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Carrier-facilitated transport of Glycine leucine, and valine across the liquid membrane using anthraquinone derived podands

Anshumala Vani
anshumala_vani@rediffmail.com
Vikram University, Ujjain, Madhya Pradesh

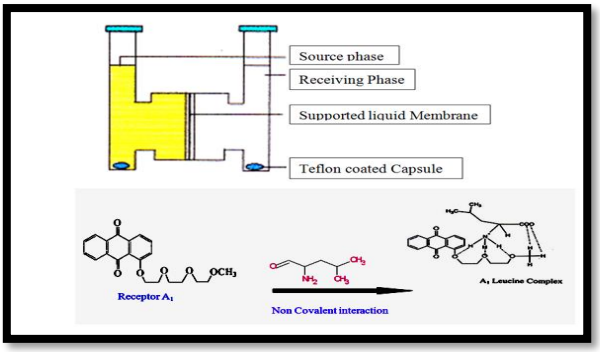
Mukesh Vani
vani_mukesh@rediffmail.com
Vikram University, Ujjain, Madhya Pradesh

Uma Sharma
vanimukesh9@gmail.com
Vikram University, Ujjain, Madhya Pradesh

ABSTRACT

Liquid membrane system mimics membrane mediated processes using designed carriers for transport of substrate based on molecular recognition has potential applications in developing of novel separation system. We have designed and synthesized a new series of redox switched anthraquinone derived podands (receptor) 1-(1-anthraquinonloxy), 3,6,9 triaoxanonane–9–methane (A_1) 1-(1- anthraquinonloxy), 3, oxapentane – 5 – methane (A_2),1-(anthraquinonloxy), 3 methoxy methane (A_3), 1,5 bis (2-(2-(2-(2- hydroxyethoxy) ethoxy) ethoxy) anthrancene 9-10 dione (A_4), 1,5 bis (2-(2-(2-hydroxyethoxy)ehoxy)ethoxy)anthracene-9-10 dione (A_5), 1,5 bis -(2-(2- hydroxyethoxy) ethoxy)ethoxy)anthracene-9-10 dione (A_6) have been characterized by M.P., TLC, IR, H^1NMR, Mass spectral analysis and cyclic voltammetry and used as a carrier in liquid-liquid extractionbulk liquid membrane, supported liquid membrane transport of amino acids. Quinone moiety present in these receptors not only act as redox centers but also act as a ligating site to interact substrate.The binding affinity of these synthesized receptors towards amino acid have been investigated and characterized in solid state as soft material and explored in solution state by liquid-liquid extraction, BLM,SLM system. Recognition of amino acid by synthesized receptor retained in both solid as well as solution state. The trend of transport of amino acid is lecucine>valine>glycine. Receptor A_4,A_5,A_6 are bibracchial podands proved to be good extractant and poor carrier than single armed podands A_1,A_2,A_3. Selectivity and specificity signify their scope in separation and used in fabrication of biosensors and redox scitchable devices.

Keywords – *Redox switched receptors, Amino acids*, BLM, SLM



Carrier facilitated transport of amino acids through Supported Liquid Membrane (SLM)

I. INTRODUCTION

Liquid membranes are a unique tool for selective transport of substrate and strongly dependent on the ability to design and synthesis of receptors with the potential to achieve recognition of substrate leads in developing separation system[1] (Luccio 2002).

The lariat ethers derived from anthraquinone have been concerned with electrochemical switching. With these considerations we synthesized novel anthraquinone-derived lariat ethers and studied their binding properties with Glycine leucine, valine.(Vani et al 2010)[2] Liquid membrane transport is an effective method for estimating the complexation properties of Glycine leucine ,valine. This capability underlies the use of anthraquinone-derived redox switched (Bhatnagar et al 2004) [3]lariat ethers as selective ligands for extraction, separation and liquid membrane(Tomar et al 2008)[4] transport of amino acids and in fabrication of sensors and molecular devices.

II. MATERIALS AND METHOD

Chemicals

The reagents used for the synthesis of receptors are chloroanthraquinone,1,5-dichloroanathraquinone (Lancaster, Ward Hill, MA, USA), sodium hydride (MERCK, Nerul, Navi Mumbai, India), tetraethyleneglycol and methoxy methanol (Fluka, Buchs, Switzerland).Solvents CH 2 Cl 2 , THF, CH 3 OH, C 6 H 6 , CHCl, CH 2 Cl 2 and CCl 4 were obtained from Qualigens (Mumbai, India). Glycine, valine, leucine were obtained from Lancaster. For the cyclic voltammetric studies $1*10^{-3M}$ stock solution of sample was prepared indimethyl formamide (DMF), 1M KCl and Britton Robinson(BR) buffer (pH 6.5) was used as supporting electrolyte.

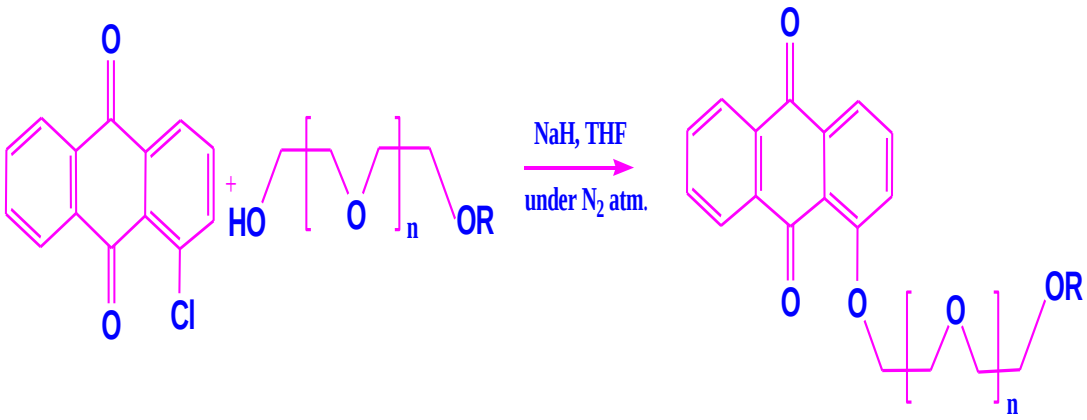
Instruments

Melting point was measured by the melting point apparatus Boss 165, Elemental analysis (C, H,N) were obtained from CDRI Lucknow using elemental analyser Carlo Erba 1108, BASI Epsilon electrochemical system (model no. C31276) was used for cyclic voltammetric studies .IR spectra were recorded on FTIR spectrophotometer(Perkin-Elmer BX 70836) at the School of Studies in Chemistry and Biochemistry, Vikram University,Ujjain. and ^{1}HNMR spectra recorded on NMR spectrophotometer (varian 350) at 400 MHz, Amino acids were estimated by spectrophotometer Perkin Elmer 70836.

III. EXPERIMENTAL METHODS

Redox switched anthraquinone derived podands (A1-A6) have been synthesized as shown in Schemes reported by Echegoyen (Echegoyen et al)[5] and published in previous papers Isolation (Bhatnagar et al 2007-08)[6,7] and liquid-liquid extraction (Mishra et al. 1999)[8] studies have been carried out to know the affinity of anthraquinone derived receptors and the selectivity was determined by bulk liquid membrane (BLM), (Sharma et al 2020) [9]and supported liquid membrane transport studies (Mishra et al. 2002)[10].

Scheme

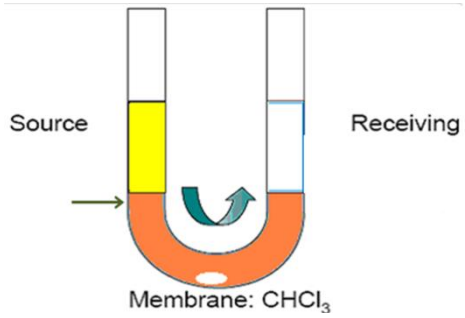


Isolation studies

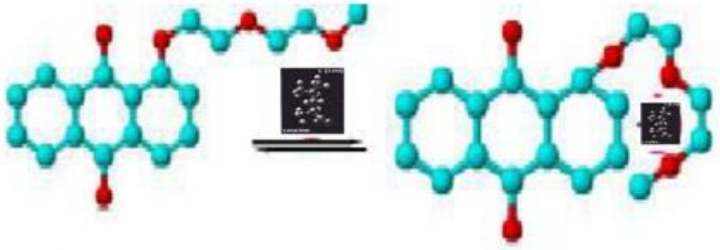
The isolation[11] studies were performed by mixing different proportion of amino acid and sugars with receptor (A1-A6) in different solvents like methanol, ethyl, acetate, isporopanol, acetonitrile, chloroform, Carbon tetrachloride, dichloromethane. The mixture was heated on a water bath for 2 to 3 minutes and then allowed to crystallize at room temperature. Crystallization generally occurs within two to three days shiny crystals were obtained. The crystals were vacuum filtered and recrystallized from same solvent from which they have isolated. The characterization of isolated compounds were carried out by melting point determination and confirmed by elemental and spectral analysis (CHN estimation, IR, ^{1}HNMR) as shown in table.

Extraction Procedure

For extraction[12] 10 mL of sugar and amino acid solution was vigorously stirred with 10 mL of receptor solution in an organic solvent ($CHCl_3$) in a small beaker using magnetic stirrer. The beaker was covered and stirred for 4 hours. After 4 hours, the mixture was allowed to stand for 5 minutes for the separation of two phases. The depleted aqueous phase was removed and the amount of sugar and amino acid extracted by the receptor was determined by its difference in concentration in aqueous phase before and after extraction by spectrophotometer.



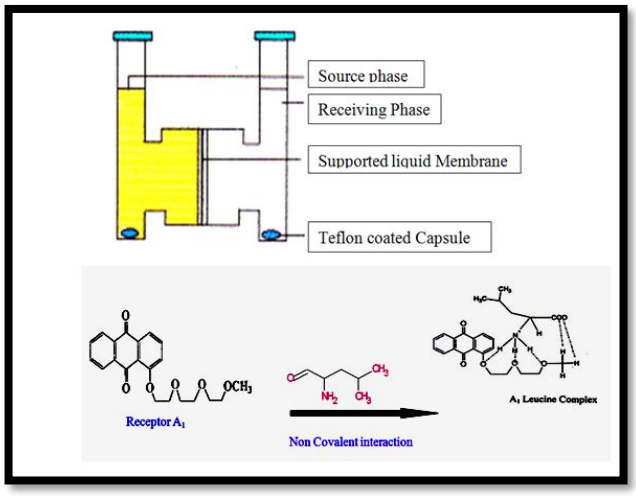
Bulk Liquid Membrane System (BLM)

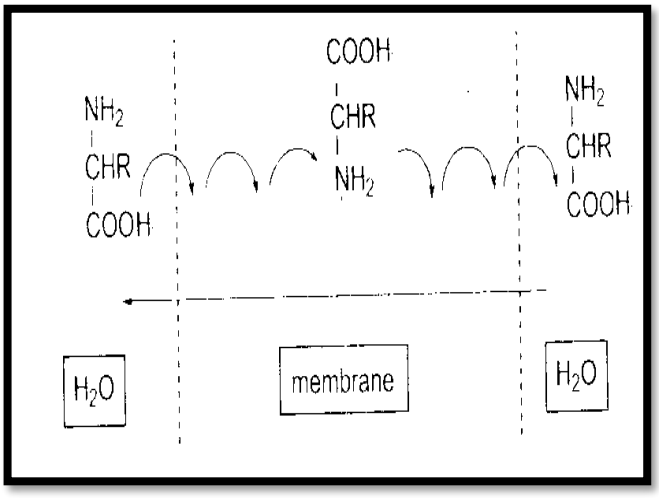


Transport experiments[13] were performed in a U-tube glass cell in which 25 mL of receptor solution in $CHCl_3$ was placed in the bottom of the U-tube serving as the membrane. 10 mL of aqueous solution of sugar and amino acid was placed in one limb of the U-tube serving as source phase and 10 mL of double distilled water was placed in another limb of the U-tube, which served as the receiving phase. The two aqueous phase i.e. source and receiving phase floating on the organic membrane phase respectively in two limbs of the U-tube. The membrane phase was constantly stirred using magnetic stirrer. The samples were withdrawn from source and receiving phase after 24 hours and amount of sugar and amino acid transported was determined by Spectrophotometer. Apparatus set up are shown in figure.

Supported Liquid Membrane Studies (SLM's)

In SLM study membrane support was achieved by immersing PTFE, onion, dialysis membrane in the receptor solution in $CHCl_3$[14,15]. The supported liquid membrane was positioned between two cylindrical half-cells. One cell compartment (source phase) contained an aqueous solution of the amino acid and the other cell compartment contained the receiving phase (50 mL) double distilled water separated by membrane having an effective diameter of 1 cm. Both the phases were stirred with magnetic stirrer at room temperature. The sample was withdrawn from the receiving phase after 24 hours and analyzed for samples by using spectrophotometer.





SLM transport of Amino Acid

IV. RESULTS & DISCUSSION

Liquid –Liquid extraction and bulk liquid membrane (BLM) Rhaizada et al (2010), supported liquid membrane (SLM) transport experiments of biological impotant amino acids were performed using redox-switched anthraquinone derived podands. Blank

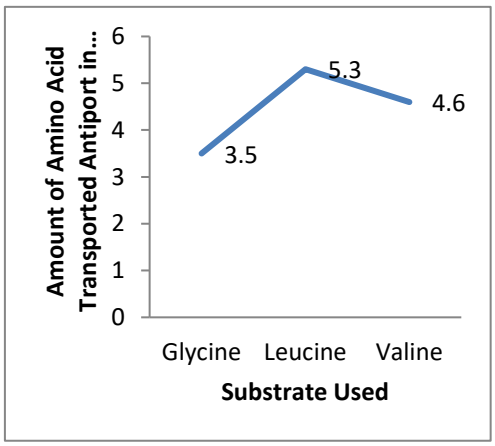
experiments were carried out for extraction and transport studies for amino acid in which membrane was devoid of carrier. No leakage of amino acid from source phase into organic phase was observed. All measurements were performed in duplicate to check reproducibility.

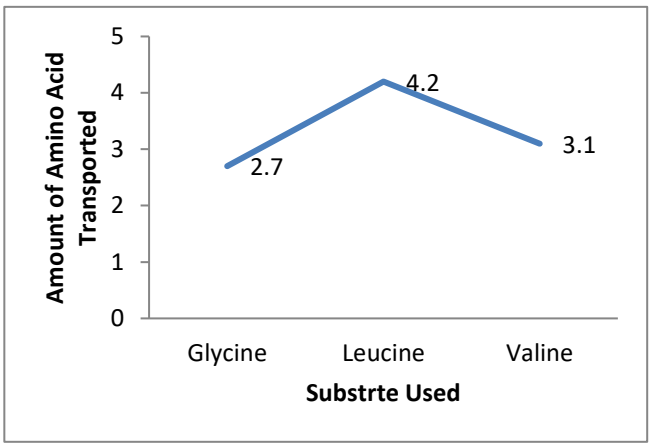
Effect of concentration

Amino acids as well as receptors concentration variation have been studied. The optimum concentration of amino acids and receptors (A1-A6) for extraction, bulk liquid membrane transport, and supported liquid membrane transport studies is found to be 0.1M to 0.3 M and $1x10^{-2}$ M, respectively.

Effect of pH

Facilitated proton driven transport enhances glycine, leucine, valine transport rate by receptor A_1 as shown in FIG.1 pH value of source phase maintained as 9.5 which increases amount of transport of amino acid than neutral and acidic this is due to the existence of anionic form of amino acid by deprotonation. pH value of the source was maintained as 3.4 which increases amount of transport of amino acid than neutral medium. Amount of amino acid transported in a acidic medium is less than basic medium this indicates complexation of amino group of amino acid with receptor.





Effect of Oxidsed and reduced state redox-switched anthraquinone derived podands

Extraction and. transport of amino acids [16,17] with redox-switched anthraquinone derived podands have been carried out with two different forms of receptors i.e. oxidesed and reduced state. Redox switched functional molecule present in synthesized receptor switched them between oxidsed and reduced state provide ligating site towards glycine, leucine, valine in solid state (isolation studies) investigated as soft material and demonstrated in solution state by liquid- liquid extraction, bulk liquid membrane, BLM, supported liquid membrane system SLM.

The trend of transport of amino acid is leucine > valine > glycine Table-1 and for extraction is glycine > valine > leucine Table-2. Extraction and transport carrier ability depends on hydrophobicity of amino acids. Receptor A4 ,A5 ,A6 are bibracchial podands [6] proved to be good extractant and poor carrier than single armed podands A1 , A2, A3.

Effect of nature of membrane:

In case of supported liquid membrane [18,19] system the nature of membrane also plays an important role during transport of amino acids. SLM consists of PTFE, Onion, dialysis as membrane support impregnated with receptor solution in $CHCl_3$. Supported liquid membrane configuration is more advanced and efficient than bulk liquid membrane system. In SLM(system(Table-3) receptor molecule have fixed mobility on the membrane support, provide stable conformation to the receptors. SLM results explained on the basis of relay mechanism. All receptors show higher transport of amino acid with Onion membrane as compared to PTFE and dialysis membrane. The hydrophobicity and porosity of the membrane plays an important role in transport studies. Recognition of amino acid by synthesized receptor retained in both solid (isolation studies) as well as solution state (BLM, SLM).

Figure-1

Amount of amino acid extracted after 4 h at $1x10^{-2}$ M with receptor A_1 to A_3 in oxidized and reduced state

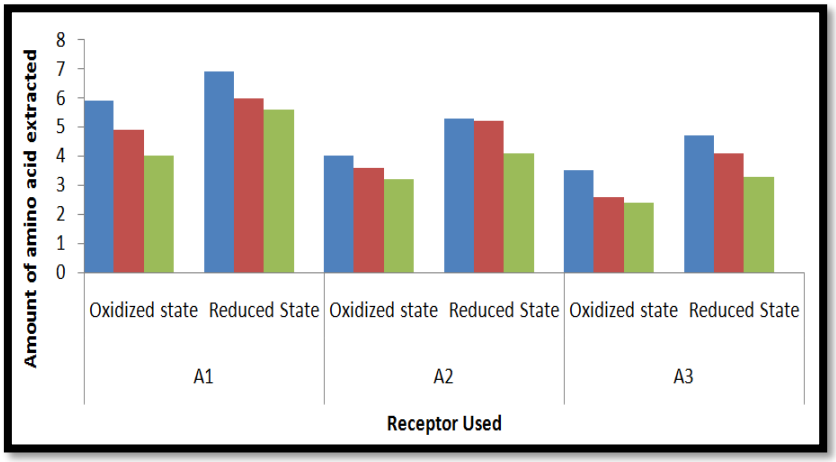


Figure-2 Amount of amino acid transported after 24 h at $1x10^{-2}$ M with receptor A_1 to A_3 in oxidized and reduced state

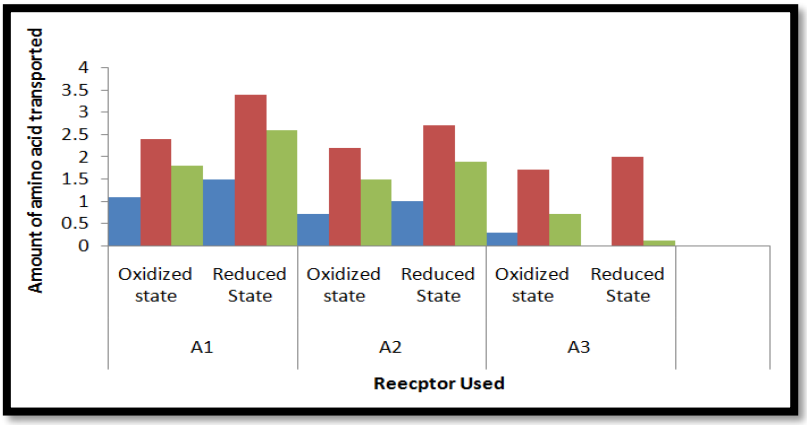


Figure 3- Amount of amino Acid transported with receptors A_1 to A_6 at $1x10^{-2}$ M through SLM by using onion membrane as a support

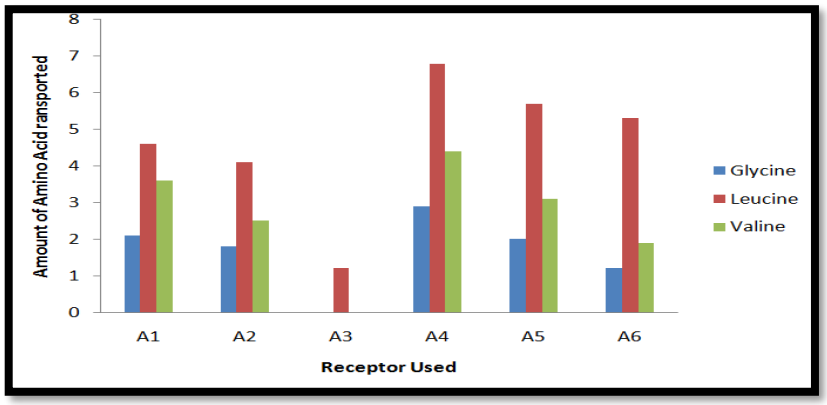


Figure 4- Onion Member after transport

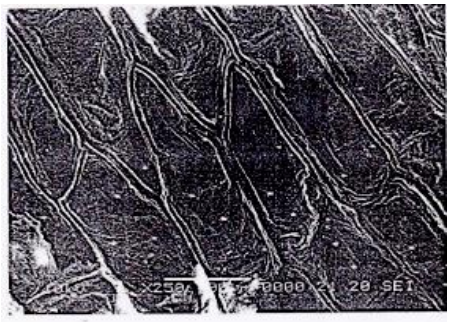
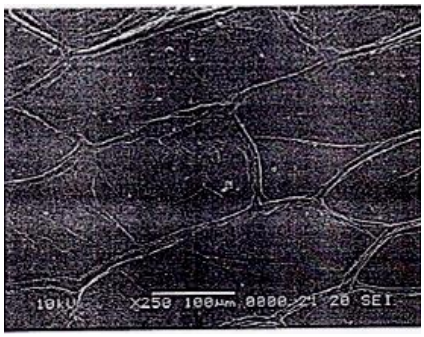


Figure 5- Onion Member before transport



V. CONCLUSION

The experimental results suggest that SLM has the advantage of higher transport rates. Onion membrane is better support for the transport of amino acids. The hydrophobicity and porosity of the membrane affects SLM transport

VI. ACKNOWLEDGEMENTS

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VII. ABBREVIATIONS

m.p.	*melting point*
IR	*Infra Red*
1H NMR	*Proton nuclear magnetic resonance*
BLM	*Bulk Liquid Membrane*
SLM	*Supported Liquid Membrane*
CV	*Cyclic Voltammetry*

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