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Complexation of Some Amino Acids and Peptides by *p*-Sulfonatocalix[4]arene and Hexasodium *p*-Sulfonatocalix[6]arene in Aqueous Solution

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Abstract

The stability constants ($\log K$), the reaction enthalpy (ΔH) and entropy (ΔS) of the complexes formed between some amino acids (glycine, L-alanine, L-valine, L-leucine, L-phenylalanine, L-tryptophan, L-threonine, and L-lysine) and peptides (glycyl-glycine, glycyl-L-alanine, glycyl-L-leucine, glycyl-L-phenylalanine, L-leucyl-glycine, L-leucyl-L-alanine, glycyl-L-valine, L-leucyl-glycyl-glycine, and glycyl-glycyl-glycine) with *p*-sulfonatocalix[4]arene and hexasodium *p*-sulfonatocalix[6]arene in aqueous solutions by means of calorimetric titration have been investigated. The reported results demonstrate that the amino acids and peptides under study form complexes with both *p*-sulfonatocalix[4]arene and hexasodium *p*-sulfonatocalix[6]arene. In the case of the amino acids and peptides the complexation with water-soluble calixarenes in aqueous solution is favored by enthalpic contributions and disfavored by entropic contributions. However, no influence of the ring size of the calixarenes upon the complexation is observed. By comparison with the reaction of the sodium salt of phenol-4-sulfonic acid with amino acids a macrocyclic effect in case of the calixarenes is possible.

Introduction

Calixarenes and their derivatives are attractive hosts for certain neutral and charged inorganic and organic species in solution, the solid state [1] and in the gas phase as well [2]. It is known that calixarene molecules exhibit a big sterical flexibility by comparing with cyclodextrins, and therefore there is a possibility to using calixarenes in a wide field of applications [3]. There are many studies dedicated to calixarenes and their derivatives, most of them directed toward the selective complexation of biological substrates [4–12].

Remarkable progress has been achieved in the synthesis of calixarene derivatives used as chemical sensors [13], enzyme mimetics and allosteric molecules [14]. Recently, the development of calixarene-based ionophores, which allow sterically fine-tune complexation of alkali ions has been the subject of a few studies [15, 16]. A resorcinol-derived calixarene has been shown by Schneider *et al.* [17] to form complexes with organic ammonium ions. The water soluble *p*-sulfonatocalix[n]arenes (n = 4, 6, 8) synthesized mainly by Shinkai *et al.* [18] and Ungaro *et al.* [19] are able to recognize compounds of biological interest in aqueous solution. It has been found that water-soluble calix[n]arene derivatives are able to catalyze aldol-type condensation and Michael addition reactions of activated methyl and methylene compounds smoothly in aqueous NaOH solution [20]. The complexation properties of water-soluble calixarenes towards organic ions [21], amino acids [22], small neutral organic molecules such as alcohols, ketones and nitriles [23] in aqueous solution have been extensively investigated by ^{1}H NMR spectroscopy, calorimetric and microcalorimetric titration [24, 25]. The obtained results show that the inclusion capabilities of the investigated hosts are correlated with their conformational properties [23]. The studies have shown that *p*-sulfonatocalix[4]arene is able to complex α-amino acids by inserting the aromatic or aliphatic group into the calixarene cavity [22]. An interesting study regarding the acid-base properties of water soluble *p*-sulfonatocalix[6]arenes has been reported by Arena *et al.* [26]. In addition, the ^{1}H and ^{13}C NMR studies of the complex formed between tetrasodium *p*-sulfonatocalix[4]arene with trimethylanilinium chloride and 1-adamanthyltrimethyl-ammonium chloride in D_2O showed that the guest is bound to the cone-shaped cavity [27]. The results suggest that in acidic aqueous solution the phenyl moiety is bound to the calixarene cavity whereas in neutral medium both the ammoniomethyl and the phenyl moiety are nonselectively bound to the calixarene cavity. This conclusion was confirmed by X-ray crystallographic studies [27]. Using microcalorimetric titration of *p*-sulfonatocalix[4]arene with alkyl diammonium ions at pH 7.1 in an aqueous solution Stödeman *et al.* [28] have studied the aspects of interactions between the above-mentioned compounds. The complexation of basic amino acids arginine and lysine by *p*-sulfonatocalix[4]arene by means ^{1}H NMR spectroscopy [29] and microcalorimetry [30] has shown that 1 : 1 complexes between these amino acids and calixarene in water have been formed. Similarly reasoning,

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the study of the complexation of *p*-sulfonatocalix[4]arene with some amino acids as guests by means of reversed-phase high-performance liquid chromatography (RP-HPLC) and ^{1}H NMR experiments has been reported [31]. The results obtained suggest that various interactions such as hydrophobic, ion-pairing, aromatic-aromatic and electrostatic may occur between the amino acids under study and *p*-sulfonatocalix[4]arene.

By far the majority of the studies that involve water-soluble calixarenes have been focused on the recognition of ionic metal species, ammonium ions and amino acids [5, 6], whereas only a few of them have been dedicated to the recognition of peptides [32, 33]. A thermodynamical study concerning the binding of dipeptides and tripeptides bearing lysine or arginine by water soluble *p*-sulfonatocalix[n]arenes (n = 4, 6 and 8) have been studied by NMR and microcalorimetric techniques [32]. The complexation has been controlled by the favourable enthalpy obtained by the inclusion of the apolar part of the peptide into the hydrophobic cavity of *p*-sulfonatocalix[n]arenes (n = 4, 6 and 8) through van der Waals interactions. Also, an important role is played by the entropy accompanying the desolvation of the charged groups upon ionic interaction [32].

In a previous study the determination of complex stabilities between different cyclodextrins and *p*-tert-butylcalix[n]arenes (n = 4, 6) in aqueous solutions using a spectrometric method has been reported [34]. In this work we have investigated the complexation of some amino acids and peptides with *p*-sulfonatocalix[4]arene and hexasodium *p*-sulfonatocalix[6]arene in aqueous solutions by means of calorimetric titration. The stability constants of the complexes investigated have been determined.

Experimental

The following amino acids and peptides: glycine (Gly), L-alanine (L-Ala), L-valine (L-Val), L-leucine (L-Leu), L- phenylalanine (L-Phe), L- tryptophan (L- Trp), L-threonine (L-Thr), L-lysine (L-Lys), glycyl-glycine (Gly-Gly), glycyl-L-alanine (Gly-L-Ala), glycyl-L-leucine (Gly-L-Leu), glycyl-L-phenylalanine (Gly-L-Phe), L-leucyl-glycine (L-Leu-Gly), L-leucyl-L-alanine (L-Leu-L-Ala), and L-leucyl-glycyl-glycine (L-Leu-Gly-Gly) from Fluka and glycyl-L-valine (Gly-L-Val) and glycyl-glycyl-glycine (Gly-Gly-Gly) from Sigma were of the highest purity commercially available. They were used without further purification. The calixarene, *p*-sulfonatocalix[4]arene hydrate was obtained from Acros Organics and hexasodium *p*-sulfonatocalix[6]arene (Figure 1) was synthesized, purified and characterized as described in the literature [35]. Reagent-grade water produced by a Milli-Q filtration system (Millipore) was used.

The stability constants and reaction enthalpies in aqueous solutions were determined by means of calorimetric titrations (Tronac Calorimeter Model 450). The solution of the ligand (0.01–0.02 mol/L) was added continuously to a solution of the amino acid or peptide (0.001–0.002 mol/L). The heat, Q, produced during the titration is related to the reaction enthalpy ΔH, after correction for all non-chemical heat effects, by the following equation:

$$Q = \Delta n \Delta H.$$

With Δn as the number of moles of the complex formed. In the literature the mathematical treatment of the experimental data has been described in detail [36].

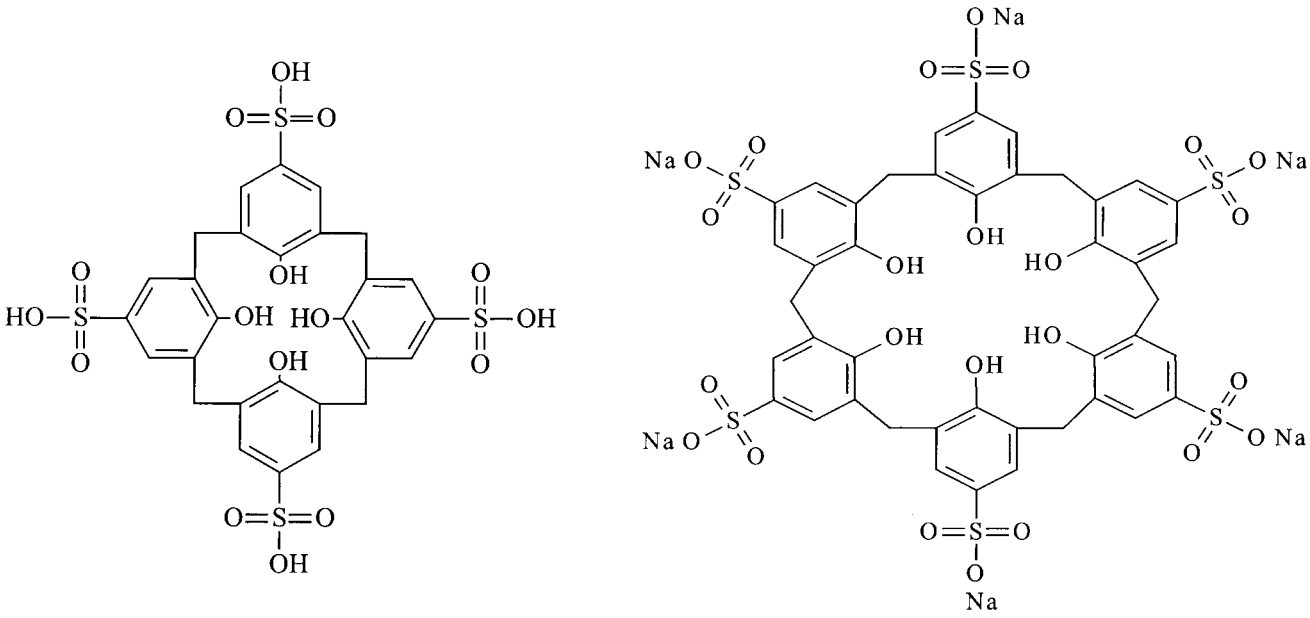
Table 1. Stability constants $\log K$ (K in M^{-1}) and thermodynamic values ΔH and $T\Delta S$ (in kJ mol^{-1}) for the complexation of some amino acids by *p*-sulfonatocalix[4]arene in aqueous solution at 25 °C

Amino acids	$\log K$	$-\Delta H$ (kJ/mol)	$T\Delta S$ (kJ/mol)
Gly	2.74 ± 0.02	38.3 ± 1.2	-22.7 ± 2.3
	2.26[31]		
L-Ala	3.22 ± 0.02	30.4 ± 0.09	-12.0 ± 1.3
	2.82[31]		
L-Val	3.20 ± 0.0	46.7 ± 1.7	-28.5 ± 1.8
	1.20[22]		
L-Leu	3.08 ± 0.02	51.7 ± 2.1	-34.2 ± 1.5
	1.70[22]		
L-Phe	3.14 ± 0.01	36.0 ± 1.62	-18.1 ± 1.6
	1.80[22]		
	2.77[31]		
L-Trp	3.13 ± 0.03	33.4 ± 1.8	-15.6 ± 2.2
	1.40[22]		
	3.18[31]		
L-Thr	3.19 ± 0.05	28.9 ± 1.5	-10.7 ± 2.0
L-Lys	3.83 ± 0.02	20.4 ± 1.3	1.8 ± 1.7
	2.87[30]	14.4	2.0
	3.23[37]		

Results and discussion

The values of the stability constants and thermodynamic parameters for the complexation of some α-amino acids by *p*-sulfonatocalix[4]arene in aqueous solution are given in Table 1. The study was carried out under non-buffered conditions. It is well known that amino acids exist in neutral aqueous solution as zwitterions. For comparison results given in the literature by different methods are included. These values differ for several orders of magnitude for same of the complexes.

One can see from Table 1 that *p*-sulfonatocalix[4]arene forms relatively strong complexes with the amino acids studied in present work. The amino acid, glycine, which contains no side chain presents a low value of stability constant, $\log K = 2.74$ by means of calorimetric titration comparing with the amino acids under study. L-Phe and L-Trp with aromatic side chains, actually for L-Trp the aromatic side chain is sterically much larger, the values of stability constants are nearly identical in our conditions. The aromatic-aromatic interactions between the aromatic groups of *p*-sulfonatocalix[4]arene with aromatic ring of L-Phe and L-Trp respectively are responsible for complex formation. The complexation of *p*-sulfonatocalix[4]arene



a b

Figure 1. Chemical structures of water soluble calixarenes used: (a) *p*-sulfonatocalix[4]arene, (b) hexasodium *p*-sulfonatocalix[6]arene.

with the trimethylanilinium ion with a value of apparent K_a of 5600 M^{-1} is known [27]. Because of the difference in the pH values of the two measurements a comparison is difficult to make. The association constants for L-Phe and L-Trp obtained from ^{1}H NMR [22] at pD = 7.3 are lower than those obtained by our experiments. Instead comparing the association constants determined by RP-HPLC [31] for L-Phe and L-Trp, the values found are in accordance with the results of present study. The amino acid L-Lys shows the highest value of stability constant, $\log K = 3.83$. In the conditions of this work, the favourable interactions between positively charged amino acid and the negatively charged sulfonatocalix[4]arene are involved. It was reported that the crystal structure of the Lys-*p*-sulfonatocalix[4]arene complex shows that the Lys side chain is folded on binding into cavity [37, 38]. From the data given in Table 1 one can see that L-Ala displays a strong binding to *p*-sulfonatocalix[4]arene with a $\log K = 3.22$. The RP-HPLC studies [31] have also reported a large value of association constant for the complexation of L-Ala (K_a = 675 M^{-1}) [31] with *p*-sulfonatocalix[4]arene. Similarly with L-Ala, the L-Val shows the high value for stability constant ($\log K = 3.20$). The association constant of L-Val with *p*-sulfonatocalix[4]arene determined by ^{1}H NMR studies [22] at pD 7.3 is 16, this being lower than observed in present experiments. For L-Leu, the stability constant determined is $\log K = 3.08$, higher than that it was observed by ^{1}H NMR measurements [22]. One also can see from Table 1 that by calorimetric titration a large value of stability constant has been obtained for L-Thr ($\log K = 3.19$).

By comparing the association constants obtained by calorimetric titration with those determined by RP-HPLC [31], NMR [22] and microcalorimetry [30], the results are quite different. Direct comparison is difficult because of the differences in conditions such as pH, solvent polarities and experimental methodology (RP-HPLC, NMR, microcalorimetry, calorimetric titration).

The values of the stability constants determined by ^{1}H NMR titration experiments [22] for L-Val, L-Leu, L-Phe and L-Trp with *p*-sulfonatocalix[4]arene in aqueous solutions at pD = 7.3 are approximately an order of magnitude lower than those obtained by RP-HPLC [31] and two order of magnitude lower compared with those obtained by calorimetric titration.

In the case of Gly, L-Ala, L-Trp, and L-Phe the values of stability constants determined by calorimetric titration are comparable with those obtained by RP-HPLC [31]. Even no complex formation could be detected with L-Ala using ^{1}H NMR [22].

Except the values of L-Leu, L-Thr and L-Lys all values of the reaction enthalpies are quite similar. The values of ΔH obviously result from electrostatic interactions between the protonated amino group of the amino acids and the phenolic hydroxyl groups of the calixarenes. The complex formation is favored by enthalpic contributions and disfavoured by entropic contributions. Except L-Lys, all values of ΔS for the other amino acids under study are negative. The orientation between guest and host molecules is important. During the complex formation no or only few solvent molecules are liberated. As a result the negative values of the reaction entropy are observed. Unfortunately no thermodynamic values from the literature are known for comparison.

The stability constants of *p*-sulfonatocalix[4]arene and hexasodium *p*-sulfonatocalix[6]arene formed with peptides (Table 2 and Table 3) are identical within the experimental

Table 2. Stability constants $\log K$ (K in M^{-1}) and thermodynamic values ΔH and $T\Delta S$ (in kJ mol^{-1}) for the complexation of some peptides by *p*-sulfonatocalix[4]arene in aqueous solution at 25 °C

Peptides	$\log K$	$-\Delta H$	$T\Delta S$
Gly-Gly	2.99 ± 0.03	42.1 ± 0.7	-25.1 ± 0.6
Gly-L-Ala	3.21 ± 0.01	39.7 ± 0.2	-21.4 ± 0.2
Gly-L-Val	3.24 ± 0.02	39.5 ± 1.2	-21.1 ± 1.1
Gly-L-Leu	3.22 ± 0.02	51.6 ± 0.9	-33.2 ± 1.0
L-Leu-Gly	3.23 ± 0.01	68.9 ± 1.3	-50.5 ± 1.4
L-Leu-L-Ala	3.23 ± 0.02	56.1 ± 1.9	-37.7 ± 1.8
Gly-L-Phe	3.23 ± 0.04	38.8 ± 0.8	-20.4 ± 0.6
Gly-Gly-Gly	3.11 ± 0.03	41.1 ± 0.5	-23.4 ± 1.2
L-Leu-Gly-Gly	3.12 ± 0.01	79.1 ± 2.4	-61.1 ± 2.4

Table 3. Stability constants $\log K$ (K in M^{-1}) and thermodynamic values ΔH and $T\Delta S$ (in kJ mol^{-1}) for the complexation of some peptides by hexasodium *p*-sulfonatocalix[6]arene in aqueous solution at 25 °C

Peptides	$\log K$	$-\Delta H$	$T\Delta S$
Gly-Gly	3.30 ± 0.02	43.6 ± 0.9	-24.7 ± 1.8
Gly-L-Ala	3.47 ± 0.04	38.2 ± 1.2	-18.4 ± 2.2
Gly-L-Val	3.21 ± 0.01	40.7 ± 1.7	-22.4 ± 1.9
Gly-L-Leu	3.19 ± 0.03	60.6 ± 0.8	-42.4 ± 2.4
L-Leu-Gly	3.21 ± 0.02	49.0 ± 1.3	-30.7 ± 2.0
L-Leu-L-Ala	3.16 ± 0.01	52.7 ± 1.4	-34.7 ± 1.6
Gly-L-Phe	3.28 ± 0.02	46.9 ± 1.1	-28.1 ± 1.1
Gly-Gly-Gly	3.25 ± 0.04	47.9 ± 0.7	-29.3 ± 1.7
L-Leu-Gly-Gly	3.22 ± 0.03	52.7 ± 1.5	-34.3 ± 2.0

error. Surprisingly, no effect of the ligand size upon the complexation of peptides is found. Also due to the electrostatic interactions between guest and host molecules nearly identical results are observed in the case of the reaction enthalpies and entropies. The values of the reaction enthalpies are slightly higher than those with the amino acids. This effect is compensated by the reaction entropy. With increasing molecular size of the peptides the values of the reaction entropy increase too.

For a more detailed discussion of different effects influencing the complex formation of amino acids and peptides with *p*-sulfonatocalix[n, n = 4, 6]arenes more experimental results are necessary.

A comparison between linear oligomers and the corresponding macrocyclic calix[n]arene derivatives should give some information about the presence of a macrocyclic effect in case of the complex formation with calixarenes. Such a macrocyclic effect has already been discussed in detail for the reactions of polyethers and crown ethers with cations [39, 40]. A macrocyclic effect has been reported in case of the extraction of lanthanides with calixarenes and analogues noncyclic ligands [41].

In Table 4 some results are summarized for the reaction of the sodium salt of phenol-4-sulfonic acid with few amino

Table 4. Stability constants $\log K$ (K in M^{-1}) and thermodynamic values ΔH and $T\Delta S$ (in kJ mol^{-1}) for the complex formation of some amino acids with phenol-4-sulfonic acid sodium salt in aqueous solution at 25 °C

Amino acids	$\log K$	$-\Delta H$	$T\Delta S$
Gly	2.49 ± 0.02	1.5 ± 0.2	12.7 ± 1.2
L-Ala	2.42 ± 0.01	1.8 ± 0.4	12.0 ± 0.9
L-Val	2.61 ± 0.03	0.9 ± 0.2	14.0 ± 1.5
L-Thr	2.61 ± 0.02	1.8 ± 0.3	13.1 ± 1.9

acids. The values of the stability constants, reaction enthalpies and entropies are nearly identical. This is not surprising due to the electrostatic interactions between the protonated amino groups and the phenol group. However, the values of the reaction enthalpies are much smaller compared with those observed with the calixarenes. The macrocyclic structure of the ligands obviously plays an important role for the complex formation. More experimental work about the reaction between noncyclic oligomers (n = 4–6) and amino acids is necessary to verify a marocyclic effect in case of calixarenes.

Conclusions

The complexation of some amino acids and peptides by water soluble calixarenes: *p*-sulfonatocalix[4]arene and hexasodium *p*-sulfonatocalix[6]arene in aqueous solution by means of calorimetric titration has been studied. The stability constants, enthalpies and entropies of complexation have been evaluated. There are no significant differences between the values of stability constants of peptide complexes formation with the calixarenes under study. As in the case of complexes of amino acids with water soluble calixarenes, the complexation of peptides with the same ligands is favored by enthalpic contributions. In order for a better understanding of the binding processes and of the existence of a macrocyclic effect in case of calixarenes further studies are in progress.

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