

Microcalorimetric titration of a tetra-*p*-sulphonated calix[4]arene with α,ω -alkyl diammonium ions in an aqueous solution

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Abstract

25,26,27,28-Tetrahydroxycalix[4]arene-5,11,17,23-tetrasulphonate was in a heat-conduction calorimeter titrated with α,ω -alkyl diammonium ions, $^+H_3N(CH_2)_nNH_3^+$ $n=(3-7)$, in an aqueous solution at pH 7.1. Apparent concentration binding constants (K_c) and enthalpy changes are reported for a 1 : 1 binding model at minimized concentration ranges. The standard Gibbs energy change, $\Delta G^0 = -RT \ln K_c$, has a non-linear dependence of the alkyl chain length, n . The interaction is strongest at $n \geq 5$. A similar trend is observed for the enthalpy change. However, the fit of the experimental data to the 1 : 1 model was quite poor and neither 1 : 2 nor 2 : 1 models gave any further improvement. Concentration-dependent results were also obtained. It is therefore concluded that the interaction observed is more complex. © 1998 Elsevier Science B.V.

Keywords: Alkyl ammonium ions; Aqueous solution; Calixarene; Calorimetric titration; Interaction model

1. Introduction

Calixarenes is a class of macrocyclic compounds of fundamental interest and growing technical importance in various areas. The calixarenes are cavity-shaped oligomers, built up from phenol units linked together via alkylidene groups to ring systems. Applications are found in catalysis, enzyme mimics, chemical analysis, ion sequestering, ion-selective electrodes, phase transfer, binding and separation of organic compounds, field effect transistors, accelerators for instant adhesives, stabilizers for organic polymers, attachment to polymers and pollutant extraction [1–5]. These compounds can be manufactured on

large scale from inexpensive starting materials, be easily chemically derivatized and provide for rational choice of ring size. Other important aspects of the calixarenes are high melting points, high thermal and chemical stability, low solubility, low toxicity and, with derivatization, optical activity [1–6]. Looking for new possibilities within this field, water-soluble calixarenes have recently been synthesized, mainly by Shinkai and co-workers [6,7] and Ungaro and co-workers [8].

We have earlier carried out a calorimetric titration study on 25,26,27,28-Tetrahydroxycalix[4]arene-5,11,17,23-tetrasulphonate (CATS), Fig. 1, and monoammonium ions, $H(CH_2)_nNH_3^+$, $n=(3-7)$ [9]. Other calorimetric studies on calixarenes, conducted by Danil de Namor and coworkers [10–13], involve binding to metal ions and the heat of solution in organic solvents. The protonation of CATS and its

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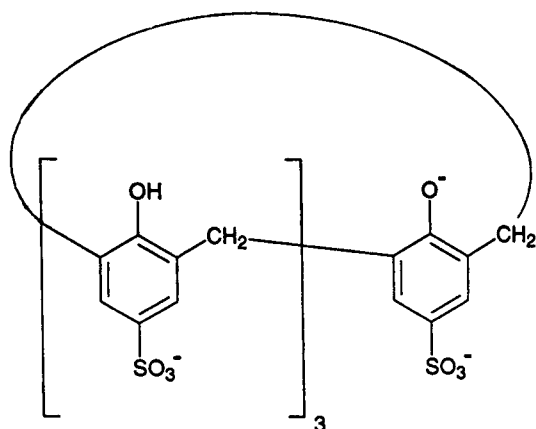


Fig. 1. 25,26,27,28-Tetrahydroxycalix[4]arene-5,11,17,23-tetrasulphonate (CATS). At pH 7.1, used in the present experiments, one hydroxyl group is deprotonated.

calix[6]analogue has also been calorimetrically studied by Arena et al. [14]. For reviews on microcalorimetric studies on calixarenes and other macrocyclic compounds (see Refs. [11,15]).

By use of NMR-techniques, equilibrium constants for the binding of CATS, its calix[6]- and calix[8]-analogue to the trimethylanilinium cation and the adamantyltrimethylammonium cation has been determined by Araki et al. [7]. A weak interaction of CATS and ethanol has also been studied by Arena et al. [16] using NMR measurements. Of particular interest to the present work, the binding constants for the interaction of a water-soluble polyphenolate, another anionic macrocyclic structure having similarities to CATS, and aliphatic ammonium ions, were as well determined by Schneider and co-workers, by an NMR technique [17,18]. In the present work, we report microcalorimetric results on the interactions among alkyl diammonium ions, $^+H_3N(CH_2)_nNH_3^+$, and CATS in an aqueous solution.

2. Experimental

25,26,27,28-Tetrahydroxycalix[4]arene-5,11,17,23-tetrasulphonate (CATS) of unspecified purity was purchased from Janssen. The sample batch was recrystallised four times from propanol–water mixtures and once from a methanol–water mixture, always using boiled reagent-grade water produced by a Milli-Q

filtration system (Millipore). The purified batch was equilibrated for several days over saturated $Ca(NO_3)_2$, providing for a relative humidity of 51% [19]. From Karl–Fischer titration (Metrohm Coulometer), the hydration state of CATS was found to be 8.79% taking into account the sample for solution preparation while weighing.

1,3-propanediamine and 1,4-butanediamine, both of 99% purity, or better, were purchased from Fluka, 1,5-Pentanediamine (98%) and 1,6-hexanediamine (of 99.5% purity or better) were received from Janssen and 1,7-heptanediamine (98%) was obtained from Sigma (the purities stated by the manufacturers). The samples were used as received. Disodiumhydrogenphosphate and sodiumdihydrogenphosphate were of puriss quality. The diamines were converted to diammonium ions by the addition of hydrochloric acid in stoichiometric amounts. The sulphonic acid groups of CATS were neutralized by 4 mol of sodium hydroxide per mole CATS. The diammonium ion solutions and the CATS solution were diluted by $0.00918 \text{ mol l}^{-1}$ phosphate buffer and pH was adjusted to 7.1 by disodiumhydrogenphosphate or sodiumdihydrogenphosphate of the same concentration. All the sulphonate groups and one of the four phenolic hydroxyl groups are at this pH deprotonated, according to the pK_a values of the hydroxyl groups ($pK_{a1}=3.26\pm 0.02$, $pK_{a2}=11.8\pm 0.3$, $pK_{a3}=12.8\pm 0.3$, $pK_{a4}=\text{ca. } 14$), as reported by Yoshida et al. [20] and Arena et al. ($pK_{a1}=3.34$, $pK_{a2}=11.5$) [21].

All solutions were prepared in boiled reagent-grade water, produced by a Milli-Q filtration system (Millipore).

The isothermal calorimetric experiments were carried out in a 1-ml stainless-steel titration vessel at the prototype of TAM (Thermometric AB, Sweden) [22].

The instrument was calibrated electrically by use of an insertion heater positioned in the calorimetric vessel (charged with water) and by dissolution of propan-1-ol in water [23]. The values, obtained by the two methods, for the calibration constant agreed within 0.5%. Titration of 18-crown-6 with $BaCl_2$ was used as a test process and agreed within the limits of error with the results earlier reported by Briggner and Wadsö ($K_c=5900\pm 200 \text{ l mol}^{-1}$, $\Delta H^0=-31.42\pm 0.20 \text{ kJ mol}^{-1}$) [23]. All measurements were performed at a stirring speed of 100 revolutions per min, using a gold propeller. Injections were made

stepwise at 3–12 min intervals and the calorimetric heat response was dynamically deconvoluted by employment of the instrumental time constant and computational routines earlier described [24,25].

An aliquot of 0.3 ml of 2.5 mmol l⁻¹ CATS was titrated with ten portions of 40 μl of 0.4 mmol l⁻¹ propyl diammonium ion. For $n=(4-7)$, 0.7 ml of 0.1 mmol l⁻¹ CATS was titrated with ten portions of 4–10 μl of 4 mmol l⁻¹ alkyl diammonium solution. In these experiments, three-to-five titration series were carried out at the temperatures 288.15, 298.15 and 308.15 K. For hexyl diammonium ion, titration of 0.9 ml 1 mmol l⁻¹ CATS with 14 portions of 5 μl 25 mmol l⁻¹ diammonium ion was carried out at 288.15 and 298.15 K. In a single experiment, 0.7 ml of 1 mmol l⁻¹ CATS was titrated with 14 portions of 23 μl of 4 mmol l⁻¹ pentyl diammonium ion at 288.15 K. It is not meaningful to carry out measurements at even lower concentration ranges, due to the sensitivity (noise-to-signal ratio) of the instrumental setup. For propyl diammonium ion, the measurements

could not be carried out at the lower concentration range (0.1 mmol l⁻¹ CATS), due to the low value of the equilibrium constant [26]. In all cases, the experimental data were corrected for heat of dilution of the titrand, obtained from separate and analogous dilution experiments.

Values for concentration equilibrium constants and enthalpy changes were calculated from non-linear regression analysis according to Marquardt [27], including an algorithm to eliminate linear parameters [28]. Models 1 : 1, 1 : 2 and 2 : 1 were tested. Each titration series was separately treated in the regression analysis.

3. Results

The results of the fitting of experimental data to a 1 : 1 binding model are summarized in Table 1 and in Figs. 2 and 3. The Gibbs energy change is largest (most negative) at $n=5$. It is also observed that the

Table 1

Apparent thermodynamic properties for the binding of 25,26,27,28-Tetrahydroxycalix[4]arene-5,11,17,23-tetrasulphonate (CATS) to α,ω -alkyldiammonium ions, $^+H_3N(CH_2)_nNH_3^+$, $n=(3-7)$, in dilute aqueous solution at pH 7.1, assuming a 1 : 1 model

n	T/K	Number of titrations	$K_c/(l\ mol^{-1})$	$\Delta H^0/(kJ\ mol^{-1})$	$G^0\ a/(kJ\ mol^{-1})$
3	288.15	4	$3.7 \times 10^3 \pm 2 \times 10^3$ ^b	-12.2 ± 2.2 ^b	-19.7 ± 1.9 ^b
	298.15	3	$8.0 \times 10^3 \pm 7 \times 10^2$ ^b	-10.2 ± 0.6 ^b	-22.3 ± 0.25 ^b
	308.15	4	$2.8 \times 10^3 \pm 3 \times 10^2$ ^b	-10.0 ± 0.6 ^b	-20.3 ± 0.25 ^b
4	288.15	3	$1.7 \times 10^4 \pm 1.1 \times 10^3$	-24.2 ± 0.6	-23.3 ± 0.3
	298.15	3	$3.3 \times 10^4 \pm 8.5 \times 10^3$	-20.5 ± 0.2	-25.8 ± 0.8
	308.15	3	$4.9 \times 10^4 \pm 1.2 \times 10^4$	-16.8 ± 1.1	-27.7 ± 0.9
5	288.15	5	$9.7 \times 10^4 \pm 3.7 \times 10^4$	-27.4 ± 1.8	-27.5 ± 1.1
		1	$(8 \times 10^4 \pm 5 \times 10^4)$ ^b	(-21 ± 1.2) ^b	(-27.0 ± 2.3) ^b
	298.15	3	$6.0 \times 10^4 \pm 8.5 \times 10^3$	-25.8 ± 0.9	-27.3 ± 0.4
	308.15	5	$1.1 \times 10^5 \pm 3.7 \times 10^4$	-26.7 ± 1.7	-29.7 ± 1
6	288.15	5	$8.4 \times 10^4 \pm 4.9 \times 10^4$	-25.3 ± 3.8	-27.2 ± 2.1
		3	$(8.7 \times 10^4 \pm 8 \times 10^4)$ ^b	(-23.5 ± 0.8) ^b	(-27 ± 6) ^b
	298.15	3	$4.5 \times 10^4 \pm 7.4 \times 10^3$	-28.7 ± 0.5	-26.6 ± 0.5
		8	$(1.6 \times 10^5 \pm 7 \times 10^4)$ ^b	(-20.9 ± 1.6) ^b	(-29.7 ± 1.4) ^b
	308.15	3	$4.5 \times 10^4 \pm 2.6 \times 10^3$	-29.7 ± 5.4	-27.4 ± 0.1
7	288.15	5	$4.1 \times 10^4 \pm 1.6 \times 10^4$	-31.4 ± 4.1	-25.4 ± 1.1
	298.15	3	$3.7 \times 10^4 \pm 1.3 \times 10^4$	-31.2 ± 1.8	-26.1 ± 1.1
	308.15	4	$4.6 \times 10^4 \pm 4.7 \times 10^3$	-24.5 ± 0.6	-27.5 ± 0.3

^a $\Delta G^0 = -RT \ln K_c/(l\ mol^{-1})$.

^b These results were obtained at elevated concentration ranges, cf. experimental.

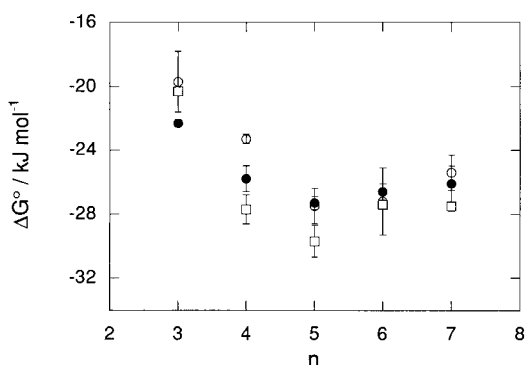


Fig. 2. ΔG^0 for the binding of CATS to alkyl diammonium ions, ${}^+\text{H}_3\text{N}(\text{CH}_2)_n\text{NH}_3^+$, versus alkyl chain length, n , at the temperatures 288.15 K (○), 298.15 K (●) and 308.15 K (□).

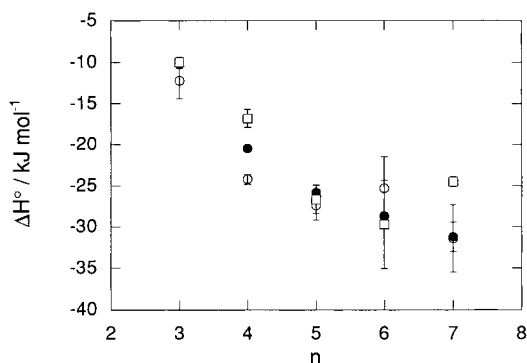


Fig. 3. ΔH^0 for the binding of CATS to alkyl diammonium ions, ${}^+\text{H}_3\text{N}(\text{CH}_2)_n\text{NH}_3^+$, versus alkyl chain length, n , at the temperatures 288.15 K (○), 298.15 K (●) and 308.15 K (□).

enthalpy change increases (become more negative) and tend to level-off at $n \geq 5$. The Gibbs free energy changes were calculated as $\Delta G^0 = -RT \ln K_c$. The uncertainties of K_c and ΔH^0 were obtained from the diagonal of the variance–covariance matrix of the regression analysis. The error in ΔS^0 was obtained from simple propagation of error calculations, being aware that ΔH^0 and ΔG^0 are statistically correlated. However, at all concentration ranges and temperatures studied, the residuals obtained have non-random and similar behavior, Fig. 4. For $n=(5, 6)$, the residuals at the higher concentration range, *cf. experimental*, were of the order of 0.5 mJ. For $n=3$ at the higher concentration range and for $n=(4-7)$ at the lower concentration range, the residuals were of the order of the standard deviation obtained in the electrical calibra-

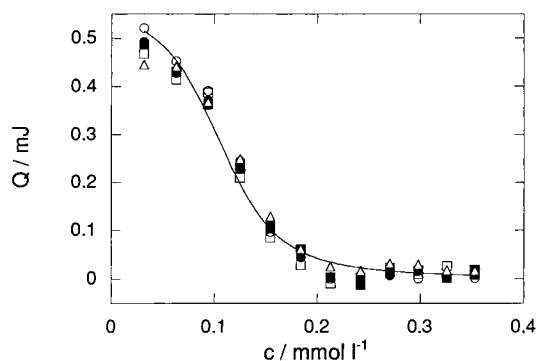


Fig. 4. A typical titration curve; the calorimetric response of the titration of 0.7 ml 0.1 mM CATS with pentyl diammonium ion at 288.15 K. Calorimetrically detected exothermal heat, Q , is plotted versus final concentration (after injection) of diammonium ion, c . The data are corrected for the heat of dilution of the diammonium ion, determined in separate experiments. The five different symbols indicating the data points refer to five different titration series and the regression line result from calculation on the five titration series taken together, by use of a 1 : 1 binding model. However, the data presented in Table 1 result from individual treatment of the titration series.

tion of the instrument, 10–50 μJ , or slightly larger. Further, the different values, in particular for hexyl diammonium ion at 298.15 K, for K_c and ΔH^0 , were obtained at different concentration ranges. No further improvement was obtained when using 1 : 2 or 2 : 1 binding models. Therefore, the results are reported as apparent properties, obtained when using the 1 : 1 model.

Table 2 and Figs. 5 and 6 present a comparison of the present results and the earlier study regarding the interactions of CATS and monoalkylammonium ions, $\text{H}(\text{CH}_2)_n\text{NH}_3^+$ [9]. In both studies, the data treatment was based on a 1 : 1 binding model. The difference in Gibbs energy change,

$$\Delta\Delta G^0 = \Delta G^0_{\text{diammonium ion}} - \Delta G^0_{\text{monoammonium ion}}$$
 become more negative for $3 < n < 5$ and levels off at $n \geq 5$. The same trend is observed for the corresponding property $\Delta\Delta H^0$.

4. Discussion

The residual patterns obtained for the 1 : 1, 1 : 2 and 2 : 1 models tested are possibly influenced by the fact that concentrations rather than activities are used in the data treatment. However, excellent fit was obtained

Table 2

Differences in apparent thermodynamic binding properties of CATS, $\Delta\Delta X^0 = \Delta X_{N2}^0 - \Delta X_{N1}^0$; $X=(G,H)$, in dilute aqueous solution at pH 7.1, assuming a 1 : 1 model. The indices N2 and N1 refer to diammonium ions, $^+H_3N(CH_2)_nNH_3^+$ and monoammonium ions [9], $H(CH_2)_nNH_3^+$, respectively, $n=(3-7)$

n	T/K	$\Delta\Delta H^0/(kJ\ mol^{-1})$	$\Delta\Delta G^0\ a/(kJ\ mol^{-1})$
3	288.15	4±2	3±2
	298.15	6.7±0.6	1.2±0.3
	308.15	7.6±0.6	3.1±0.2
4	288.15	-7.4±0.6	-0.8±0.3
	298.15	-2.6±0.2	-2.9±0.8
	308.15	2±1	-4.8±0.9
5	288.15	-9±2	-6±1
	298.15	-5.6±0.9	-5.6±0.4
	308.15	-6±2	-8±1
6	288.15	-7±4	-7±2
	298.15	-8.3±0.5	-6.0±0.5
	308.15	-8±5	-6.8±0.1
7	288.15	-14±4	-6±1
	298.15	-10±2	-7±1
	308.15	-1.8±0.6	-8.3±0.3

^a $\Delta G^0 = -RT \ln K_c/(l\ mol^{-1})$.

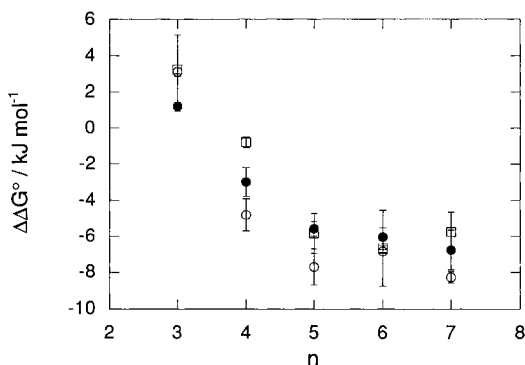


Fig. 5. $\Delta\Delta G^0 = \Delta G_{N2}^0 - \Delta G_{N1}^0$ for the binding of CATS to alkyl diammonium ions (N2), $^+H_3N(CH_2)_nNH_3^+$ and alkyl ammonium ions (N1), $H(CH_2)_nNH_3^+$ [9], versus alkyl chain length, n . The data refer to the temperatures 288.15 K (\square), 298.15 K (\bullet) and 308.15 K (\circ).

for the experimental data on the binding of CATS to the monoammonium ions [9], at experimental conditions identical to the higher concentration ranges used in the present study, when using a 1 : 1 binding model. The same purification batch of CATS was used for the monoammonium ions and in the present measure-

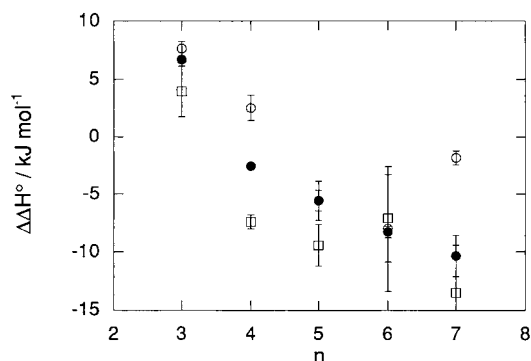


Fig. 6. $\Delta\Delta H^0 = \Delta H_{N2}^0 - \Delta H_{N1}^0$ for the binding of CATS to alkyl diammonium ions (N2), $^+H_3N(CH_2)_nNH_3^+$ and alkyl ammonium ions (N1), $H(CH_2)_nNH_3^+$ [9], versus alkyl chain length, n . The data refer to the temperatures 288.15 K (\square), 298.15 K (\bullet) and 308.15 K (\circ).

ments. For the monoammonium ions, the residuals between experimental data and the fitted function showed random behavior and were of the order of 45 μJ or less, corresponding to the standard deviation obtained in electrical calibrations of the microcalorimetric system employed. It is therefore believed that the interactions of CATS and the diammonium ions are more complex than as described by 1 : 1, 1 : 2 or 2 : 1 models. The bifunctionality of the diammonium ions may lead to higher ordered structures, in coexistence with the 1 : 1 complex. Another possibility is that more than one type of 1 : 1 complex is formed. Further, for each type of 1 : 1 complex, different conformations may exist and there would be distributions of values for the thermodynamic properties. These possibilities can hardly be taken into account. The statistical correlation among the fitting parameters would be large, leading to results suffering from poor precision. Many fitting parameters can also lead to deceptive results, since many types of data can be fitted to such models. Since large errors in the fitting parameters, K_c and ΔH^0 , were obtained, due to unsatisfactory fit to the model used, we do not find it meaningful to derive values for ΔS^0 or ΔC_p^0 .

However, assuming that the derived data are approximately correct for a particular 1 : 1 complex formed at low concentration, a few conclusions can be made. The non-linear chain-length dependencies of ΔG^0 and ΔH^0 suggest that the different alkane diammonium ions bind in different modes to the tunable CATS structure. In the study on the binding of CATS

to the alkane monoammonium ions [9], using a 1 : 1 model, strongly decreasing (less negative) values for ΔG^0 were obtained for increasing alkyl chain length. In contrast, for the alkane diammonium ions, the Gibbs energy change is increasing (become more negative) for increasing chain length and levels off at $n \geq 5$. It is also found that the diammonium ions bind stronger than the monoammonium ions at $n \geq 4$. Similar trends are obtained for the enthalpy changes, suggesting that the distance between the ammonium groups is suited for the distances between anionic groups of CATS, at $n \geq 5$. The 1 : 1 complex formation would be regarded as an ion exchange among the reactants and the counter ions. However, are the alkyl diammonium ions interacting mainly with the sulphate groups or are they (partially) included in the cavity? For the monoammonium ions [9], large and negative heat capacity changes, typical for dehydration of apolar surfaces, support the view of inclusion complex formation.

Further studies using calorimetric and other techniques, at different concentrations and pH, are needed for better understanding of the present results. The primary data of this work are available from this laboratory on request.

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