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Binding of inorganic and organic cations by *p*-sulfonatocalix[4]arene in water: a thermodynamic study

Christine Bonal,* Yaël Israëli, Jean-Pierre Morel and Nicole Morel-Desrosiers

Laboratoire de Thermodynamique des Solutions et des Polymères, UMR CNRS 6003, Université Blaise Pascal (Clermont-Ferrand II), 24 Avenue des Landais, 63177 Aubière Cedex, France

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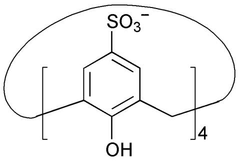
We report a microcalorimetry study of the association of various inorganic and organic cations with *p*-sulfonatocalix[4]arene at 298.15 K. First, we have studied the electrostatic attraction between host **1** and seven rare-earth-metal cations representative of the whole lanthanide series (La^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+} and Yb^{3+}) in an acidic solution (pH 2). In order to compare the charge effects in the electrostatic interactions we have also studied the attraction between host **1** and two alkaline-earth-metal cations (Ca^{2+} and Mg^{2+}). Next, we investigated the binding of a series of quaternary ammonium cations in an acidic solution (pH 2). For each system, both the apparent association constant and enthalpy of complexation have been extracted from the calorimetric data. In all cases, our results are consistent with the formation of 1 : 1 complexes. Whereas for the inorganic cations (alkaline-earth-metal and lanthanide cations) the association process is enthalpically unfavoured ($\Delta_r H° > 0$) and entropically favoured ($\Delta_r S° > 0$), the complexation is driven by a favourable enthalpy change for the organic cations. These thermodynamic properties show that the organic and inorganic cations bind in very different modes.

Introduction

The inclusion chemistry of calix[4]arenes has been extensively discussed in several books[1–3] and review articles.[4–7] A characteristic feature of the calixarenes is their insolubility in water and their low solubility in organic solvents. By introducing sulfonic acid groups at the *p*-position of the hydroxycalix[4]arenes, Shinkai *et al.*[8] first synthesized some water-soluble calix[4]arenes. The *p*-sulfonatocalix[4]arene, **1**, has been found to have a solubility at least as great as 0.1 mol dm^{-3}.[1] With the advent of this solubility data, potentiometric and calorimetric measurements of pK_a values have yielded data for several OH groups of compound **1**.[9–11]



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The *p*-sulfonatocalix[4]arene is able to complex a variety of metal and organic cations in water. The binding of cations in water is a complicated phenomenon in which electrostatic forces, van der Waals forces and hydrophobic effects play a major role but other factors also have to be considered. For instance, the weak cation–π interactions between the positive charge of the cation and an electron rich aromatic ring could be of special importance, particularly in biological recognition.[12] Thus, in order to characterize further the driving forces involved in the complexation by water soluble calixarenes, we have determined by microcalorimetry the thermodynamic parameters of association of various inorganic and organic cations with *p*-sulfonatocalix[4]arene.

Firstly, we have studied the electrostatic attraction between host **1** and seven rare-earth metal cations representative of the whole lanthanide series (La^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+} and Yb^{3+}) in an acidic solution (pH 2). Lanthanide cations have a common oxidation state of +3 (Ln^{3+}). They behave as hard acids with a strong affinity for hard bases like oxygen and negatively charged groups and they form essentially electrostatic bonds. Because of the increasing industrial interest in lanthanides from different fields the results of the present work are considered not only to study the interactions that occur between two highly charged species but also to be of some direct relevance to the understanding of the characteristics of lanthanide complexes. Previously, Shinkai's group[13] studied by pHmetry the binding properties of **1** with all the lanthanides in alkaline aqueous solution (pH 11.7). The anion was treated as a diprotic acid releasing two protons on the formation of a complex with a metal ion. Their results showed that the overall stability constants are very high—around 20 log units—and increase slightly along the series. However, results obtained in an alkaline solution can not be extended to an acidic medium. There is indeed a pH dependence of the extent of complexation of a lanthanide cation by the calixarene because of the acid–base properties of this macrocycle.

To compare charge effects in the electrostatic interactions we have also studied the attraction between host **1** and two alkaline-earth-metal cations (Ca^{2+} and Mg^{2+}).

Our early interest to understand the nature of the interactions between the *p*-sulfonatocalix[4]arene and various inorganic and organic cations in aqueous solution also led us to investigate the binding of a series of quaternary ammonium cations in an acidic solution (pH 2). Only a few examples of association equilibrium constants and thermodynamic parameters for complexes of calixarenes and organic molecules in aqueous solution are known[14] and in only three cases[15–17] have the thermodynamic parameters for the complexation of alkylammonium cations by host **1** in water been determined. Lehn *et al.*[15] have studied the binding of acetylcholine and other quaternary ammonium cations by sulfonated calixarenes at pH 7.3 by ^1H NMR. They have estimated the association constants of **1** with $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(C_3H_7)_4N^+$, $(C_4H_9)_4N^+$. Their results

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showed that the calixarene forms remarkably stable complexes with all the cationic ammonium substrates studied and the large shielding effects obtained by ^{1}H NMR indicate that inclusion of the substrate into the aromatic cavity of the calixarene probably takes place. Stödeman *et al.*[16] applied microcalorimetry to the thermodynamic characterization of the complexation of **1** by alkylammonium ions $H(CH_2)_nNH_3^+$, $n = 3$–7 at pH 7.1 and 298.15 K. Their results pointed out that the binding mode of the calixarene varies with the chain length of the alkylammonium ions and the thermodynamic properties observed originate from different types of forces in interplay. Finally, Arena *et al.*[17] have been interested by the inclusion of symmetrical tetramethylammonium cation in various calixarenes. In particular they determined by direct calorimetry the association constant of this ion with **1** at pH 7.3.

In the present paper the association constant, the enthalpy and entropy changes for the complexation of host **1** with inorganic cations (alkaline-earth-metal and lanthanide cations) and organic cations (quaternary ammonium cations) in water at pH 2 are reported. Comparison of such parameters provides a general understanding of both the similarities and the differences in the complexation behavior. In fact, ΔH and ΔS values are interpreted in terms of the importance of the various interactions responsible for complexation, and analysed in the context of the enthalpy–entropy compensation effect.

Experimental

Solutions

The 25,26,27,28-tetrahydroxy-5,11,17,23-tetrasulfocalix[4]arene was bought from Acros: water analysis showed it to be hexahydrated. $LaCl_3 \cdot 6H_2O$, $La(NO_3)_3 \cdot 6H_2O$, $NdCl_3 \cdot 6H_2O$, $SmCl_3 \cdot 6H_2O$, $EuCl_3 \cdot 6H_2O$, $GdCl_3 \cdot 6H_2O$, $DyCl_3 \cdot 6H_2O$ and $YbCl_3 \cdot 6H_2O$ were bought from Strem Chemicals (purity, 99.9%) and used as received. $CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 6H_2O$ were obtained from Merck and used as received. $(CH_3)_4NBr$ (Merck, 99%), $(C_2H_5)_4NBr$ (Fluka, 99%) $(C_3H_7)_4NCl$ (Alfa, 99%) and $(C_4H_9)_4NBr$ (Fluka, 99%) were dried at 373 K, stored in a desiccator and used without futher purification. CH_3NH_3Cl and $C_2H_5NH_3Cl$ were bought from Fluka (99%) and used without further purification.

All the solutions were prepared by weight from triply distilled water. The pH of the calixarene and lanthanide or quaternary ammonium cation solutions was set at 2 with 0.01 mol kg^{-1} HCl.

Stock solutions of the lanthanide salts, *ca.* 0.1 mol kg^{-1}, were analysed for cation concentration by titration with Titriplex III (Merck) following classical methods. These stock solutions were diluted so that the concentration of the lanthanide cation was fixed to 0.001 mol kg^{-1}.

Microcalorimetry

All the measurements were performed using a multichannel microcalorimeter (LKB – Thermometric 2277 Thermal Activity Monitor) equipped with a titration–perfusion vessel. Suurkuusk and Wadsö[18] have thoroughly described this twin thermopile heat-conduction calorimeter and analysed its performance.

The experiments were carried out using a 1 mL glass vessel fitted with a gold stirrer. The vessel was charged with 0.9 mL of lanthanide solution or alkylammonium cation solution and 10 μL of calixarene solution was injected in each step using a Lund syringe pump (Thermometric) equipped with a 250 μL Hamilton syringe fitted with a gold cannula. 20 injections were made for each titration experiment. The solution molalities were, prior to titration, 0.01 mol kg^{-1} for the calixarene and 0.001 mol kg^{-1} for the alkaline-earth-metal, lanthanide or alkylammonium cation. Static and dynamic calibrations were used; the power values observed upon titration ranged from 30 to 100 μW.

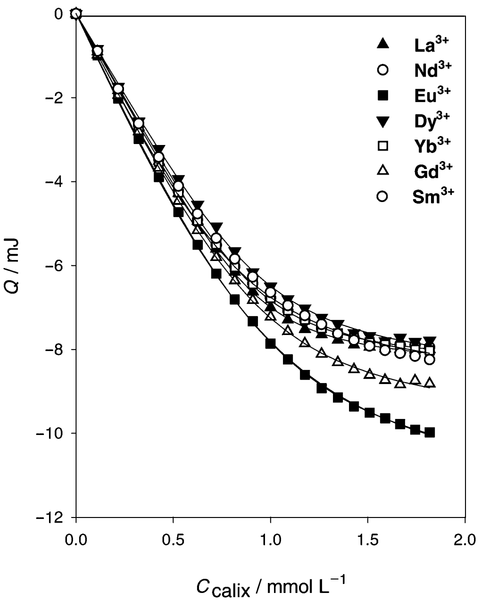

Fig. 1 Heat effects determined by microcalorimetry for the complexation of Ln^{3+} *versus* the concentration of the *p*-sulfonatocalix[4]arene anion (see Experimental section).

Table 1 Thermodynamic parameters characterizing the complexation of lanthanide and alkaline-earth metal cations by the *p*-sulfonatocalix[4]arene in water at 298.15 K and at pH 2[a,b]

Cations[c]	log$K$[a]	$\Delta_rG°$	$\Delta_rH°$	$T\Delta_rS°$
La^{3+}	4.23	−24.1 ± 0.3	9.2 ± 0.1	33.3 ± 0.4
La^{3+}[d]	4.23	−24.1 ± 0.4	8.5 ± 0.2	32.6 ± 0.6
Nd^{3+}	4.08	−23.3 ± 0.3	9.5 ± 0.2	32.8 ± 0.5
Sm^{3+}	3.82	−21.8 ± 0.2	10.4 ± 0.2	32.2 ± 0.4
Eu^{3+}	3.83	−21.9 ± 0.2	12.5 ± 0.2	34.4 ± 0.4
Gd^{3+}	3.94	−22.5 ± 0.3	9.8 ± 0.3	32.2 ± 0.6
Dy^{3+}	3.88	−22.1 ± 0.3	10.1 ± 0.2	32.3 ± 0.5
Yb^{3+}	3.81	−21.8 ± 0.3	10.0 ± 0.2	31.8 ± 0.5
Ca^{2+}	3.32	−19 ± 1	3.0 ± 0.4	22 ± 1
Mg^{2+}	3.30	−18.8 ± 0.8	4.7 ± 0.5	23.5 ± 1.0

[a] Molar scale. [b] $\Delta_rG°$, $\Delta_rH°$ and $T\Delta_rS°$ in kJ mol^{-1}. [c] Counter-ion: Cl$^-$. [d] Counter ion: NO$_3^-$.

Separate dilution experiments were performed. The heats of dilution of calixarene were found to be negligible. Each experiment was repeated twice for reproducibility.

Values for the apparent association constant K' and apparent standard enthalpy of reaction $\Delta_rH'°$ in a given medium were calculated by use of the Digitam 4.1 minimization program (Thermometric). The two series of data obtained for each system were treated simultaneously in the regression analysis. Under the present conditions, the apparent values are close to standard values and will thus be designated by K and $\Delta_rH°$ throughout the text.

Results and discussion

The thermic effects observed upon complexation of the lanthanide cations by host **1** at pH 2 are plotted *vs.* the concentration of **1** in Fig. 1. The K and $\Delta_rH°$ values deduced from the nonlinear regression fit of the microcalorimetric data are reported, with the estimated standard errors, in Table 1. The corresponding $\Delta_rG°$ and $T\Delta_rS°$ values are also given. In order to study the anion effect, $LaCl_3$ has been replaced by $La(NO_3)_3$ and the K and $\Delta_rH°$ values obtained are also reported in Table 1. Obviously, changing the counter-ion does not induce significant

Table 2 Thermodynamic parameters characterizing the complexation of alkylammonium cations by the *p*-sulfonatocalix[4]arene anion in water at 298.15 K and at pH 2[a,b]

Cations	$\log K$[a]	$\Delta G°$	$\Delta_r H°$	$T\Delta_r S°$
NH_4^+	—	—	—	—
$(CH_3)_4N^+$	4.40	−25.1 ± 0.2	−26.0 ± 0.2	−0.9 ± 0.4
$(C_2H_5)_4N^+$	4.67	−26.7 ± 0.4	−41.2 ± 0.8	−14.5 ± 1.2
$(C_3H_7)_4N^+$	4.47	−25.5 ± 0.3	−23.8 ± 0.3	1.7 ± 0.6
$(C_4H_9)_4N^+$	4.21	−24.0 ± 0.3	−21.6 ± 0.5	2.4 ± 0.8
$CH_3NH_3^+$	2.65	−15.1 ± 0.4	−11.5 ± 0.5	3.6 ± 0.9
$C_2H_5NH_3^+$	3.58	−20.4 ± 0.4	−16.5 ± 0.5	3.9 ± 0.9

[a] Molar scale. [b] $\Delta_r G°$, $\Delta_r H°$ and $T\Delta_r S°$ in kJ mol^{-1}.

effects: the K and $\Delta_r H°$ values found for the two salts are, within the experimental uncertainties, identical. No association between La^{3+} and the anions arise under the conditions used here.[19]

At pH 2, all the phenolic hydroxy groups of **1** are protonated according to the pK_a values.[9–11] Consequently, the lanthanide cations form electrostatic bonds only with the four sulfonate groups located on the upper rim of the calixarene. We have also studied, under similar conditions, the interaction of La^{3+} with *p*-hydroxybenzenesulfonic acid but no association has been detected by microcalorimetry. This underlines the importance of the preorganized structure of the calixarene which favours a multi-site interaction with the lanthanide cation.

One sees that host **1** forms rather stable 1 : 1 complexes with the lanthanide cations cited above. It can be noticed that $\Delta_r G°$ decreases slightly from La^{3+} to Sm^{3+} and then remains almost constant till Yb^{3+}. In all cases, the association process is enthalpically unfavoured ($\Delta_r H° > 0$) and entropically favoured ($\Delta_r S° > 0$). The positive enthalpy and entropy changes are essentially due to the partial desolvation of Ln^{3+} and SO_3^- upon interaction and from the consequent release of water molecules. The association of host **1** with a lanthanide cation, which is strongly entropy-driven, is a remarkable example of a process involving strong electrostatic interactions.

$\Delta_r H°$ increases slightly from La^{3+} to Eu^{3+}, then decreases up to Yb^{3+}. The $\Delta_r H°$ values do not differ significantly across the lanthanide series. This is still an indication that non-specific electrostatic interactions play a major role in the association process. But if we examine in detail these $\Delta_r H°$ values, a small discontinuity is observed in the middle of the series. It is now fairly well established that the lighter lanthanide cations are nine-coordinated in water whereas the heavier lanthanide cations are eight-coordinated.[20] This inner-sphere hydration number change is probably the main factor explaining this small discontinuity observed for the $\Delta_r H°$ values in the middle of the series. Such behaviour has often been observed for other lanthanide complexes.[21]

In order to examine the influence of the charge of the cation we have also studied the complexation of Ca^{2+} and Mg^{2+} by **1** at pH 2. The thermodynamic properties deduced from the microcalorimetric data are reported in Table 1. Here again the association process is enthalpically unfavoured and entropically favoured, which indicates that the electrostatic interactions are driving the complexation. However, the association with Ca^{2+} and Mg^{2+} is smaller than with a lanthanide cation because of a less important desolvation of the divalent cation.

The K and $\Delta_r H°$ values characterizing the complexation of the quaternary ammonium cations by **1** in water at pH 2 are reported in Table 2. The corresponding $\Delta_r G°$ and $T\Delta_r S°$ values are also given. NH_4^+ has also been studied under the same conditions but no complexation has been observed. In order to complete the series obtained by Stödeman *et al.*[16] for alkylammonium ions, we have also studied the interaction of **1** with methylammonium and ethylammonium cations in water at pH 2. The results are reported in Table 2. Stödeman *et al.*[16] adjusted the pH of their solutions to 7.1 by addition of disodium hydrogenophosphate or sodium dihydrogenophosphate buffer. At this pH, all the sulfonate groups and one of the four phenolic hydroxy groups are deprotonated according to the pK_a values.[9–11] But, Arena *et al.*[17] showed that the association process is charge assisted and that the presence of sulfonate groups at the upper rim of the calixarene enhances the efficiency of binding of the ammonium cation. This implies that the positively charged ammonium cation is located nearby the negatively charged sulfonate groups and that the phenolate group does not play a major role in the association process. The modes of binding should thus be the same both at pH 2 and 7.1.

The $\log K$ values reported in Table 2 are of the same order of magnitude as those found for the lanthanides. However, the affinity of **1** for the organic cations results from a large negative change in $\Delta_r H°$ (−41.2 kJ mol^{-1} for Et_4N^+) and a small change in $T\Delta_r S°$ (except for Et_4N^+). These thermodynamic properties show that the organic and inorganic cations bind in very different modes. For all the organic cations studied here, the interaction process is enthalpy-driven. According to Lehn *et al.*,[15] there is inclusion of the quaternary ammonium cation into the cavity of the calixarene. Then, the major contribution to the enthalpy of complexation of these species comes from the van der Waals interactions associated with the inclusion of the alkyl chains. The role of the hydrophobic interactions is more difficult to evaluate. However we know that they give a positive contribution to $T\Delta_r S°$. Even if the entropic terms we have obtained are small it can be noticed that the sign of the change is always positive (except for Et_4N^+), which indicates that the desolvation of the alkyl chain also leads to a positive contribution to the $T\Delta_r S°$ term. Our results for the alkylammonium cations seem to be consistent with this interpretation. For these cations, the interaction is governed by the inclusion of the alkyl group within the cavity. A more negative enthalpy change shows that the ethylammonium cation binds more strongly than the methylammonium cation. The thermodynamic properties obtained by Stödeman *et al.*[16] for the alkylammonium ions, $H(CH_2)_nNH_3^+$ with $n = 3–7$, indicate that the enthalpy change levels off at larger chain lengths. The entropy change shows decreasing values for increasing alkyl chain length and, consequently, the association constant slowly decreases. One interpretation is that increasing alkyl chain length leads to a more important loss of degrees of freedom. $\Delta_r H°$ is negative and this indicates that the contribution of electrostatic interactions to the inclusion process is probably small. For all these species, the thermodynamic properties show that the electrostatic contribution is not predominant in the association process.

We have compared our $\log K$ values for the tetraalkylammmonium cations with those obtained by proton NMR.[15,17] Even if the values of the stability constants are not exactly the same, the selectivity we observe ($Et_4N^+ > Pr_4N^+ \approx Me_4N^+ > Bu_4N^+$) is in good agreement with the one reported by Lehn *et al.*[15]

The thermodynamic parameters show that the chain-length dependence is not linear within the R_4N^+ series. We notice that $\Delta_r G°$, $\Delta_r H°$ and $T\Delta_r S°$ go through a minimum for Et_4N^+. This suggests that the tetraethylammonium ion forms a tight inclusion complex ($\Delta H \ll 0$ and $T\Delta S < 0$).[22] Furthermore, the negative $T\Delta_r S°$ value reveals an important loss of degrees of freedom probably due to the insertion of more than one ethyl group into the cavity, as confirmed by CPK (Corey–Pauling–Koltun) models. For Me_4N^+, which can penetrate more deeply, the $T\Delta_r S°$ value is much smaller, in agreement with a less important loss of degrees of freedom. The small positive $T\Delta_r S°$ values obtained for Pr_4N^+ and Bu_4N^+ probably imply the insertion of only one alkyl chain. This is confirmed by the fact that the thermodynamic properties for the complexation of the tetrabutylammonium cation [$\log K$ (molar scale) = 4.21, ΔH = −21.6 kJ mol^{-1}, $T\Delta S$ = 2.4 kJ mol^{-1}] are similar to those

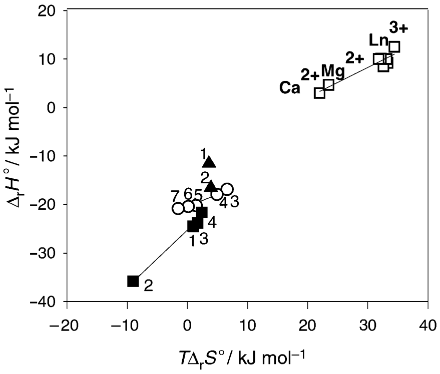

Fig. 2 $\Delta_r H°$ *versus* $T\Delta_r S°$ for the binding of the *p*-sulfonatocalix[4]arene anion to inorganic cations (□), to alkylammonium ions $H(CH_2)_n$-NH_3^+ with $n = 1–2$ at pH 2 (▲), with $n = 3–7$ at pH 7 (○)[16] and to tetraalkylammonium ions $(H(CH_2)_n)_4N^+$ with $n = 1–4$ (■).

for the complexation of the butylammonium cation [log*K* (molar scale) = 4.0, $\Delta H = -18$ kJ mol^{-1}, $T\Delta S = +5$ kJ mol^{-1}].[16]

In Fig. 2, we have plotted $\Delta_r H°$ against $T\Delta_r S°$ for the complexation of the three families of ions. For each of them a roughly linear relationship is observed. The very different positions of the straight lines for the organic and inorganic cations emphasize the fact that the interactions responsible for the complexation processes are totally different. Furthermore, within the organic series the correlations underline the peculiar behaviour described above.

In conclusion, we have carried out a thermodynamic characterization of the complexation of the *p*-sulfonatocalix[4]arene with various inorganic and organic cations in aqueous solution at pH 2. The thermodynamic quantities allow us to better identify the type of interactions controlling the association processes. It is interesting to note that the lanthanide cations are able to form stable 1 : 1 complexes with this type of host; complexation is enthalpically unfavoured and entropically favoured which indicates that electrostatic interactions are driving the association process. Results with alkyl and tetraalkylammonium cations highlight the difficulty in characterizing the driving forces leading to complexation. Here the process is essentially enthalpically favoured which indicates that the major contributions come from the van der Waals interactions with some contributions of hydrophobic interactions. These data also show that the interpretation becomes complicated with systems for which there are simultaneously inclusion of the alkyl chain and electrostatic interactions. This kind of work calls for further investigation in particular for a better understanding of the complex structure. We are currently performing molecular dynamics simulations of these complexes in aqueous solution.

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