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Abstract

Microcalorimetric titrations have been performed in acidic aqueous solution at 25 °C to calculate the complex stability constants ($K_S$) and thermodynamic parameters ($\Delta H^\circ$, $\Delta S^\circ$, and $\Delta G^\circ$) for the stoichiometric 1:1 complexation of lanthanoid(III) nitrates (La-Gd, Tb) with 5,11,17,23-tetrasulfonato-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)calix[4]arene (2) and 5,11,17,23-tetrasulfonato-thiacalix[4]arene (3). Using the present and previous reported data on water-soluble calix[4]arenesulfonates (1) and structurally related analogues 2 and 3, the complexation behavior is discussed comparatively from the thermodynamic point of view. Possessing four carboxyls at the lower rim of parent calix[4]arenesulfonate (1), the derivative 2 displays the enhanced binding abilities for Sm$^{3+}$. As compared with 1 and 2, $p$-sulfonatothiacalix[4]arene (3) gives not only the lower binding constants for all of lanthanoid(III) ions but also lower cations selectivity.

Thermodynamically, the resulting complexes of lanthanoid(III) ions with 1 and its derivatives 2 and 3 is absolutely entropy-driven in aqueous solution, typically showing larger positive entropy changes. These larger positive entropy changes ($\Delta S^\circ$) and somewhat smaller positive enthalpy changes ($\Delta H^\circ$) are directly contributed to the complexes stability as a compensative consequence.

Keywords: Microcalorimetric titration; Thermodynamic parameter; Enthalpy–entropy relationship; Calixarene; Lanthanoid

1. Introduction

It is well documented that the calixarenes and their derivatives can be taken as acceptor-selected binding cation/molecule to form the host–guest complexes or supramolecular species [1]. Therefore, a lot of calixarene derivatives have been designed and synthesized in order to alter the original cation/molecule binding ability and selectivity. Indeed, some calixarene derivatives with donating or non-donating side-arms attached to the lower rim can enhance not only the binding abilities of cation/molecule but also the selectivities [2]. However, little concern was focused on the complexation thermodynamics of calixarenes with ionic or molecular guests in aqueous and other polar solvents [3], probably due to the low solubility. Our recent studies [4] on alternatively lower-rim-modified 1,3-bis(cyanomethoxy) and -bis(2-aminoethoxy)-calix[4]arenes displayed remarkably different cation binding abilities and selectivity profiles upon complexation with light lanthanoids(III), giving much higher complex stability constants ($K_S$) for La$^{3+}$ and Ce$^{3+}$. An X-ray crystallographic study suggests that such a critical change in complexation behavior might be related to the original structures in the solid state, since the calixarene ring is distorted as a result of the repulsive interaction between the dipoles of 1,3-bis(2-aminoethoxy) groups. More recently, we demonstrated that the 5,11,17,23-tetra-tert-butyl-25,27-bis-[2-[N-(2-hydroxy-3-methoxybenzylidene)amino]ethoxy]-26,28-dihydroxy-calix[4]arene showed a global enhancement of $K_S$ for all light lanthanoids [5], displaying a unique selectivity profile with a broad peak at Nd$^{3+}$ and a sharp spike at Eu$^{3+}$. On the other hand, calixarenes could be modified via sulfonation at the upper rim, and then transformed into water-soluble molecular receptors, i.e. calixarenesulfonates, which have also been studied on the binding to several guest molecules and/or cations [6–12].
These results prompted us to further investigate the complexation thermodynamics of water-soluble calix[4]arene derivatives with lanthanoid(III) nitrates in acidic aqueous solution.

In the present study, we report the results of our investigation on the complexation thermodynamics of some lanthanoid(III) nitrates \((\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{and Tb})\) with 5,11,17,23-tetrasulfonato-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)calix[4]arene (2) and 5,11,17,23-tetrasulfonato-thiacalix[4]arene (3), using microcalorimetric titration. The thermodynamic parameters for the complexation of some lanthanoid(III) nitrates with calix[4]arene derivative possessing four carboxyls (2) and p-sulfonatothiacalix[4]arene (3), along with those for the parent calix[4]arenesulfonates (4) [12], will serve our further understanding of this thermodynamically less investigated area of calixarene chemistry [3b]. It is another point of interest to examine the thermodynamic consequence, as well as the scope and limitations, of the donating side-arm of interest to examine the thermodynamic consequence of the thermodynamic parameters of the complexation reaction of cyclohexanol with β-cyclodextrin. The results obtained were shown to be in good agreement with previous results reported [15,16]. Thus, titration microcalorimetry allows us to determine simultaneously the enthalpy and equilibrium constant from a single titration curve. Each microcalorimetric titration experiment consisted of 30 successive injections, a constant volume (9 μl per injection) of calixarene solution was injected into the reaction cell (1.4227 ml) charged with a lanthanoid(III) nitrates solution, and initial concentrations of aqueous lanthanoids(III) and calixarenesulfonates solution in each run are 1.0 and 10 mM, respectively. The calixarenesulfonates (1–3) solution was, respectively, added to the acidic aqueous solution to determine the heat of dilution, which was measured in each run using the same number of injections and concentration of calixarenesulfonates as used in the titration experiments. The separate dilution enthalpies of calixarenes and lanthanoid(III) nitrates determined in these control experiments were subtracted from the enthalpies measured in the titration experiments. The ORIGIN software (Microcal Inc.), which was used to calculate the equilibrium constant and standard molar enthalpy of reaction from the titration curve, gave a standard deviation based on the scatter of the data points in a single titration curve.

2. Experimental

2.1. Materials

Water-soluble calix[4]arenes, i.e. 5,11,17,23-tetrasulfonato-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)calix[4]arene (2) [13] and 5,11,17,23-tetrasulfonato-thiacalix[4]arene (3) [14a], were prepared according to the literature procedures previously. Water is distilled twice. The pH of calixarenes and lanthanoid cation solution was set at 2 with 0.01 M HCl. Lanthanoid(III) nitrates \((\text{Ln} = \text{La}–\text{Gd}, \text{Tb})\) were prepared by dissolving the corresponding oxides of 99.99% purity (Baotou Rare Earth Chemical Co.) in 50% aqueous nitric acid while heating for about 10 min. After evaporation, the solid residue was dried in vacuo over \(\text{P}_2\text{O}_5\) for several days to give a powdery product. The lanthanoid(III) nitrates, i.e. \(\text{La(NO}_3\text{)}_3\cdot3\text{H}_2\text{O}, \text{Ce}(\text{NO}_3\text{)}_3\cdot3\text{H}_2\text{O}, \text{Pr(NO}_3\text{)}_3\cdot3\text{H}_2\text{O}, \text{Nd(NO}_3\text{)}_3\cdot3\text{H}_2\text{O}, \text{Sm(NO}_3\text{)}_3\cdot3\text{H}_2\text{O}, \text{Eu(NO}_3\text{)}_3\cdot3\text{H}_2\text{O}, \text{Gd(NO}_3\text{)}_3\cdot3\text{H}_2\text{O}, \text{and Tb(NO}_3\text{)}_3\cdot6\text{H}_2\text{O}\), were used without further purification [14b].

3. Results

Assuming 1:1 stoichiometry [17] for the complexation of \(\text{Ln(NO}_3\text{)}_3\) \((\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{and Tb})\) with water-soluble calix[4]arene derivatives 2 and 3, the complex stability constant \((K_1)\) and the enthalpy change \((\Delta H)\) were calculated by using the 1:1 binding mode:

\[
K_1 = \frac{[\text{calix} \cdot \text{Ln}]}{[\text{calix}] \cdot [\text{Ln}^3\text{+}]} 
\]

For each lanthanoid–calixarene 1:1 combination, the measurement was independently repeated two or three times to check the thermodynamic quantities obtained. No serious deviation was found in the fitting process, verifying the 1:1 stoichiometry of complexation as assumed above. A representative result of microcalorimetric titration curve of \(p\)-sulfonatothiacalix[4]arene with \(\text{Nd}^{3+}\) is shown in Fig. 1. In addition to the 1:1 binding mode, calculation has also been performed based on the 2:1 binding model, which found that these calculations had uncertainties and serious deviation. The fitting analysis used was “one set of binding sites”...
Fig. 1. Typical calorimetric titration showing binding of host 3 to Nd\textsuperscript{3+} at 25°C in aqueous solution: (a) raw data for sequential 9µl injections of host 3 (10.0 mM) into Nd\textsuperscript{3+} (1.0 mM; ITC cell volume: 1.4277 ml); (b) heats of reaction as obtained from the integration of the calorimetric traces.

Table 1

<table>
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<th>Ligand</th>
<th>Cation</th>
<th>log K\textsubscript{S}</th>
<th>−ΔG\textsuperscript{o}</th>
<th>ΔH\textsuperscript{o}</th>
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<td>1</td>
<td>La\textsuperscript{3+}</td>
<td>4.23</td>
<td>24.1 ± 0.3</td>
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<td>Nd\textsuperscript{3+}</td>
<td>4.08</td>
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<td>32.8 ± 0.3</td>
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<td>Sm\textsuperscript{3+}</td>
<td>3.82</td>
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<td>10.4 ± 0.2</td>
<td>32.2 ± 0.4</td>
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<tr>
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<td>Eu\textsuperscript{3+}</td>
<td>3.63</td>
<td>21.9 ± 0.2</td>
<td>12.5 ± 0.2</td>
<td>34.4 ± 0.4</td>
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<td>Gd\textsuperscript{3+}</td>
<td>3.94</td>
<td>22.5 ± 0.3</td>
<td>9.6 ± 0.3</td>
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<td>3.73 ± 0.03</td>
<td>21.3 ± 0.4</td>
<td>5.1 ± 0.5</td>
<td>26.5 ± 0.3</td>
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<td>Ce\textsuperscript{3+}</td>
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<td>21.8 ± 0.1</td>
<td>5.1 ± 0.3</td>
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<td>Pr\textsuperscript{3+}</td>
<td>3.97 ± 0.04</td>
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<td>26.7 ± 0.5</td>
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Values are the averages of more than three independent measurements in pH = 2 acidic aqueous solution.
plexation with the parent calix[4]arenesulfonates (1) are also included in Table 1.

4. Discussion

4.1. Substituted effects

As can be seen from Table 1, the binding constants, the relative cation selectivity, and the thermodynamic parameters for the complexation of calix[4]arenesulfonates (1) with lanthanoid(III) ions are influenced by several factors of the relative size between host 1 and cation diameter, and surface charge density of cation, and so on. It is interesting to note that the introduction of carboxyls to the parent calix[4]arenesulfonates (1) or methylene substituted by sulfur to give calix[4]arene derivatives 2 and 3 alters not only significantly the intrinsic rigidity and bind site of 1, but also the binding ability and the relative cation selectivity. In order to visualize the cation’s binding properties and relative cation selectivity of hosts 1–3, the changing profile of log $K_3$ is plotted as a function with reciprocal ionic radius of lanthanoids in Fig. 3.

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4.2. Thermodynamic parameters

To elucidate the thermodynamic origins of cation binding ability and relative cation selectivity, thermodynamic quantities upon the complexation between water-soluble calix[4]arene derivatives 1–3 and lanthanoids are also listed in Table 1. As can be recognized readily from Table 1, all the values of the enthalpy changes ($\Delta H^\circ$) and the entropy changes ($\Delta S^\circ$) of the resulting complexes are positive. These results indicate that the complexation of calix[4]arenes (1–3) with lanthanoid(III) ions examined is driven predominantly by the favorable entropic change, typically showing large positive entropy changes ($T\Delta S^\circ = 26–34$ kJ mol$^{-1}$) and somewhat smaller positive enthalpy changes ($\Delta H^\circ = 4–12$ kJ mol$^{-1}$). One possible explanation for the complexation of the large entropy-driven is that, both dissociated trivalent lanthanoid(III) ions and free calixarene derivatives are heavily solvated by ion–dipole and hydrogen-bonding interactions, respectively. Therefore, the cation binding of water-soluble calixarene derivatives with lanthanoids in acidic aqueous solution demands entirely the extensive desolvation of interaction between host and guest cation, affording the highly positive entropy change upon complexation, as observed in the case of complexation with crown ether in methanol [18,19].

Significantly, three water-soluble calixarene derivatives give the lowest complexes stability constants for Eu$^{3+}$ among lanthanoids, but the much larger positive enthalpy changes ($\Delta H^\circ$) and entropy changes ($\Delta S^\circ$) at the same
time. This means that the complexation of Eu(III) with water-soluble calixarene in aqueous solution is favored predominantly by the entropic gain, which is however canceled by similarly large unfavored enthalpic changes. From the previous reports, it may be deduced that the lighter lanthanoid(III) ions are nine-coordination in water, whereas the heavier lanthanoid(III) ions are eight-coordination [20,21].

The different hydration numbers may be explained by larger lanthanoid(III) ions possessing high electropositivity and small cation radius. Therefore, comparing to those relative extrathermodynamic parameters we reported previously [24], it can be found from Table 2 that calixarene shows larger intercepts for the complexation with trivalent lanthanoid ions than those for crown ether complexation with lanthanoid ions or alkali and alkaline earth metals, which indicated that trivalent lanthanoid ions possessing high electropositivity and small cation radius could occur in very extensive desolvation. These extrathermodynamic parameters for the larger slope (α) and intercept (TDAS) indicated that the complexation of calixarene derivatives with trivalent lanthanoid ions could occur even in the absence of enthalpic stabilization due to the entropic gains from the extensive desolvation of the host and guest molecules, especially the complexation of trivalent lanthanoid ions in aqueous and other polar solvents. Therefore, the enthalpy–entropy compensation effect could serve to understanding of the host–guest complexation behavior [25].

4.3. Enthalpy–entropy compensation

Using the present and the previous reported data [4,5], the entropy changes (TDAS) were plotted against the enthalpy changes (ΔHf) to give an excellent regression line (correlation coefficient r = 0.948) of a large slope (α = 0.88) and intercept (TDAS0 = 22.5 kJ mol⁻¹) upon complexation of calixarene derivatives with the trivalent lanthanoid ions, as shown in Fig. 4 and Table 2. Although the available data size is still limited (number of data sets (α) = 38), the excellent regression line reveals that the compensatory enthalpy–entropy relationship is generally valid for the complexation thermodynamics of calixarene derivatives with lanthanoids [3]. According to our previous report [23], the slope (α) and intercept (TDAS0) can be taken as quantitative measures of the conformational changes and the degree of desolvation induced by complex formation. Therefore, comparing to those relative extrathermodynamic parameters we reported previously [24], it can be found from Table 2 that calixarene shows larger intercepts for the complexation with trivalent lanthanoid ions than those for crown ether complexation with lanthanoid ions or alkali and alkaline earth metals, which indicated that trivalent lanthanoid ions possessing high electropositivity and small cation radius could occur in very extensive desolvation. These extrathermodynamic parameters for the larger slope (α) and intercept (TDAS0) indicated that the complexation of calixarene derivatives with trivalent lanthanoid ions could occur even in the absence of enthalpic stabilization due to the entropic gains from the extensive desolvation of the host and guest molecules, especially the complexation of trivalent lanthanoid ions in aqueous and other polar solvents. Therefore, the enthalpy–entropy compensation effect could serve to understanding of the host–guest complexation behavior [25].

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