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Extraction behaviour of amino acid esters by functionalised calix[4]arenes

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Abstract Calixarenes **2–4**, **6** and **7** in the cone conformation variously substituted by acid or amido functions, glycolic chains and hydroxyl groups were synthesised. They have been used in extraction of native amino acid and amino acid esters.

Keywords Calixarenes · Synthesis · Extraction

Introduction

Calixarenes are cup-shaped molecules that can form inclusion complexes with a wide range of guest species. Calixarenes contain a repeating phenolic unit forming a macrocycle via methylene bridges [1–4]. They have a vase-like structure defined by an upper rim, lower rim and a central annulus. The polar and non-polar nature of the cavities enables them to interact with a wide range of guests species, depending on the binding groups substituted ate each rim and the number of repeating units in the macrocycle. As such, they belong to a broad range of compounds, such as crown-ethers, cryptands, cucurbiturils and cyclodextrins [5], which are known to form host-guest complexes in solution. Calixarenes have been used as sensor devices, as toxic metal-removal agents in waste treatment, as catalysts, as liquid crystals, and as synthetic ionophores in transmembrane ion transport [6–8]. There are studies dedicated to the molecular inclusion of biological substrates, like biogenic amines, amino acids, and peptides. Likewise, numerous studies have been focused on the ability of calixarenes to form complexes with amino acids and their derivatives, on the basis of their importance in natural living processes. The molecular recognition of amino compounds by calixarene derivatives involving multiple noncovalent interactions like hydrogen bonds, van der Waals forces, π–π stacking, cation-π, and hydrophobic effects depends on the type, the shape, and the flexibility of the receptor and the substrate as well [9, 10]. The remarkable host-guest properties of calix[6]arene tris-carboxylic acid derivatives toward ammonium ions in solution and in solid state have also been reported [11]. Moreover, functionalized calixarenes have been proved to be appropriate receptors acting as extractants in solvent extraction as well as carriers through liquid membranes for separation of various compounds [7, 12–15].

The ability of calix[6]arene carboxylic acid derivatives to act as extractants for aromatic amino acids, nucleotide bases, such as adenine, and catecholamine has been reported by Oshima et al. [16, 17]. The driving force of the complexation was established to be the electrostatic interaction between the amino group of the amino acid and the oxygen atoms of the calix[6]arene. Several synthetic receptors based on calixarene for chiral recognition of amino acids have been made available. Thus, Okada et al. [18] prepared calix[4]arene having chiral pendant groups and subsequently used them to selective extraction and transport of some amino acid ethyl and methyl esters, and Z-amino acid carboxylates into CH_2Cl_2. The efficiency of

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extraction was explained by the hydrophobicity of the amino acids and the extractability of receptors was increased by replacing the methyl group with the ethyl group. Shinkai et al. [19] have proved by spectroscopic means that pseudo-C_2-symmetrical homooxacalix[3]arene exhibited enantiomeric recognition properties towards alanine ethyl ester and phenylalanine ethyl ester. Chiral separation of zwitterionic form of aromatic amino acids by calix[4]arene-based α-aminophosphonates through a supported liquid membrane composed of a porous polymeric support was reported by Antipin et al. [20].

In the present article we report our recent results on the extraction of amino acid native and ester derivatives (see Chart 1) by calix[4]arenes **2–4**, **6** and **7** variously substituted by acid or amido functions, glycolic chains and hydroxyl groups (see Chart 2).

Experimental section

Syntheses

All reagents and solvents for synthesis were commercial and used without further purification. Uncorrected melting points (Mps) were taken on a Buchi 500. ^{1}H NMR spectra ($CDCl_3$, 300 MHz, in ppm from tms) were recorded on a Bruker SY 200. FAB(+) MS spectra were measured on a Biflex Bruker. The elemental analyses were carried out at the Service de Microanalyse de l'ULP at Strasbourg.

Preparation of **2–4**, **6** and **7**

Hydrolyses

Calixarenes **2** [21] and **6** [22] have already been already published. However our method of preparation is different.

Preparation of ***2*** 25,27-dihydroxy-26,28-dimethylester-*p-tert*-butylcalix[4]arene (**1**) [23, 24] (0.500 g, 0.63 mmol), KOH (0.353 g, 6.30 mmol) and a 1:1 mixture of ethanol:water (20 mL) stirred at reflux 21 h. Solvents were evaporated to dryness. Dichloromethane was added with 1 N HCl and water until pH = 3. The organic layer is dried over $MgSO_4$. After filtration and evaporation of the solvents **2** was obtained as a white solid (0.376 g, 78%). Mp = 217–220 °C. ^{1}H NMR δ (ppm) 9.03 (s, 2H, COO***H***), 7.80 (s, 2H, O***H***), 7.08 (s, 4H, Ar***H***), 6.97 (s, 4H, Ar***H***), 4.71 (s, 4H, ArOC***H₂***), 4.18 (d, J = 13.0 Hz, 4H, AB system ArC***H₂***Ar), 3.46 (d, J = 13.0 Hz, 4H, AB system ArC***H₂***Ar), 1.27 (s, 18H, C(C***H₃***)$_3$), 1.08 (s, 18H, C(C***H₃***)$_3$).

Preparation of ***6*** 25,26,27,28-tetramethylester-*p-tert*-butylcalix[4]arene (**5**) [25] (0.300 g, 0.32 mmol), KOH (0.353 g, 6.3 mmol) and a 1:1 mixture of ethanol:water (15 mL) were refluxed with stirring during 22 h, Solvents were evaporated to dryness. Dichloromethane was added with 1 N HCl and water until pH = 3. The organic layer is dried over $MgSO_4$. After filtration and evaporation of the solvents **6** was obtained as a white solid (0.282 g, 85%). Mp = 246–247 °C. ^{1}H NMR δ (ppm) 9.52 (s, 4H, COO***H***), 6.95 (s, 8H, Ar***H***), 4.55 (s, 8H, ArOC***H₂***), 4.32 (d, J = 12.0 Hz, 4H, AB system ArC***H₂***Ar), 3.30 (d, J = 12.0 Hz, 4H, AB system ArC***H₂***Ar), 1.08 (s, 36H, C(C***H₃***)$_3$).

Aminolyses

Aminolyses reactions were carried out according to prescriptions described by us [26].

Preparation of ***3*** 25,27-dihydroxy-26,28-dimethylester-*p-tert*-butylcalix[4]arene (**1**) (0.810 g, 1.01 mmol), commercial 2-amino-1,3-propanediol (0.323 g, 3.24 mmol) and 1:1 mixture of methanol:toluene (10 mL) were refluxed for 16 h. The solvents were removed by evaporation under reduced pressure. The residue was triturated and precipitated with methanol. Filtration gave pure **3** as white solid (0.520 g, 57%). Mp = 169–172 °C. ^{1}H NMR δ 9.20 (d, J = 7.0 Hz, 2H, N***H***), 7.44 (broad s, 2H, ArO***H***), 7.09 (s, 4H, Ar***H***), 6.86 (s, 4H, Ar***H***), 4.61 (s, 4H, ArOC***H₂***), 4.22 (d, J = 13.3 Hz, 4H, AB system, ArC***H₂***Ar), 3.86 (m, 8H, CHC***H₂***OH), 3.47 (d, J = 7.0 Hz, 2H, NHC***H***), 3.43 (d, J = 13.3 Hz, 4H, ArC***H₂***Ar), 2.65 (broad s, 4H, CH$_2$O***H***), 1.28 (s, 18H, C(C***H₃***)$_3$), 0.99 (s, 18H, C(C***H₃***)$_3$). MS-FAB positive m/z = 933.477 (M-H + Na), 895.818 (M-H$_2$O + 2 H) (calculated mw = 971.24). (calculated mw = 911.19). Anal. calcd. for $C_{54}H_{74}O_{10}N_2$:C, 71.18; H, 8.19. Found C, 70.60; H, 8.02.

Preparation of ***4*** 25,27-dihydroxy-26,28-dimethylester-*p-tert*-butylcalix[4]arene (**1**) (1.021 g, 1.26 mmol), commercial tris(hydroxymethyl)aminomethane (0.916 g, 7.56 mmol) and a 1:1 mixture of methanol:toluene (16 mL) were refluxed for 4 days. The solvents were removed by evaporation under reduced pressure. The residue was triturated and precipitated with methanol. Filtration gave pure **4** as a white solid (0.751 g, 61%). Mp = 224–228 °C. ^{1}H NMR δ 8.51 (s, 2H, N***H***), 7.10 (s, 4H, Ar***H***), 6.72 (s, 4H, Ar***H***), 6.46 (broad s, 2H, ArO***H***), 4.53 (s, 4H, ArOC***H₂***), 4.19 (s, 4H, ArOC***H₂***), 4.14 (d, J = 13.0 Hz, 4H, ArC***H₂***Ar), 3.86 (m, 8H, CHC***H₂***OH), 3.39 (4H, d, J = 13.0 Hz, ArC***H₂***Ar), 1.62 (broad s, 6H, CH$_2$O***H***), 1.31 (s, 18H, C(C***H₃***)$_3$), 0.89 (s, 18H, C(C***H₃***)$_3$). MS-FAB positive m/z = 993.487 (M-H + Na), 955.813 (M-H$_2$O + 2 H) (calculated mw = 971.24). Anal. calcd. for: $C_{56}H_{78}O_{12}N_2$:C, 69.25; H, 8.09. Found C, 70.11; H, 7.82.

Preparation of **7** 25,26,27,28-tetramethylester-*p-tert*-butylcalix[4]arene (**5**) (3.751 g, 4.00 mmol), commercial 2-(2-aminoethoxy)ethanol (4.211 g, 40.02 mmol) and a 1:1 mixture of methanol:toluene (50 mL) were refluxed for 10 days. Precipitation with methanol gave pure **7** as a white solid (2.80 g, 57%). Mp 244–246 °C. ^{1}H-NMR ($CDCl_3$), 8.20 (t, $J = 5.0$ Hz, 4H, N***H***), 6.80 (s, 8H, Ar***H***), 4.63 (s, 8H, ArOC***H*****$_2$**), 4.55 (d, $J = 13.0$ Hz, 4H, AB system, ArC***H*****$_2$**Ar), 3.55 (s, 36 H, (C***H*****$_2$**)$_2$O(C***H*****$_2$**)$_2$OH), 3.74 (q, $J = 6.5$ Hz, 8 H, C***H*****$_2$**NH), 3.35 (d, $J = 13.0$ Hz, 4H, AB system, ArC***H*****$_2$**Ar), and 1.06 (s, 36H, C(C***H*****$_3$**)$_3$). MS-FAB positive *m/z* = 1228.70 (calculated mw = 1229.56). Anal. calcd. for $C_{68}H_{100}O_{16}N_4$:C, 66.43; H, 8.20. Found: C, 67.89; H, 8.37.

Extraction experiments

The following amino acid derivatives: L-tryptophane methylester hydrochloride (L-TrpOMe), L-phenylalanine methylester hydrochloride (L-PheOMe), L-tyrosine methylester hydrochloride (L-TyrOMe), and native L-tryptophane (L-Trp), L-phenylalanine (L-Phe), and L-tyrosine (L-Tyr) were obtained from Fluka at the highest purity commercially available and employed without further purification (Chart 1). The organic solvent chloroform was distilled before use. Distilled (Millipore) water was used throughout the experiments.

Liquid–liquid extraction

The extraction experiments of amino acids from water into chloroform were performed according to Pedersen's procedure [27]. Equal volumes of 2.5×10^{-4}–1.0×10^{-3} M of amino acid methylester or native amino acid at pH ≈ 5.5 in aqueous phases (5 mL) were extracted with chloroform solution (5 mL) of calixarene derivatives 5.0×10^{-4}–1.0×10^{-4} M. The pH was measured by a digital MV-870 Pracitronic pH-metre with glass electrode and saturated calomel electrode. Chloroform and water were saturated with each other to prevent volume change during extraction. The phases were mixed and shaken for 30 min at 25 ± 1 °C. The pH of the aqueous solutions was adjusted by the hydrochloric acid. The extractability was calculated as $E[\%] = \frac{(A_0 - A)}{A_0} \times 100$, where A_0 and A are the absorbances of the aqueous phases before and after the extraction with calixarenes, respectively. The absorbance was determined by spectrophotometric measurements carried out by means of an UV-Vis Spectrometer JASCO V-530. Each experiment was repeated five times.

Results and discussion

Synthesis of the calixarenes derivatives **2–4**, **6** and **7**

Calixarenes **2–4**, **6** and **7** were obtained from the corresponding methylesters **1** [23, 24] and **5** [25] by alcoholic hydrolysis in the presence of an excess of KOH followed by acidification with 1 N HCl (to give diacetic **2** and tetraacetic **6**) and by aminolysis (to give diamido **3** and **4**, and tetraamido **7**). Aminolyses were carried out according to preparations published by us [26] by refluxing the methylesters **1** and **5** with an excess of chosen amines in 1:1 mixture of methanol:toluene (see Experimental). Calixarenes **2–4, 6** and **7** were fully characterized by ^{1}H NMR, mass spectrometry and microanalysis. They were shown to adopt the cone conformation due to the presence at ~3 ppm and 4 ppm of characteristic AB systems for the ArCH_2Ar methylene protons in the macrocycle.

Extraction of amino acids by **2–4**, **6** and **7**

The liquid–liquid extraction of some native and methylesters aromatic amino acids from aqueous phase (pH ≈ 5.5) into chloroform phase was performed with calixarene derivatives **2–4**, **6**, and **7**. The values of extractabilities of L-Trp and L-Trp-OMe by using calixarene derivatives **2–4**, **6** and **7** are presented in Fig. 1. The order of decreasing extraction of L-TrpOMe for the employed extractants is the following: **7** (65%) > **4** (61%) > **2** (50%) > **3** (41%) > **6** (5%)**.** Receptor **6** exhibited limited extraction abilities

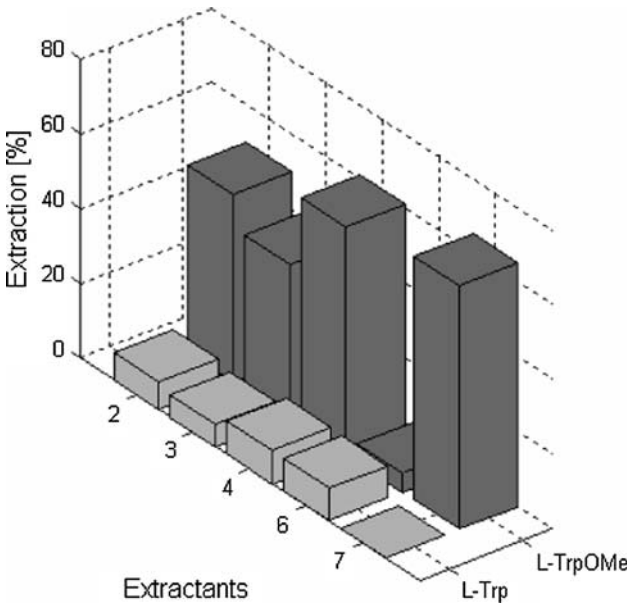


Fig. 1 L-TrpOMe and L-Trp extraction (%) by calixarene derivatives **2–4**, **6** and **7**

towards L-TrpOMe. The highest L-TrpOMe extraction was observed for the tetraamido **7** and diamido **4** calix[4]arene derivatives as extractants. The results pointed out that the structure of calix[4]arenes is one of the most important parameter for the recognition of L-TrpOMe.

Very large differences in percentage extraction between L-TrpOMe and L-Trp were obtained. Thus, the extraction values of native L-Trp were relatively small being within the interval 5.8–10% as a function of the extractant. The re-extraction of L-TrpOMe by **2–4**, **6** and **7** from the organic phase into the acidic aqueous phase (pH = 1.3) was performed. A percentage ranging from 65% to 97% tryptophane was recovered in the acidic aqueous phase for the corresponding receptors.

The extraction yields of L-PheOMe and L-Phe from the aqueous phase into chloroform phase by using calixarene derivatives **2–4**, **6** and **7** are given in Fig. 2.

The sequence of the decreasing extraction yields of L-PheOMe with calixarene derivatives **2–4**, **6** and **7** as extractants was the following: **4** (21%) > **7** (13%) > **2** (12%) > **3** (11%) > **6** (8%). The diamido **4** calix[4]arene provided the highest affinity towards L-PheOMe but less than L-TrpOMe in the same conditions of the experiment. As in the case of L-Trp, the native L-Phe extracted with the same receptors, showed lower extraction yields ranging from 4% to 9%.

The re-extraction of L-PheOMe by **2–4**, **6** and **7** receptors in the acidic phase occurred with yields between 56% and 95%.

The extraction behaviour of L-TyrOMe and L-Tyr by calixarene derivatives **2–4**, **6** and **7** presented in Fig. 3 shows the following sequence of extractability: **2** (23%) > **4** (16%) > **7** (6%) > **3** (3%). By using the receptor **6**, the extractability of L-TyrOMe is <3%. The liquid–liquid extraction of L-Tyr with the same calixarene derivatives indicated that only **4** and **7** exhibit extractabilities for this native aromatic amino acid. As one can see, the hydrophobicity of amino acid is another important factor for extraction behaviour. L-Trp is more hydrophobic than L-Phe and L-Tyr [28]. The re-extraction of L-TyrOMe with receptors **2**, **4**, and **7** in the acidic aqueous phase was also performed and the results were ranging from 20% to 50%.

The extraction yields of L-TrpOMe, L-PheOMe and L-TyrOMe with calix[4]arene diamide **4**, as a function of

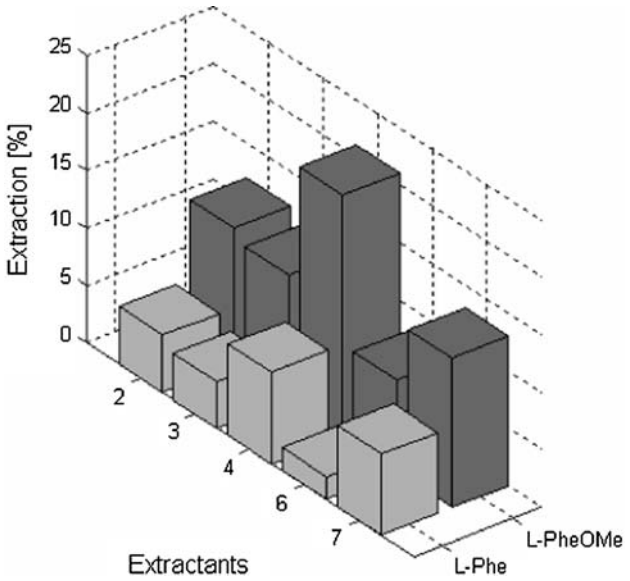


Fig. 2 L-PheOMe and L-Phe extraction (%) by calixarene derivatives **2–4**, **6** and **7**

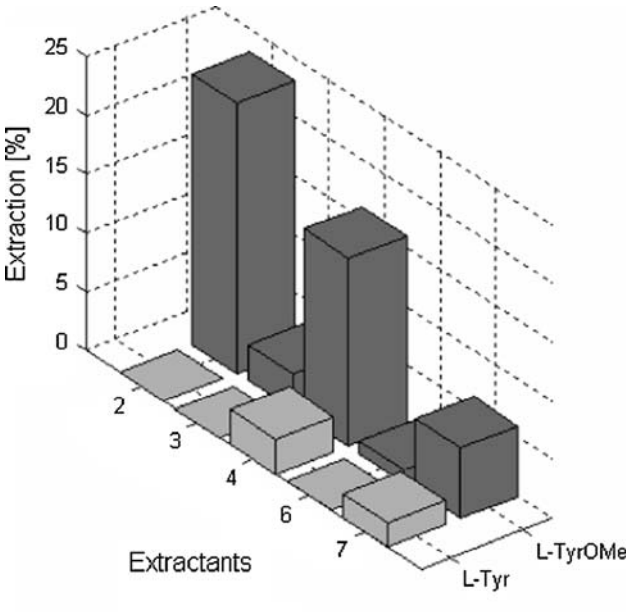


Fig. 3 L-TyrOMe and L-Tyr extraction (%) by calixarene derivatives **2–4**, **6** and **7**

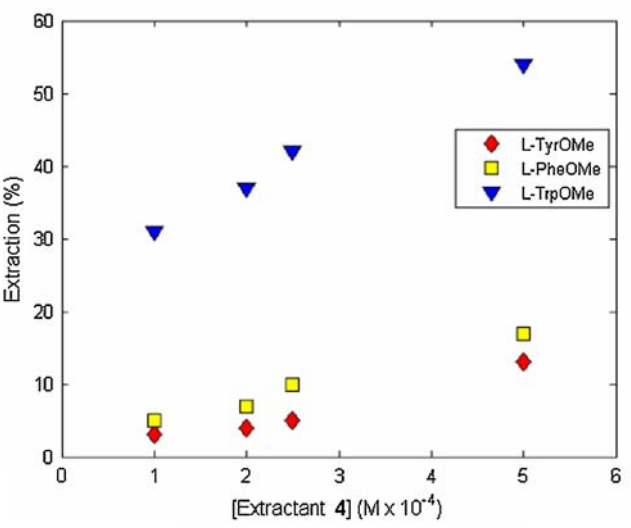


Fig. 4 Extraction behaviour of amino acid methylesters (1.0×10^{-3} M) with calix[4]arene derivative **4** at pH = 5.5

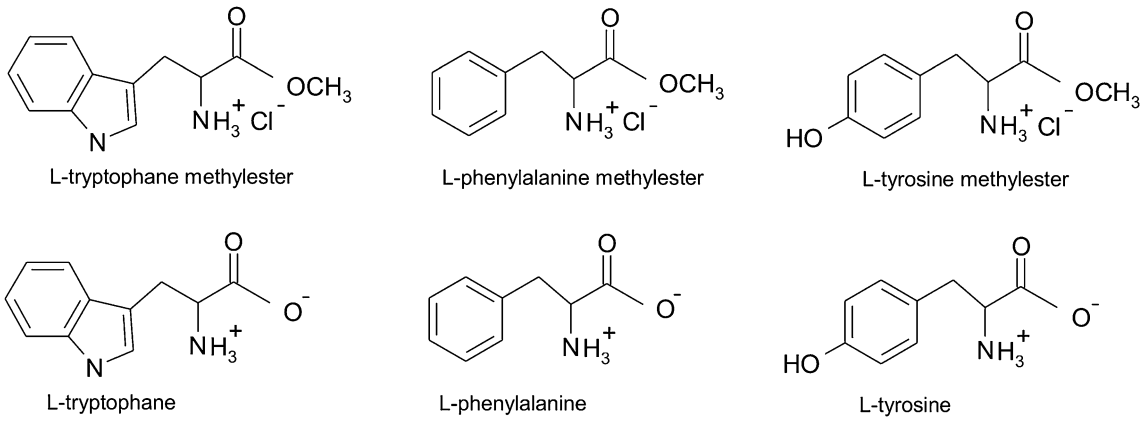
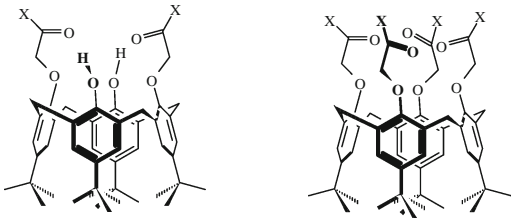


Chart 1 Chemical structures of the native and methylester amino acids



1 X = OCH_3
2 X = OH
3 X = $NHCH(CH_2OH)_2$
4 X = $NHC(CH_2OH)_3$
5 X= OCH_3
6 X = OH
7 X = $NH(CH_2)_2O(CH_2)_2OH$

Chart 2 Chemical structures of calixarenes **1–7**

extractant concentration are displayed in Fig. 4. It can be observed that the extraction of L-TrpOMe is comparatively larger than the one corresponding to L-PheOMe and L-TyrOMe. As such, the extractant **4** selectively behaves in extracting the above aromatic amino acids. The structure of the amino acids, and particularly their hydrophobicity, are primarily responsible for this behaviour.

Conclusions

The experimental results suggest that aromatic amino acid methylesters are extracted from aqueous phase into organic phase and the extractability is essentially controlled by the structure of the calix[4]arene derivative and the nature of the amino acid. Based of the obtained results in these experiments, we may conclude that the synthesized calix[4]arene derivatives can be used without counterion. The functional groups introduced on the calixarene structure are an important factor in affinity towards amino acids. One can assume that the functionalities, mainly the OH groups, glycolic chains, and amido functions known for their ability to form hydrogen bonds, oxygen-cation interactions and electrostatic interactions may play a role in the binding of the amino acid ester through the interactions with the ammonium cation. The existence of such interactions have to be taken into account when knowing that the calix[4]arene unit was declared to be too small in size for the inclusion of the amino acids used. The studies will be extended to membrane transport processes of amino acids for their optimal separation.

References

1. Gutsche, C.D.: Calixarenes. The Royal Society of Chemistry, Cambridge (1989)
2. Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J. (eds.): Calixarenes 2001. Kluwer Academic Publishers, Dordrecht (2001)
3. Asfari, Z., Harrowfield, J., Vicens, J. (eds.): Calixarenes 50th Anniversary: Commemorative Volume. Kluwer Academic Publishers, Dordrecht, The Netherlands (1994)
4. Vicens, J., Harrowfield, J. (eds.): Calixarene in the Nanoworld. Springer, Dordrecht (2006)
5. Mustafina, A.R., Skripacheva, V.V., Konovalov, A.I.: Outer-sphere association of calixarenes and other macrocyclic ligands with metal complexes as the basis for the design of molecular devices. Russ. Chem. Rev. **76**, 917–930 (2007). doi:10.1070/RC2007v076n10ABEH003727
6. Coleman, A.W., Perret, F., Moussa, A., Dupin, M., Guo, Y., Perron, H.: Calix[n]arenes as protein sensors. Top. Curr. Chem. **277**, 31–88 (2007). doi:10.1007/128_2007_115
7. Cragg, P.J., Iqbal, K.S.J.: Transmembrane ion transport by calixarenes and their derivatives. Dalton Trans. **1**, 26–32 (2007)
8. Lumetta, G.L., Rogers, R.D., Gopalan, A.S. (eds.): Calixarenes for Separations. ACS Symposium series 757. American Chemical Society, Washington (2000)
9. Gutsche, C.D.: Calixarenes Revisited. The Royal Society of Chemistry, Cambridge (1998)
10. Böhmer, V., Vicens, J. (eds.): Calixarenes: a Versatile Class of Macrocyclic Compounds. Kluwer Academic Publishers, Dordrecht, The Netherlands (1991)
11. Le Gac, S., Giorgi, M., Jabin, I.: Calix[6]arene tris-carboxylic acid derivatives: X-ray and NMR characterization of their remarkable host-guest properties toward ammonium ions. Supramol. Chem. **19**, 185–197 (2007). doi:10.1080/10610270600967038

12. Mutihac, L., Buschmann, H.-J., Diacu, E.: Calixarene derivatives as carriers in liquid membrane separation. Desalination **148**, 253–256 (2002). doi:10.1016/S0011-9164(02)00706-3
13. Mutihac, L., Buschmann, H.-J., Tudorescu, A., Mutihac, R.: Some aspects of extractibility and transport of amino acids esters by calixarenes. J. Incl. Phenom. Macrocycl. Chem. **47**, 123–128 (2003). doi:10.1023/B:JIPH.0000011735.27476.61
14. Nakashima, K., Oshima, T., Goto, M.: Extraction of amino acids by calixarenes in an aliphatic organic solvent. Solv. Extr. Res. Dev. Jpn. **9**, 69–79 (2002)
15. Ludwig, R.: Calixarenes in analytical and separation chemistry. Fresenius J. Anal. Chem. **367**, 103–128 (2000). doi:10.1007/s002160051611
16. Oshima, T., Goto, M., Furusaki, S.: Extraction behavior of amino acids by calix[6]arene carboxylic acid derivatives. J. Incl. Phenom. Macrocycl. Chem. **43**, 77–86 (2002). doi:10.1023/A:1020451421666
17. Oshima, T., Oishi, K., Ohto, K., Inoue, K.: Extraction of catecholamine by calixarene carboxylic acid derivatives. J. Incl. Phenom. Macrocycl. Chem. **55**, 79–85 (2006). doi:10.1007/s10847-005-9022-9
18. Okada, Y., Kasai, Y., Nishimura, J.: The selective extraction and transport of amino acids by calix[4]arene-derived esters. Tetrahedron Lett. **36**, 555–558 (1995). doi:10.1016/0040-4039(94)02251-6
19. Araki, K., Inada, K., Shinkai, S.: Chiral recognition of α-amino acid derivatives with a homooxacalix3arene: construction of a pseudo-C_2-symmetrical compound from a C_3 symmetrical macrocycle. Angew. Chem. Int. Ed. Engl. **35**, 72–74 (1996). doi:10.1002/anie.199600721
20. Antipin, I.S., Stoikov, I.I., Pinkhassik, E.M., Fitseva, N., Stibor, I., Konovalov, A.I.: Calix[4]arene based α-aminophosphonates: novel carriers for zwitterionic amino acids transport. Tetrahedron Lett. **38**, 5865–5868 (1997). doi:10.1016/S0040-4039(97)01305-1
21. Schlientz, L.M., Hagen, K.S.: 5,11,17,23-tetra-tert-butyl-26, 28-di-hydroxycalix[4]arene-25,27-dioxy-di-acetic acid N, N-dimethylformamide trisolvate. Acta Crystallogr. C **60**, 533–535 (2004). doi:10.1107/S010827010401323X
22. Arnaud-Neu, F., Fanni, S., Guerra, L., McGregor, W., Ziat, K., Schwing-Weill, M.-J., Barrett, G., McKervey, M.A., Marrs, D., Seward, E.M.: Cation complexation by chemically modified calixarenes. Part 7. Transport of alkali cations by *p-tert*-butylcalix[*n*]arene esters and amides. J. Chem. Soc. Perkin Trans. **II**, 113–118 (1995)
23. Unob, F., Asfari, Z., Vicens, J.: An anthracene-based fluorescent sensor for transition metal ions derived from calix[4]arene. Tetrahedron Lett. **39**, 2951–2954 (1998). doi:10.1016/S0040-4039(98)00376-1
24. Oueslati, I., Abidi, R., Amri, H., Thuéry, P., Nierlich, M., Asfari, Z., Harrowfield, J., Vicens, J.: Cation and solvent-induced conformational changes of 25,27-dimethoxy-26, 28-dimethylester-p-tert-butylcalix[4]arene. Tetrahedron Lett. **41**, 8439–8443 (2000). doi:10.1016/S0040-4039(00)01230-2
25. Abidi, R., Oueslati, I., Amri, H., Thuéry, P., Nierlich, M., Asfari, Z., Vicens, J.: Synthesis, structure and complexing properties of new calix[4](aza)crowns. Tetrahedron Lett. **42**, 1685–1689 (2001). doi:10.1016/S0040-4039(00)02356-X
26. Hamdi, A., Abidi, R., Trabelsi Ayadi, M., Thuéry, P., Nierlich, M., Asfari, Z., Vicens, J.: Synthesis and cation complexation studies of a new tetra(2-pyridyl)amide calix[4]arene. Tetrahedron Lett. **42**, 3595–3598 (2001). doi:10.1016/S0040-4039(01)00532-9
27. Pedersen, C.J.: Ionic complexes of macrocyclic polyethers. J. Fed. Proc. Fed. Am. Soc. Exp. Biol. **27**, 1305–1309 (1968)
28. Tayar, N.E.I., Tsai, R.S., Carrupt, P.A., Testa, B.: Octan-1-ol-water partition coefficients of zwitterionic α-amino acids. Determination by centrifugal partition chromatography and factorization into steric/hydrophobic and polar components. J. Chem. Soc. Perkin Trans. **2**, 79–84 (1992). doi:10.1039/p29920000079