SELECTIVE MEMBRANE TRANSPORT OF AMINO ACIDS BY FUNCTIONALIZED CALIX[4]ARENES

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Introduction

Calixarenes have attracted considerable interest in the growing field of supramolecular chemistry. As cyclic oligomers are important receptors of supramolecular hosts involved in host-guest molecular recognition of various compounds as well as in analytical applications such as separation of chemical or biochemical compounds [1-3]. Derivatisation of calix[n]arenes at the upper and lower rim in order to introduce various functional groups has led to new compounds with desired properties [4,5].It is well known that the calix[4]arene cavity is not large enough to accommodate some molecules but its functionalization allows the obtaining of external binding sites appropriate to form inclusion complexes with guest molecules [2]. Our current research has focused on the transport through liquid membrane of some aromatic amino acids methylesters by using of a series of functionalized calix[4]arenes variously substituted by acid or amido functions, glycolic chains and hydroxyl groups as carriers.

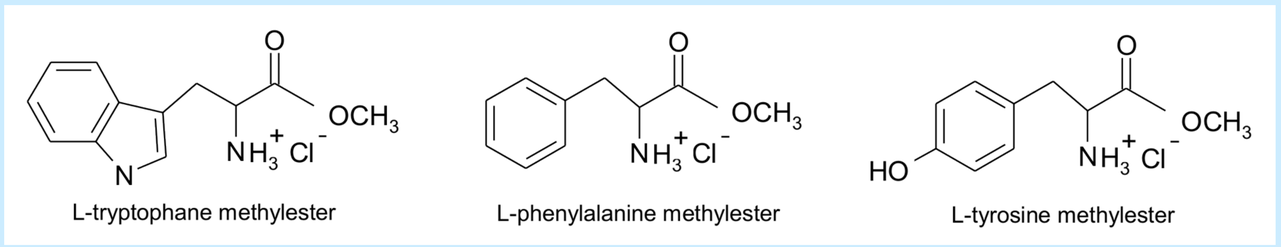
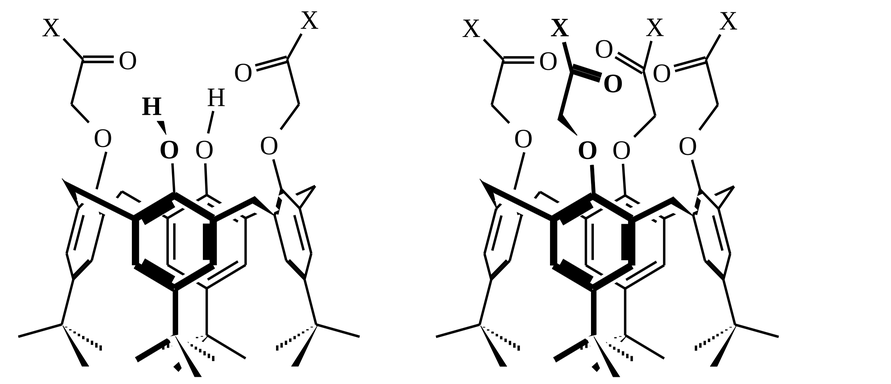


Fig. 1 *Chemical structures of the amino acids methylester*.

Experimental

The transport experiments were carried out by using a U-shaped glass tube (Fig. 4). The transport were carried out by stirring the aqueous and organic phases at 180 rpm at room temperature for 24 h.The concentration of amino acids (Fig.1) in both the aqueous phases (source – left arm in Fig.4 and receiving phase – right arm in Fig.4) was determined by UV-Vis measurements with an UV-Vis Spectrometer JASCO V-530. Each experiment was repeated three times and reproductibility was ±10%. Blank experiments were performed for reference in the absence of carrier.



1 X = OH
2 X = $NHCH(CH_2OH)_2$
3 X = $NHC(CH_2OH)_3$
4 X = OH
5 X = $NH(CH_2)_2O(CH_2)_2OH$

Fig. 2 *The chemical structure of calixarenes **1-5**.*

Results

The values of the transport yields of L-TrpOMe, L-PheOMe and L-TyrOMe through chloroform liquid membrane by means of calix[4]arene derivatives **1-5** as carriers are given in Fig.3. All calixarenes perform the transport of amino acid methylesters. As one can see from Fig. 3, the receptors **1** and **5** exhibit high transport ability towards L-TrpOMe (98% with **1** and 87% with **5**) and L-PheOMe (88% with **1** and 86% with **5**). In all our experiments, the values of amino acids methylester transport trough liquid membrane by using calix[4]arene **4** as carrier are smaller than that of calix[4]arenes **1-3** and **5**. The results pointed out that the structure of calix[4]arenes is one of the most important parameter for the recognition of aromatic amino acid methylesters. It was observed from the experimental results that the functional groups introduced on the calix[4]arene structure profoundly influence the transport abilities of calix[4]arenes.

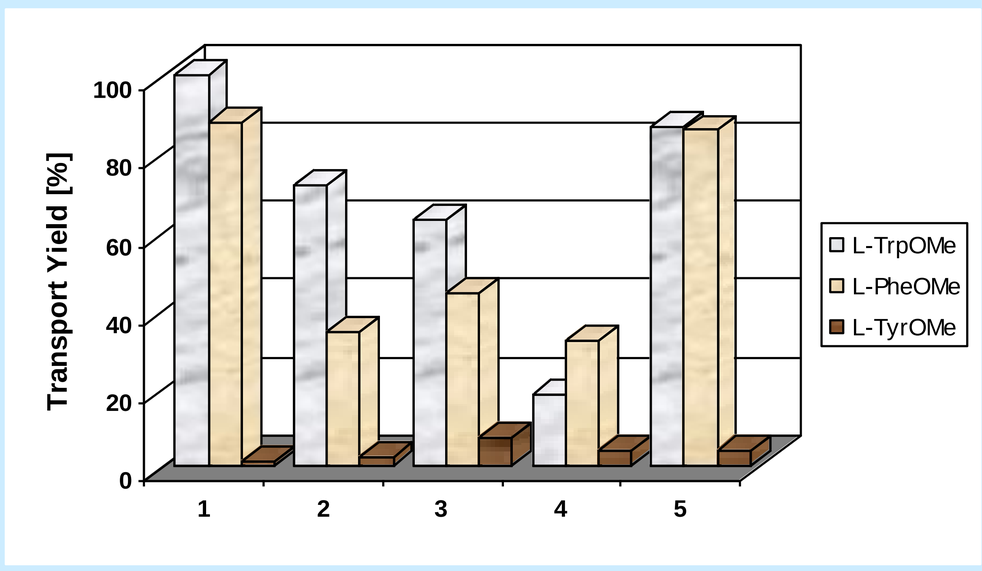


Figure 3. *Transport yields (%) of amino acids through liquid membrane by calix[4]arene derivatives **1-5** .*

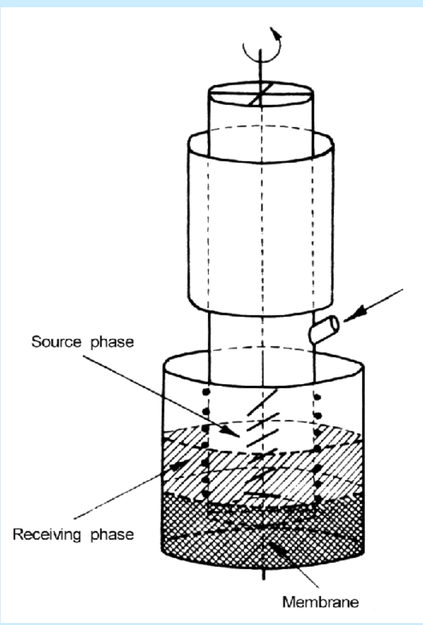


Figure 4. *The device employed in separation of some amino acids through chloroform liquid membrane*.

Conclusions

The selective active transport trough liquid membrane assisted by the pH gradient of amino acid methylesters by using a series of calix[4]arenes substituted by acid and amido functions, glycolic chains and hydroxyl groups as carriers were investigated. The experimental results suggest that aromatic amino acids methylesters are effectively transported through liquid membrane by calix[4]arenic receptors **1-5** with different yields. The transport of amino acids is controlled by factors like the functional groups introduced on the calix[4]arene structure as well as by the nature of amino acid methylesters, and the stirring time of phases. The influence of the composition and the structure of the compounds upon the partition processes occurring in triphasic systems were studied.

References

[1] Gutsche, C. D. *Calixarenes Revisited*; The Royal Society of Chemistry: Cambridge, **1998**. [2] Asfari, Z.; Böhmer, V.; Harrowfield, J.; Vicens, J. (eds.), *Calixarenes 2001*; Kluwer Academic Publishers: Dordrecht, **2001**. [3] Lumetta, G. L.; Rogers, R. D.; Gopalan, A. S. (eds.), *Calixarenes for Separations*; ACS Symposium series 757, American Chemical Society: Washington, **2000**. [4] Hamdi, A.; Lee, Y. H.; Kim, Y.; Kusumahastuti, D. K.; A., Ohto, K.; Abidi, R.; Vicens, J. *Tetrahedron Lett*. **2009**, *50*, 540. [5] Hamdi, A.; Souane, R.; Kim, L.; Abidi, R.; Mutihac, L.; Vicens, J. *J. Incl. Phenom. Macrocycl. Chem.* **2009**, *64*,95.

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