

Complexation thermodynamics of water-soluble calix[4]arene derivatives with lanthanoid(III) nitrates in acidic aqueous solution

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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 (ΔG° , ΔH° , and $T\Delta S^\circ$) for the stoichiometric 1:1 complexation of lanthanoid(III) nitrates (La-Gd, Tb) with 5,11,17,23-tetrakisulfonato-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)calix[4]arene (**2**) and 5,11,17,23-tetrakisulfonato-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 ($T\Delta S^\circ$) and somewhat smaller positive enthalpy changes (ΔH°) are directly contributed to the complexes stability as a compensative consequence.

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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 nondonating 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-

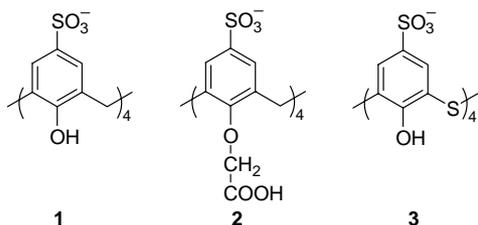
bis(cyanomethoxy) and -bis(2-aminoethoxy)-calix[4]arenes displayed remarkably different cation binding abilities and selectivity profiles upon complexation with light lanthanoids(III), giving much higher complex stability constants (K_S) for La^{3+} and Ce^{3+} . An X-ray crystallographic study suggests 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-dihydroxycalix[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].

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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-tetrakis(hydroxycarbonylmethoxy)calix[4]arene (**2**) and 5,11,17,23-tetrakis(hydroxycarbonylmethoxy)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 (**1**) [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 and heteroatom-substituted effects, using this relatively flexible calix[4]arene (**2**) and thiacalix[4]arene (**3**). Furthermore, we also examined the general validity of the enthalpy–entropy compensation effect upon the complexation of guest lanthanoid(III) ions with host calixarene derivatives.



2. Experimental

2.1. Materials

Water-soluble calix[4]arenes, i.e. 5,11,17,23-tetrakis(hydroxycarbonylmethoxy)calix[4]arene (**2**) [13] and 5,11,17,23-tetrakis(hydroxycarbonylmethoxy)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 P_2O_5 for several days to give a powdery product. The lanthanoid(III) nitrates, i.e. $\text{La}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Pr}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, and $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, were used without further purification [14b].

2.2. Apparatus procedures

Isothermal calorimetry measurements have been performed in aqueous solution at 25 °C by using a thermostated and fully computer-operated VP-ITC calorimeter purchased from Microcal Inc., Northampton, MA. The calorimetric determinations were also calibrated chemically by measurement 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 in the absence of lanthanoid(III) nitrates 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.

3. Results

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



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 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”

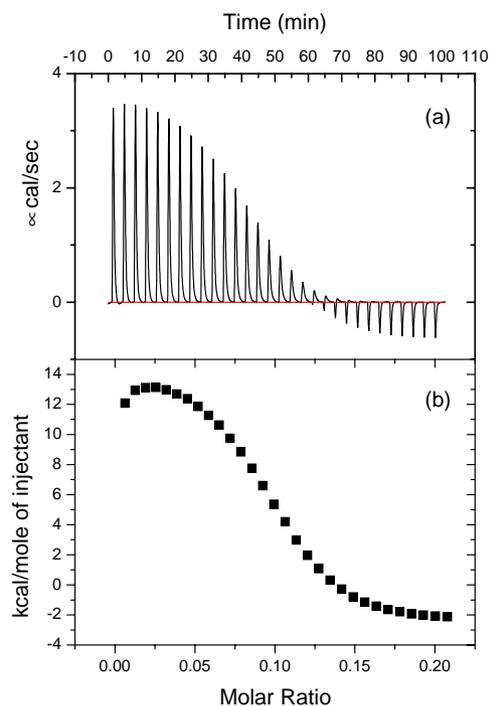


Fig. 1. Typical calorimetric titration showing binding of host **3** to Nd^{3+} at 25°C in aqueous solution: (a) raw data for sequential $9\ \mu\text{l}$ injections of host **3** (10.0 mM) into Nd^{3+} (1.0 mM; ITC cell volume: 1.4227 ml); (b) heats of reaction as obtained from the integration of the calorimetric traces.

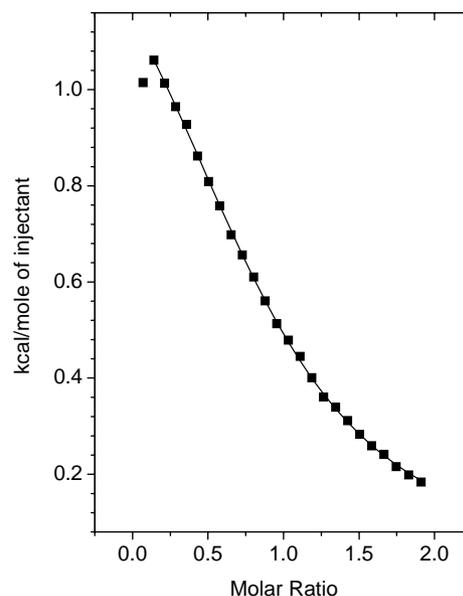


Fig. 2. "Net" heat effect obtained by subtracting the heat of dilution from the heat of reaction, which was analyzed by computer simulation using the one set of binding sites model.

model, as exemplified in Fig. 2 for the complexation of host **3** with Nd^{3+} . Then the complex stability constants and thermodynamic parameters obtained are listed in Table 1. The standard Gibbs energies of reaction, ΔG° , and standard entropies of reaction, ΔS° , given in Table 1 were calculated directly from the measured complex stability constants and standard enthalpy changes of reaction. For the comparison purpose, the thermodynamic quantities reported for the com-

Table 1

Complex stability constants ($\log K_S$) and thermodynamic parameters (in kJ mol^{-1}) for complexation of lanthanoid(III) nitrates with **1**, **2**, and **3** in $\text{pH} = 2$ acidic aqueous solution at 25°C

Ligand	Cation	$\log K_S$	$-\Delta G^\circ$	ΔH°	$T\Delta S^\circ$	References
1	La^{3+}	4.23	24.1 ± 0.3	9.2 ± 0.1	33.3 ± 0.4	[12]
	Nd^{3+}	4.08	23.3 ± 0.3	9.5 ± 0.2	32.8 ± 0.5	[12]
	Sm^{3+}	3.82	21.8 ± 0.2	10.4 ± 0.2	32.2 ± 0.4	[12]
	Eu^{3+}	3.83	21.9 ± 0.2	12.5 ± 0.2	34.4 ± 0.4	[12]
	Gd^{3+}	3.94	22.5 ± 0.3	9.8 ± 0.3	32.2 ± 0.6	[12]
2	La^{3+}	3.73 ± 0.03	21.3 ± 0.4	5.1 ± 0.5	26.5 ± 0.3	This work
	Ce^{3+}	3.82 ± 0.01	21.8 ± 0.1	5.1 ± 0.3	26.9 ± 0.4	This work
	Pr^{3+}	3.97 ± 0.04	22.7 ± 0.3	4.5 ± 0.4	27.2 ± 0.1	This work
	Nd^{3+}	4.09 ± 0.03	23.4 ± 0.6	4.0 ± 0.1	27.4 ± 0.2	This work
	Sm^{3+}	4.08 ± 0.02	23.3 ± 0.4	3.9 ± 0.1	27.2 ± 0.8	This work
	Eu^{3+}	3.51 ± 0.04	20.1 ± 0.1	7.3 ± 0.3	27.4 ± 0.1	This work
	Gd^{3+}	3.86 ± 0.05	22.0 ± 0.3	5.5 ± 0.2	27.5 ± 0.3	This work
Tb^{3+}	3.63 ± 0.01	20.9 ± 0.2	6.8 ± 0.7	27.7 ± 0.5	This work	
3	La^{3+}	3.45 ± 0.02	19.7 ± 0.1	7.2 ± 0.2	26.8 ± 0.3	This work
	Ce^{3+}	3.41 ± 0.02	19.4 ± 0.2	7.0 ± 0.1	26.5 ± 0.2	This work
	Pr^{3+}	3.42 ± 0.03	19.6 ± 0.3	6.9 ± 0.1	26.5 ± 0.3	This work
	Nd^{3+}	3.40 ± 0.01	19.4 ± 0.1	6.8 ± 0.3	26.2 ± 0.1	This work
	Sm^{3+}	3.37 ± 0.04	19.2 ± 0.2	7.2 ± 0.2	26.4 ± 0.4	This work
	Eu^{3+}	3.26 ± 0.03	18.6 ± 0.4	7.5 ± 0.3	26.0 ± 0.3	This work
	Gd^{3+}	3.30 ± 0.02	17.7 ± 0.6	9.0 ± 0.1	26.6 ± 0.1	This work
	Tb^{3+}	3.33 ± 0.02	19.0 ± 0.1	7.7 ± 0.1	26.7 ± 0.5	This work

Values are the averages of more than three independent measurements in $\text{pH} = 2$ 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 $\log K_S$ is plotted as a function with reciprocal ionic radius of lanthanoids in Fig. 3.

As can be seen from Fig. 3, the profile of K_S for *p*-sulfonatocalix[4]arene (**3**) shows the lower binding ability to all the ions examined, giving a flattening tendency. As compared with conventional *p*-sulfonatocalix[4]arene (**1**), compound **3** could decrease the original cation binding ability and relative selectivity. The lower binding constants for **3** may be attributed to the substituted sulfur atoms, possessing larger radius than carbon atoms, and thus could increase the molecular flexibility of calixarene and decrease the electrostatic interactions between sulfonate groups with cations, resulting in the K_S value to decrease nearly ca. 0.5–0.7 order magnitude for lanthanoid(III) ions examined than that for **1**.

The examination of the cation-binding ability of lanthanoids with **2** attached by four carboxyls at the lower rim

of *p*-sulfonatocalix[4]arene is also interesting. ^1H NMR investigations indicated that three host compounds all adopt cone conformations. Therefore, the different binding ability upon complexation of **2** with lanthanoid(III) ions as compared with parent compound **1** and reference compound **3** can be caused only by the substituted effect. As can be readily recognized from Fig. 3, the introduction of four carboxyls to the lower rim of *p*-sulfonatocalix[4]arene could alter not only original binding ability, but also the relative cation selectivity for lanthanoids. The profile of K_S values for **2** displays a broad peak for Nd^{3+} and Sm^{3+} . One reasonable explanation for these results is that the trivalent Nd^{3+} and Sm^{3+} are best accommodated in the preorganized 3D cavity composed of four carboxyls groups upon complexation with lanthanoid ions. Furthermore, It could be deduced that the size-fit concept is more rigorous in the complexation of trivalent lanthanoid ions upon sulfonatocalixarenes; at the same time, from Bonal et al.'s report, we also found that the preorganized structure of calixarene played an important role in multi-site interaction with the lanthanoids(III) cation [12]. Results obtained indicate the strength of binding ability of host **2** containing four carboxylic acidic groups with metal cations mainly determined by ion–ion and/or ion–dipolar interactions but not the electrostatic interaction between sulfonato groups with lanthanoids like **1** and **3** complex upon them.

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 (ΔH°) and the entropy changes (ΔS°) 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 ($T\Delta S^\circ = 26\text{--}34\text{ kJ mol}^{-1}$) and somewhat smaller positive enthalpy changes ($\Delta H^\circ = 4\text{--}12\text{ kJ mol}^{-1}$). 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 (ΔH°) and entropy changes (ΔS°) at the same

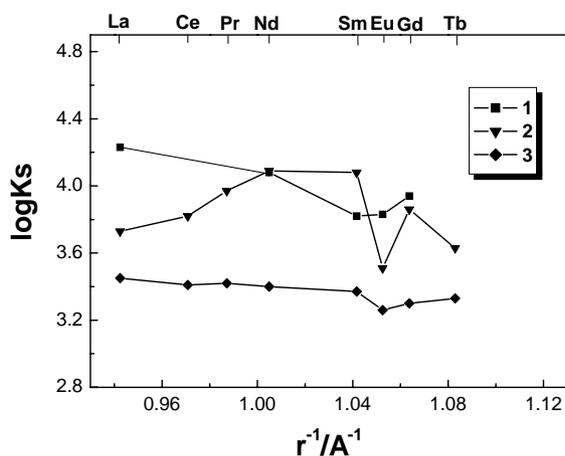


Fig. 3. Binding constants (K_S) as a function of reciprocal ionic radius for the water-soluble calixarenes (**1–3**) with lanthanoid(III) ions at 25 °C in acidic aqueous solution.

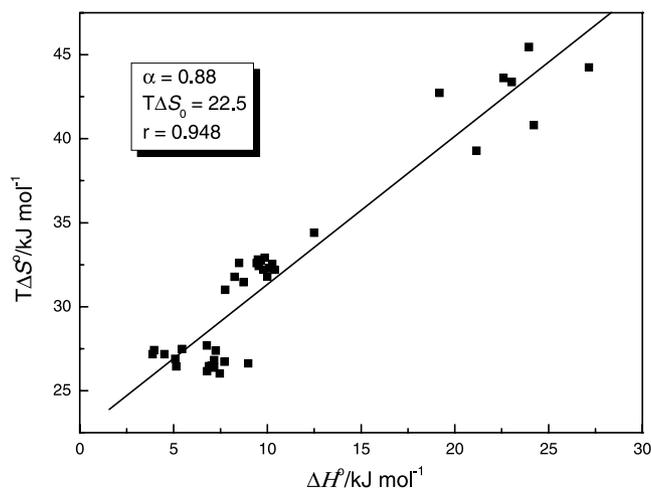


Fig. 4. Enthalpy–entropy compensation plot for complexation of lanthanoids with calixarenes.

time. This means that the complexation of Eu^{3+} 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 positive change of ΔH° values in the middle of the series. A wide variety of observations have exhibited the similar lanthanoid complex behaviors [22]. These larger positive entropy changes ($T\Delta S^\circ$) and somewhat smaller positive enthalpy changes (ΔH°) directly contributed to the complexes stability as a compensative consequence.

4.3. Enthalpy–entropy compensation

Using the present and the previous reported data [4,5], the entropy changes ($T\Delta S^\circ$) were plotted against the enthalpy changes (ΔH°) to give an excellent regression line (correlation coefficient $r = 0.948$) of a large slope ($\alpha = 0.88$) and intercept ($T\Delta S_0 = 22.5 \text{ kJ mol}^{-1}$) 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 (n) = 38), the excellent regression line reveals that the com-

Table 2
Slope (α) and intercept ($T\Delta S_0$) of the ΔH – $T\Delta S$ plot for 1:1 host–guest complexation in homogeneous solution

Host	Guest	α	$T\Delta S_0$	References
Crown ether	Cation	0.76	10.0	[25]
Glyme/podand	Cation	0.86	9.6	[25]
Cryptand	Cation	0.51	16.7	[25]
Bis(crown ether)	Cation	1.03	19.2	[25]
Crown ether	Lanthanoid	1.00	17.6	[24]
Calixarene	Lanthanoid	0.88	22.5	This work

pensatory 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 ($T\Delta S_0$) 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 ($T\Delta S_0$) 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].

Acknowledgements

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