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Host–guest interaction between water-soluble calix[6]arene hexasulfonate and *p*-nitrophenol

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Abstract

The inclusion complexation of calix[6]arene hexasulfonate with *p*-nitrophenol has been studied by photoluminescence (PL), differential scanning calorimetry (DSC) and quantum-chemical methods in aqueous media. The results indicate 1:1 complex stoichiometry. The directly measured molar enthalpy of inclusion shows strong interaction between the host and the guest, however the entropy change of the complex formation is negative and quite high. Therefore, the Gibbs free enthalpy change of the complex formation is small resulting in a relatively low complex stability. This well-known enthalpy–entropy-compensation effect is probably due to the increased freedom of guest molecules relative to the host calixarenes and also due to the increased disorder of solvent molecules after the complex has been dissociated. The good correlation between the van't Hoff enthalpy determined by PL studies and the calorimetric enthalpy reflects the two-state character of complexation. Quantum-chemical investigation suggests π–π interaction between the host and the guest in agreement with earlier results.

Keywords: Inclusion compound; Host–guest complex; DSC; Enthalpy of inclusion; Calixarenes

1. Introduction

The recognition of neutral organic molecules by synthetic receptors is a topic of current interest in supramolecular- and also in analytical chemistry [1,2]. Calix[*n*]arenes (*n* = 4–6, 8) represent a fascinating class of macrocycles due to the simplicity of their well-defined skeleton, which is associated with versatile recognition properties towards metal or organic ions and neutral molecules [3,4]. Recent reviews summarize their thermodynamic [5] and redox properties [6], applications in analytical and separation science [7], modeling of their molecular dynamics [8–10] and the extent of their metal ion binding character in solution [11,12].

The selectivity of complexation with different species can be modified by changing the cavity size and by the incorporation of functional groups in the lower and/or upper rim of the calixarene molecule. In our recent papers [13–15] the complexation behavior and the factors controlling the thermodynamic and kinetic stability or selectivity of some calixarene derivatives towards neutral π-electron deficient aromatics were reported. In addition, the binding characteristics of water-soluble calixarenes with iron ions [16] and with C_{60} fullerene [17] have also been published.

The interactions of calixarenes with neutral species involve competition between complexation and solvation processes. Non-electrostatic forces arising from the interaction of the electronic systems of neutral hosts and guests are of primary importance. For example, calixarenes and electron-deficient aromatics can form complexes predominantly through π–π type interaction, whilst the inclusion of

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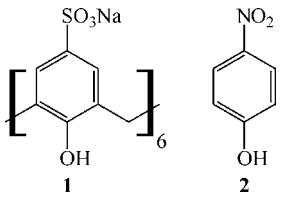

Fig. 1. Calix[6]arene-hexasulfonate sodium salt **1** as host and *p*-nitrophenol **2** as guest.

aliphatic guests into the hydrophobic cavity can be stabilized by CH–π contacts.

Calix[4]arene tetrasulfonate [18], and the thiacalix[4]arene counterpart [19] have been reported to bind small polar organic molecules (alcohols, carbonyl compounds, nitriles, acid derivatives, etc.) in aqueous solution and the complexation was monitored mostly by ^{1}H NMR spectroscopy. In these cases the importance of charge assistance of the sulfonate groups in apolar binding of the guests was confirmed. Because of the ^{1}HNMR is relatively seldom applied for identification of complexation, it may worth to note that this technique has been successfully used to identify the clathrate formation of 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl with small solvent molecules (acetone and methanol). This reaction has been also studied by means of simultaneous TG–DSC measurement using isothermal and scanning mode of operation [20].

In this paper, the interaction between calix[6]arene-hexasulfonate sodium salt **1** as a host and *p*-nitrophenol **2** as a guest (Fig. 1) in aqueous media was investigated by photoluminescence (PL), differential scanning calorimetry (DSC) and quantum-chemical methods. The stoichiometry and the van't Hoff enthalpy of the complex formation were determined by spectrofluorometric method. The calorimetric molar enthalpy of the inclusion was determined from the heat flow directly measured by DSC method. The fluorometrically determined van't Hoff enthalpy and the calorimetric enthalpy were compared to examine the two-state behavior of the formation of such a complex. Quantum-chemical investigations were carried out to determine the most stable conformation of the host–guest complex.

2. Experimental

Calix[6]arene-hexasulfonate salt **1** was prepared by the direct sulfonation of the parent calix[6]arene with concentrated sulfuric acid [21]. *p*-Nitrophenol (p.a. grade) was purchased (Merck, Germany) and used without further purification.

Calorimetric measurements were carried out with a highly sensitive nano-II-DSC 6100 (Setaram, France) instrument. The calorimeter is configurated with a platinum capillary cell (volume = 0.299 ml). The samples were pressurized to $3 \pm 0.02 \times 10^5$ Pa during all scans. Using oil rotation pump, standard degassing procedure for 15 min at about 15 Pa was applied before loading the samples into the capillary. The heat flow was scanned between 0 and 50 °C. A typical scanning rate of 0.5 K/min was applied, however it was varied from 0.1 up to 2 K/min for each sample to check the effect of diffusion of particles interacted and that of on the reaction rate of complexation. The experimental deviation of the calorimetric results were estimated to be ± 5 mJ.

To avoid any interaction other than the interaction related to the host – guest complex formation, the DSC curves of solutions of calixarene in buffer (i), calixarene in water (ii) and buffer by oneself (iii) were recorded against water. No significant differences between the curves of summed (ii) with (iii) and (i) were obtained, proving that no considerable interaction between the buffer and the host calixarene exists. Similar result was found for the guest *p*-nitrophenol species.

The PL spectra of the different solutions were investigated by means of Fluorolog τ3 spectrofluorometric system (Jobin-Yvon/SPEX). For data collection a photon counting method with 0.2 s integration time was used. Excitation and emission bandwidths were set to 1 nm. A 1 mm layer thickness of the fluorescent probes with front face detection was used to eliminate the inner filter effect.

The acid–base equilibria in the solutions of calixarene **1** was studied by potentiometry using a combined pH sensitive glass electrode (Triode pH electrode, ORION) and Orion 420 Aplus pH meter. The potentiometric measurements were carried out at 25 ± 0.1 °C. The protonation was studied in aqueous solution of **1** at concentration of 10^{-2} M with ionic strength of 0.1 M tetraethylammonium-perchlorate ($[Et_4N][ClO_4]$) background salt. The estimated error of the pH measurements was found to be about 0.02 pH unit. Values of the stepwise protonation constants K_i and the overall protonation constants β_i were computed with the HyperQuad 2000 (Protonic Software) computer program [22–24].

Both calorimetric and fluorometric experiments were carried out at pH 6.9 using phosphate buffer. 0.025 mol/kg disodium hydrogen phosphate (Merck) + 0.025 mol/kg potassium dihydrogen phosphate (Merck); pH 6.961, 6.912, 6.873, 6.843, 6.823, 6.814 at temperatures of 0, 10, 20, 30, 40, 50 °C, respectively.

The equilibrium conformations of calixarene **1** and their complexes with *p*-nitrophenol **2** were studied with semi-empirical AM1 (Austin Model) method, followed by ab initio HF/6-31G* calculations. The Fletcher-Reeves geometry optimization method was used for the investigation of the conformers. The interaction energy of the studied species was described at an ab initio level using HF/6-31G* calculation. TIP3P method [25] with extension to the solvent used [26] was applied for considering the solvent effect. All types of calculations were carried out with the HyperChem Professional 7 program package [27].

3. Results and discussion

Fig. 2 shows the distribution diagram of the differently protonated species of **1** derived from the acid–base titration

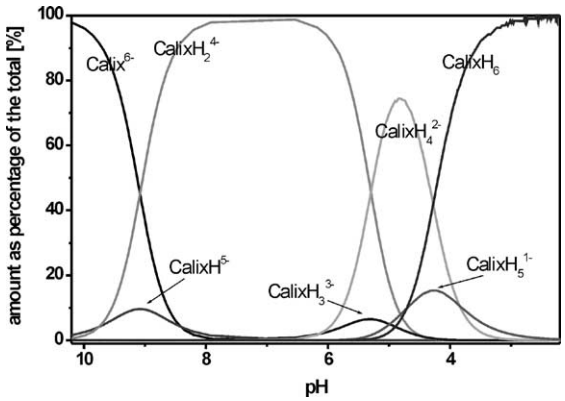

Fig. 2. Distribution diagram of the differently protonated calixarene **1** as a function of pH.

by adjusting ionic strength with 0.1 M tetraethylammonium-perchlorate background salt. Measurements were carried out under purified nitrogen atmosphere. It can be clearly seen that near pH 7, compound **1** exists in double protonated form. It has to be noted, that the distribution curve of $CalixH_2^{4-}$ has a wide maximum between pH 6 and pH 8.5 providing excellent conditions for the investigation of its host properties. Since no considerable abundance of other species has been observed at this pH range, therefore pH 6.9 was chosen for the further examinations. To minimize the effect of the temperature change on pH, phosphate buffer was used which keeps the pH constant at a wide range of temperature (see Section 2).

3.1. Effect of complexation on PL intensity

In order to investigate the interaction of **1** with **2**, 10^{-4} M solutions were prepared in phosphate buffer and the PL spectra were recorded. Their evaluation revealed that the guest molecule induced some changes in the spectra. The PL spectrum of **1** exhibits two peaks at 330 nm and at 495 nm, the intensities of which were decreased in the presence of **2** (Fig. 3). According to our earlier results [13–17] we supposed that the spectral changes were induced by the formation of an inclusion complex. Since *p*-nitrophenol **2** also shows considerable emission and its emission band overlaps with the 495 nm band of **1**, the 330 nm peak of calixarene was used for the determination of complex stability.

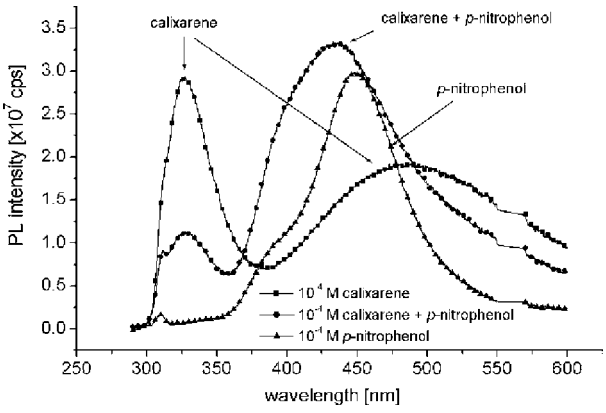

Fig. 3. The change of the PL spectra of calixarene derivative **1** obtained in the absence and in the presence of 10^{-4} M *p*-nitrophenol.

3.2. Determination of the complex stoichiometry and complex stability

Assuming a 1:1 stoichiometry, the complexation reaction can be written as follows ("H" refers to host while "G" means the guest):

$$H + G \overset{K_s}{\rightleftharpoons} HG \tag{1}$$

It is well known that in this particular case the concentration of the complex formed can be expressed as the function of the initial concentrations ($[H]_0$ and $[G]_0$):

$$[HG] = \frac{1}{2}\left\{\left([H]_0 + [G]_0 + \frac{1}{K_s}\right) \pm\sqrt{\left([H]_0 + [G]_0 + \frac{1}{K_s}\right)^2 - 4[H]_0[G]_0}\right\} \tag{2}$$

Assuming that the observed PL signal varies linearly with the concentration of the complex formed, ΔF is described by Eq. (3).

$$\Delta F = f_{HG}[HG] \tag{3}$$

wherein $\Delta F = F - F_0$ is a difference between the PL intensity obtained with the calixarene/*p*-nitrophenol system and that of the free calixarene with the same concentration. The measure of the PL signals, f_{HG} can be obtained for the individual HG species relative to the PL signal of pure calixarene species at the same concentrations. By definition,

$$f_{HG} = \left.\frac{F([G]) - F([HG])}{F([H])}\right|_{[HG]=[H]} \tag{4}$$

Job's method [28] is widely used for the spectroscopic determination of complex stability constants also in calixarene chemistry [29–33]. The stability constant of the inclusion complex can be determined by the curve fitting of Eq. (3) to the experimental data using the expression of [HG] from Eq. (2).

However, it is known that the equilibrium in similar systems strongly depends on the temperature [e.g. [34]]. The thermodynamic parameters for the individual complexes formed in the calixarene/*p*-nitrophenol system can be determined from the van't Hoff equation:

$$\ln K = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{5}$$

where ΔG is the Gibbs energy change, ΔS the entropy change and ΔH the enthalpy change associated with complex formation.

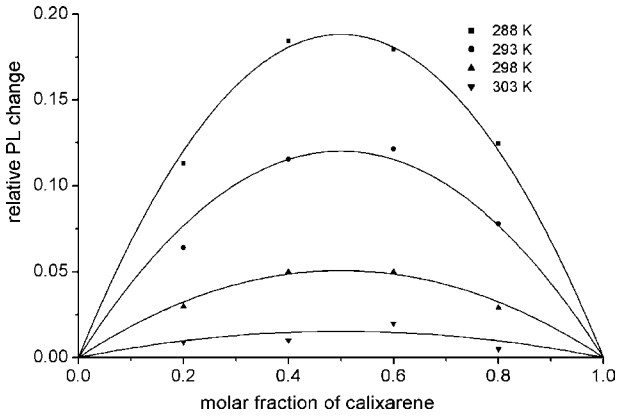

Fig. 4. Job's plot of calixarene **1**–*p*-nitrophenol system at different temperatures.

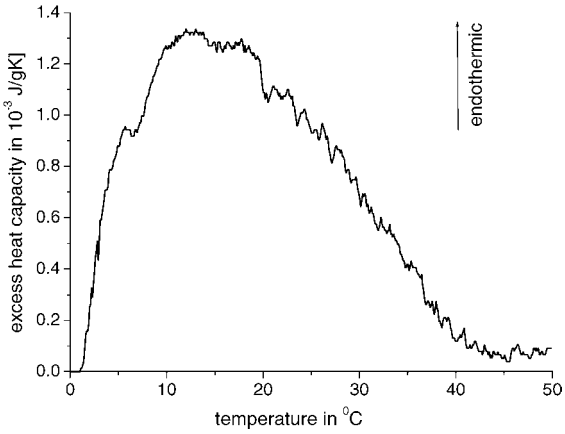

Fig. 5. The excess heat capacity of the equimolar (10^{-3} M) mixture of **1** and **2** recorded against the phosphate buffer. Scanning rate is 1 K/min.

Inserting Eq. (5) for the formation constants into the Eqs. (2) and (3), the fluorescence change in Eq. (3) can be expressed as a function of the ΔH, ΔS values and the f_{HG} coefficient.

The thermodynamic parameters associated with the K value were determined from the Job's curves by an iterative solution of Eqs. (2) and (3) using the expression of K value from the van't Hoff equation (Eq. (5)).

In order to determine the thermodynamic parameters mentioned above, 10^{-3} M stock solutions of **1** and **2** were mixed in four different [H]/([G] + [H]) ratio by stepwise addition of $n \times 300\,\mu l$ host to $(5 - n) \times 300\,\mu l$ guest solutions (n = 1–4) keeping 10^{-3} M total concentration ([G] + [H]). The measurements were carried out at four different temperatures and the iterative curve-fitting procedure was done simultaneously for the experimental data (Fig. 4). The plot of ΔF as a function of molar fraction of host gives an excellent fit, verifying the 1:1 complex stoichiometry assumed above. Table 1 summarizes the thermodynamic parameters determined from PL studies.

3.3. DSC measurements on the host–guest system

Fig. 5 shows a typical DSC scan of the mixture of equimolar (10^{-3} M) solutions of **1** and **2** recorded against the phosphate buffer with a scanning rate of 1 K/min. The excess heat capacity was calculated by substraction of the baseline (see later). The broad DSC curve reflects to fast dissociation process compared to the speed of change of concentration. This change is induced by the decreased complex stability at higher temperature, and therefore, its speed is determined by the scanning rate. This shape of the DSC curve is usual in case of weak host–guest complexes [20].

Fig. 6 shows the excess heat capacity of the equimolar mixture of **1** and **2** scanned by the rate of 0.5 K/min. Five different concentrations varying between 1×10^{-3} and 4.1×10^{-4} M were applied, keeping the same host–guest concentration ratio at each individual run. The more diluted solutions show lower excess heat capacities at each temperature. Furthermore, the curves display that the excess heat capacity decreases with increasing the temperature for each solution. This is consistent with the theoretical expectations: the amount of complexes, dissociated during the temperature changes in a temperature unit, decreases by increasing the temperature (see Eqs. (2) and (5)). Accordingly, the measured excess heat capacity decreases with increasing temperature. Overall, this shape of the DSC curves shows that the dissociation process is fast related to the speed of the change of complex concentration, which is induced by the change of temperature at a given scanning rate. Consequently, the system is in quasi-equilibrium state at each temperature. Therefore, the change of the host–guest complex concentration

Table 1
Thermodynamic parameters of complexation of **1** with **2**

Method	K_s (25 °C) (dm^3/mol)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/K mol)
DSC	192.6	−5.3 (5)	−68.2 (3)	−185 (9)
PL	145.4	−4.9 (4)	−66.4 (5)	−181.3 (3)

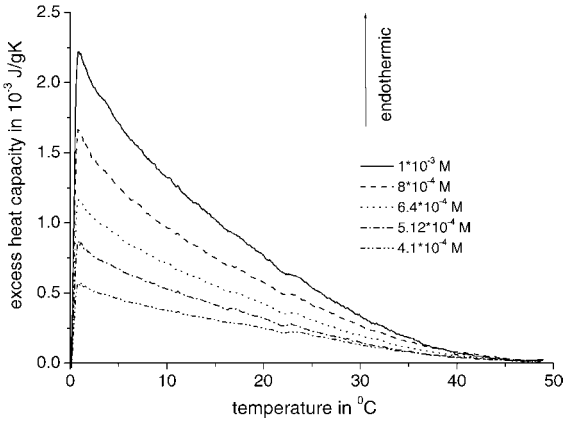

Fig. 6. Excess heat capacity of the equimolar solutions of **1** and **2** scanned with the rate of 0.5 K/min.

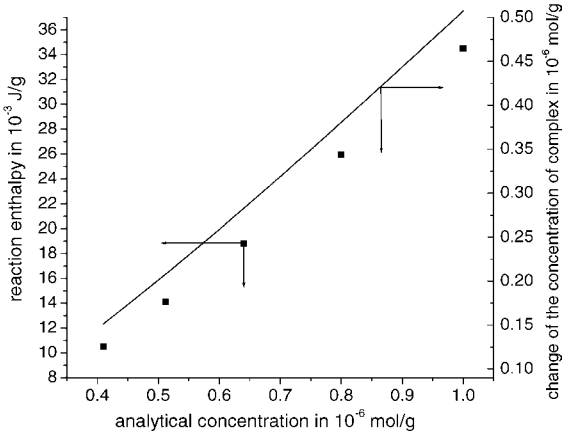

Fig. 7. The enthalpy change (■) of decomposition of the host–guest complexes (left axis) plotted against analytical concentration of equimolar solutions of **1** with **2**. The solid line shows the change of the concentration of the complex (right axis) while the temperature increases from 0 to 50 °C.

driven by the temperature change is reflected in the DSC curve.

The calculation of calorimetric enthalpies is based on the integration of the area under the excess heat capacity curve. The baseline for these calculations was generated using the software of the calorimeter: a polynomial baseline was generated by fitting it to the experimental baseline in the pre- and post-transition regions. Although this approximation of setting the baseline with a polynomial fitting was found to be widely used in such type of experiments, it is not free of an error, which is inversely proportional to the height to width ratio of the calorimetric peak. However, in our case this error was found below 0.5% of the total reaction enthalpy.

Fig. 7 shows the enthalpy changes of the dissociation plotted against the analytical concentration of equimolar solutions of **1** and **2**. The solid line shows the change of the complex concentration while the temperature increases from 0 to 50 °C. As it is well known, the concentration of a host–guest complex varies with the temperature as the complex stability constant is affected by the temperature during a DSC run. Therefore, we are unable to determine the concentration of the analyte and consequently, the thermodynamic parameters from a single DSC run.

However, using the expression of the stability constant K from the van't Hoff equation (Eq. (5)) the concentration of a 1:1 host–guest complex can be described as a function of the molar enthalpy, entropy change and of the temperature. The amount of the complex being dissociated while the temperature increases from 0 to 50 °C ($[HG]_{diss}$) can be expressed as the difference of concentrations of the complex at the two temperatures:

$$[HG]_{diss} = [HG(\Delta H, \Delta S, 0\,^{\circ}C)] - [HG(\Delta H, \Delta S, 50\,^{\circ}C)] \quad (6)$$

The reaction enthalpy measured by DSC is the product of the concentration of the complex dissociated and the molar enthalpy change of the reaction:

$$\begin{aligned}\Delta_R H &= \Delta H[HG]_{diss} \\ &= \Delta H\{[HG(\Delta H, \Delta S, 0\,^{\circ}C)] \\ &\quad -[HG(\Delta H, \Delta S, 50\,^{\circ}C)]\}\end{aligned} \quad (7)$$

After the measurements were carried out with five different, however equimolar concentrations of host and guest, iterative curve-fitting procedure by a variation of ΔH and ΔS was done for the experimental data plotted on Fig. 7. Table 1 summarizes the results determined by the procedure described above using the data of the DSC measurements. It has to be noted, that the enthalpy and entropy values in Table 1 are the averaged values over the temperature interval between 0 and 50 °C, where the complexation/decomplexation process is studied.

3.4. The stabilization energy of the inclusion complexes

The binding of *p*-nitrophenol **2** by calixarene **1** detected by PL and DSC studies, was examined by quantum-chemical method, too. The interaction energy between the host and the guest molecules was calculated by the procedure described earlier [15]. All energies were determined in the presence of solvent cage using TIP3P method [25,26], i.e. the solvation enthalpies of the interacting species were considered in this way. Only those conformations with the *p*-nitrophenol molecule located inside the calixarene cavity (i.e. interacts with calixarene from the side of the upper rim) were found

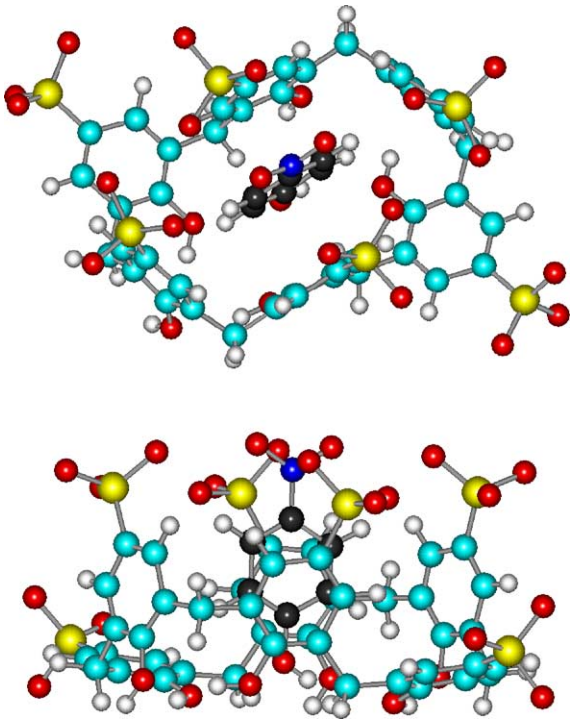

Fig. 8. Two views on the optimized structure of the inclusion complex of **1** with **2**.

stable. The stabilization energy of the complex was evaluated as the absolute value of the interaction energy, i.e. the difference between the total energy of the optimized structure of the complex and that of the separated host plus guest molecules. Fig. 8 shows the top and side view of the optimized structure of the host–guest complex. The stabilization energy was found to be 48.3 kJ/mol. This value can be compared with the enthalpy change of complexation since the entropy effect was not considered in the quantum chemical calculation. The ca. 30% deviation from the experimental value is probably due to the approximation used in the theory and also because this value is derived from the static calculation and relates to the temperature of 0 K.

4. Conclusion and summary

PL and DSC measurements have been successfully applied to study the inclusion complexation of calix[6]arene hexasulfonate with *p*-nitrophenol in aqueous solution. Both the PL and DSC signals indicate a 1:1 complex stoichiometry. The directly measured molar enthalpy of inclusion shows a strong interaction between the host and the guest. However, the entropy change during the complexation is a relatively high negative value, which decreases the Gibbs free enthalpy change of the reaction, thereby the complex stability. The highly exothermic complexation enthalpy parallel with the significant decrease of the entropy during complex formation reflects to the so-called enthalpy–entropy-compensation effect. It is probably due to the increased freedom of guest molecules relative to the host calixarenes and also due to the increased disorder of solvent molecules after the complex has been dissociated. Quantum-chemical investigation suggests that the *p*-nitrophenol guest resides in the calixarene cavity and the complex is stabilized by π–π interaction.

Acknowledgements

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