Copper, Cobalt and Nickel from multicomponent aqueous solutions, Hydrometallurgy. 5 (1980), 243.

31. R. P. Cahn, J. W. Frankenfeld, N.N. Li, D. Naden and K. N. Subramanian, Extraction of Cu^{++} by liquid membranes, Rec. Dev. Sept. Sci., 4 (1981) 51.
32. J. W. Frankenfeld and N. N. Li, Waste Water Trreatment by liquid ion exchanger in liquid membrane systems, Rec. Dev. Sept. Sci. 3 (1977) 285.
33. W. Halwachs. E. Flaschel and K.Schugeri, Liquid membrane transport, A. highly selective separation process for organic solutes, J. Membrane Sci. 6 (1980) 53.
34. Ti Kitagawa, J. Nishikawa, J. W. Frankenfeld and N. N. Li, Waste Water Treatment ny liquid membrane process. Environmemt Sci. Technol. 11 (6) (1977) 602.
35. K. Kondo, K. Kita, and F. Nakashio, Extraction Kinetics of Cu^{++} with liquid surfactant membranes containing benzoylacetone J. Chem. Eng. Jpn. 12(3), (1979) 203.
36. K. Kondo, K. Kita, and F. Nakashio, Exraction Kinetics of Cu^{++} with liuid surfactant membranes in a stirred transfer cell, J. Chem. Eng. Jpn. 14 (1), (1981) 20.
37. J. W. Frankenfield, W. J. Asdher and N. N. Li Recent Dev. In Sept, Sci. N. N. Li, Ed., Chemical rubber Co., 1978, Vol. 4 P.39.
38. W. J. Asher, K. C. Bovee, J. W. Frankenfeld, R. W. Hammilton, L. W. Henderson, P. G. Holtzapple and N. N. Li, Liquid Mebrane System directed towards chronic uremia, Kidney J., 7 (1975 5409.
39. M. P. Biechl, R. M. Izatt, J. D. Lamb and J. J. Christensen, Use of a Macrocyclic crown ether in an emulsion membrane to effect rapid separation of Pb^{++} from Cation mixture, Sept. Sci. Technol. 17 (2) (1982) 289.
40. L. Boyadzhiev and G. Kyuchoukou, Further development of Carrier Mediated extraction, J. Membrane Sci., 6 (1980), 107.
41. G. Caramatta, C. Chavarie and H. Anglino, Hydrocarbon Separation through a liquid water membrane Modelling of permeation in an emulsion drop, AICHE. J., 24 (6) (1978) 948.
42. T.H. Mangh, Liquid Membranes- New Techniques for Separation, Purification Science, 193.
43. S. W. May and N. N. Li, The immobilization of urease using liquid surfactant membranes, Biochem. Biophys. Res. Commerce, 47 (1972) 1179.
44. A. Michade, H. Bixler and R. Hodges, J. Colloid Sci., 20 : (1965) 1034.
45. R.R. Mohan and N. N. Li, Reduction and Separation of Nitrate and Nitrite by liuid membrane- Eucapsulated enzymes, Biotechnol. Bioeng., 16 (1974), 513.