Unexplored metallic cation effect in the acidity constants of p-t-butylthiacalix[4]arene, p-t-butylcalix[4]arene and p-t-butylcalix[6]arene in aqueous-organic media

Guadalupe G. Miñambres, Márcio Lazzarotto & Alicia V. Veglia

View supplementary material ⧉

Published online: 15 Jun 2017.

Submit your article to this journal ⧉

View related articles ⧉

View Crossmark data ⧉

Taylor & Francis
Taylor & Francis Group

Check for updates

Unexplored metallic cation effect in the acidity constants of *p-t*-butylthiacalix[4]-arene, *p-t*-butylcalix[4]arene and *p-t*-butylcalix[6]arene in aqueous-organic media

Guadalupe G. Miñambres[a], Márcio Lazzarotto[b] and Alicia V. Veglia[a]

[a]Facultad de Ciencia Químicas, Departamento de Química Orgánica, Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), Universidad Nacional Córdoba, Ciudad Universitaria, Córdoba, Argentina; [b]Departamento de Química Orgánica, Instituto de Química, Universidad Federal de Rio Grande del Sur, Porto Alegre, Brasil

ABSTRACT

The influence of the metallic cation of the base (Li$^+$, Na$^+$ or K$^+$) was determined on the acid–base constants of *p-t*-butylthiacalix[4]arene (**TC4**), *p-t*-butylcalix[4]arene (**CA4**) and *p-t*-butylcalix[6]arene (**CA6**) in ethanol/water in an large interval of pH values by potentiometry and spectrophotometry. The pK$_a$ values determined by both methods correlate very well and these are characteristic for each macrocycle with influence of the cation of the base without a straight evidence of an effect by the size of the metallic cation. In the case of **TC4**, pK$_{a1}$ and pK$_{a2}$ were lower to Li$^+$ and Na$^+$ than with K$^+$. For **CA4**, an effect of K$^+$ on the pK$_{a2}$ with respect to Li$^+$ was observed. A very different behaviour was observed for **CA6** with Li$^+$ and K$^+$ showing a lower pK$_{a2}$ and a higher pK$_{a3}$ than with Na$^+$. These effects were interpreted on the basis of the interaction/complexation of each cation with each macrocycle.

Receptor

Metallic cation

X = CH$_2$, S, etc.
n = 4, 6, etc.

Cation-ionized macrocycle complex
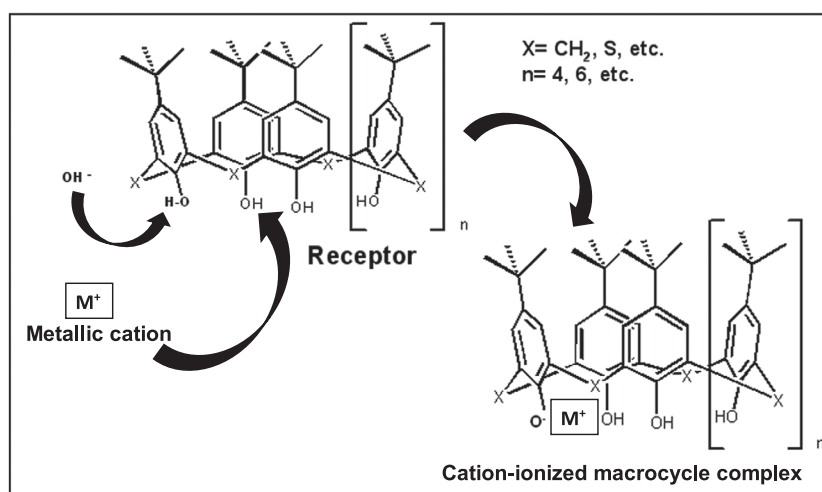
1. Introduction

In recent years molecular containers have attracted considerable attention owing to their potential application in catalysis, stabilisation of reactive intermediates, and binding, separation, and sensing of small molecules and ions (*1–3*).

Among them, a system of current interest is that formed by calix[n]arenes (**CAn**) as a result of their intrinsic shape, which makes them versatile receptors for neutral and charged molecules. The **CAn** are basket-shaped metacyclophanes synthesised first by condensation of *p*-alkyl-substituted phenols (*n* units) and formaldehyde in the presence of alkalis (*4,5*).

By other way, the thiacalix[n]arenes (**TCn**) are **CAn** where the methylene bridge has been replaced by Sulfur (S). In this case the S atom gives to the macrocycle (**TCn**) a

particular structure and electronic characteristics in comparison with the methylene group, showing different reactivity than their homologue **CAn** (*6,7*).

These macrocycles have a dual characteristic as receptors and polyprotic acid–base compounds (*8,9*). The solubility of these macrocycles depends highly of their substituents (*10*). The *p*-alkyl-phenol-macrocycles are slightly soluble in some organic solvents and practically insoluble in water (*11*). Experimental results in organic or organic mixture solvents are frequently used (*12,13*) but in aqueous–organic media (ethanol 95%) (*8*) have been scarcely reported because their poorer solubility and the impossibility of pH measures.

Water soluble derivatives have been synthesised (*14,15*) and their acid–base properties have been established as in the case of *p*-sulfonate-calix(n)arenes (*16*). The values reported indicate the dependence with the number of monomeric units and in all cases the first pK_a is lower than the corresponding phenol (pK_a ~10.0) by the formation of hydrogen bonds between the phenolate and the others phenols of the macrocycle.

In the Brönsted acid–base reactions, the nature of the counter-ion of the base used for the titration is not considered since it interacts with the solvent. But this is not probably the case with **CAn** and **TCn** since the complex formation with the counter ion could affect the stability of the system.

In order to explore experimentally this effect, in this work the polyprotic acid–base properties of *p-t*-butylthiacalix[4]arene (**TC4**), *p-t*-butylcalix[4]arene (**CA4**) (see below **TC4 y CA4** structure) and *p-t*-butylcalix[6]arene (**CA6**) in aqueous/organic media (ethanol/water 3/1 V/V) was explored together with the metallic cation effect on the acid–base constants (K_a) by potentiometry and spectrophotometry. This study makes it possible to establish the correct electronic characteristic of the macrocycle depending on the pH and the counter ion of the base employed, in order to deduce and interpret the favourable interactions with substrates of different electronic contents.
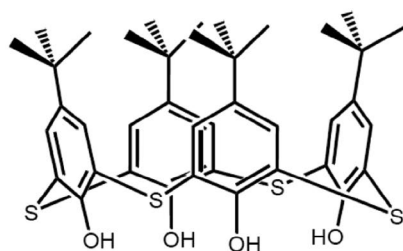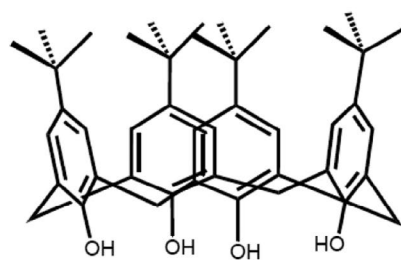
2. Experimental

2.1. Chemicals and Instruments

The water was obtained using a Millipore apparatus; ethanol was HPLC grade (Sintorgan); **CA4** and **CA6** (95% purity) (Aldrich) were used as received. **TC4** was synthesised in one pot as described in literature (*6*) and was recrystallised from chloroform and dried at 100 °C for four hours, the ESI mycroTOF-Q and ^{1}H NMR (Bruker 400 MHz) confirm the structure. The buffers used for the calibration of the pH meter, the basic and the acid solutions were prepared from commercial reagents of analytical grade. The concentrations of the concentrated basic and acid solutions were determined by potentiometric titration with primary standards (potassium biphthalate and $Na_2B_4O_7.10 H_2O$, respectively).

UV–vis spectrofluorimetric determinations were carried out on a Shimadzu UV-2101 PC or a Shimadzu UV-1800. The pH was measured using an Orion model 720 or an Orion 520 pH meter with a Ross combination pH electrode. The pH-meter was calibrated using standard buffers (pH 2.932; 4.955; 6.994 and 9.155) prepared according to literature (*17*). In all experiments the temperature was maintained at (25.0 ± 0.1) °C with a thermostatic bath.

2.2. General procedures

2.2.1. Solutions

Concentrated solutions (10 mg/5 mL) of **TC4** and **CA6** were done in chloroform and in dichloromethane for **CA4**, these solutions were stored in the refrigerator (4 °C) entrapped with aluminium foil. Stability of the stock solutions was periodically checked by spectrophotometry before preparing the appropriate dilute solutions for the determinations. The dilute solutions were prepared with no more than 1% of the concentrated solutions (chloroform or dichloromethane) in 3/1 V/V ethanol/water since this was the optimal ratio of ethanol/water supported for the high hydrophobicity of the macrocycles and the required stability of the pH meter measurements.
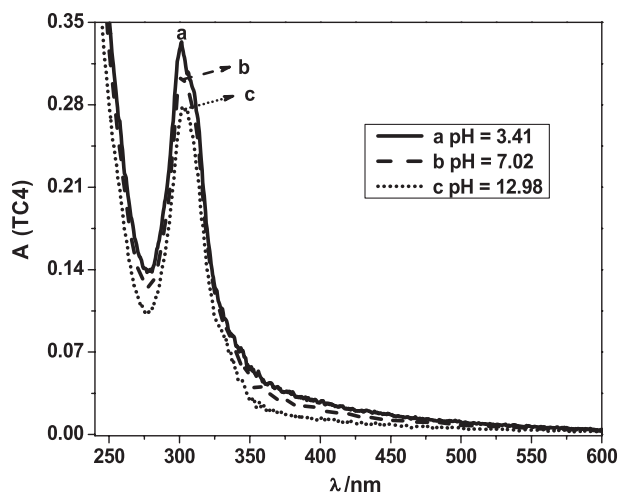

TC4 (n = 4)

CA4 (n=4)

Figure 1. UV–vis spectra of **TC4** = 2.3 µM (optical length = 4 cm) at different pH (a-3.41; b-7.02; c-12.98) in ethanol/water (3/1) and 25.0 °C.
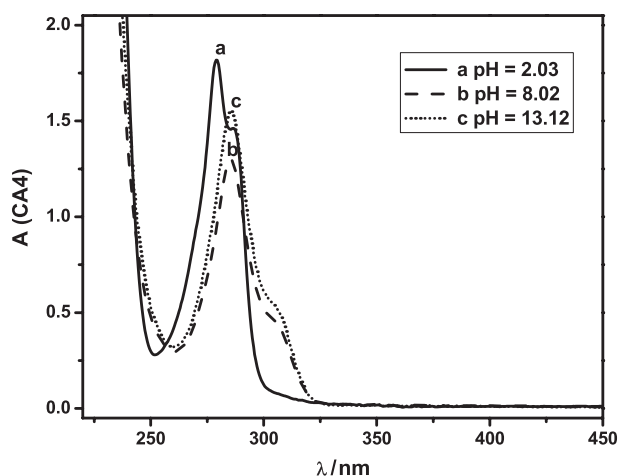

Figure 2. UV–vis spectra of **CA4** = 50 µM (optical length = 4 cm) at different pH (a-2.03; b-13.12; c-8.02) in ethanol/water (3/1) and 25.0 °C.
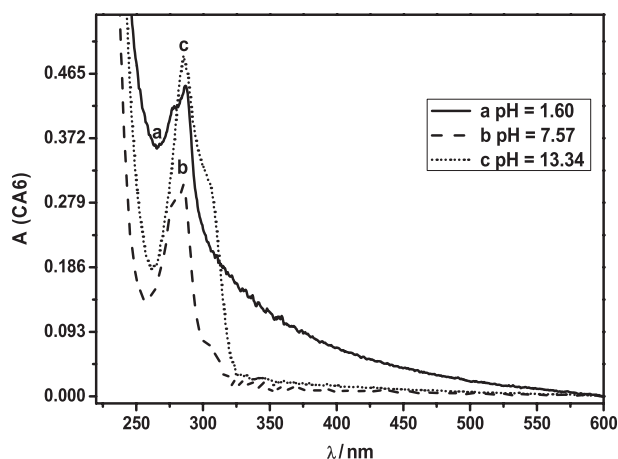

Figure 3. UV–vis spectra of **CA6** = 5.5 µM (optical length = 5 cm) at different pH (a-3.34; b-1.60; c-7.57) in ethanol/water (3/1) and 25.0 °C.

2.2.2. Potentiometric titrations

The potentiometric titrations were done from pH 2.00 to pH 12.00. Firstly the pH was changed from the nearly neutral pH of the solvent mixture (ethanol/water 3/1, pH 7.5–8.0) to pH 2.00 with small amounts of diluted HCl acid; then the pH was increased adding small volumes of the corresponding aqueous alkaline hydroxide (Li$^+$, Na$^+$ and K$^+$) of a known concentration previously determined in order to maintain the water percentage in the solvent mixture and the influence of the metallic cation in the complete interval. From the titration plots of pH vs hydroxide volume and the Equation (1) the potentiometric pK$_a$ values were calculated.

Final point Volume/2 = Volume corresponding to (pH = pK$_a$)

$$(1)$$

The pK$_a$ values and the influence of the cations (Li$^+$, Na$^+$ and K$^+$) were confirmed doing reversed titrations from pH 12.00 to acidic values with diluted HCl acid in each case. These results indicate that, in the experimental conditions used for this study, the variation of the concentration of the cation is not evidenced in the values of pKa obtained within experimental error. Also, the titrations of the initial solutions of the macrocycles in the solvent mixture (pH 7.5–8.0) with diluted HCl were performed.

2.2.3. Spectrophotometric titrations

The UV–vis spectra of the macrocycles were measured at different pH (acid, neutral and basic) in order to select the wavelengths (λ) where the differences in absorbance (A) between the protonated and deprotonated forms are higher. Quartz cells of reduced volume and masked black walls with different path length (1, 2, 4 or 5 cm) were used depending the A value.

Final solutions of 5.00 mL were done contained 20–50 µL of the concentrated solution of the macrocycle (final concentration 5.0–7.0 µM, final percentage of CHCl$_3$ or CH$_2$Cl$_2$ 1%); 20 µL of HCl of adequate concentration and variable volume of the hydroxide (10–100 µL) of the appropriate concentration; completing the volume with 3:1 ethanol: water. The temperature of the solutions was maintained at 25.0 °C for 20 min before taking the spectrum. After that the pH was measured at the same temperature. All the experiences were done by triplicate.

The plots of A at the selected λ were done at increasing pH from 2.00 to 12.00. The Equation (2) was used for fit the experimental K$_a$ values using Sigma Plot 10 or Origin 8.0 programs.

$$A_{pH} = [A_{lower} + A_{higher} \times 10^{(pH-pK_a)}] / [(10^{(pH-pK_a)}) + 1]$$

$$(2)$$

Table 1. Molar absorptivity coefficient (ε, M^{-1} cm^{-1}) for **TC4**, **CA4** and **CA6** in ethanol/water (3/1) at pH 6.00 and 25.0 °C.

TC4	$\varepsilon_{259\,nm} = 13{,}200$	$\varepsilon_{301\,nm} = 32{,}000$	$\varepsilon_{325\,nm} = 26{,}400$	$\varepsilon_{380\,nm} = 1000$
C4	$\varepsilon_{280\,nm} = 3800$	$\varepsilon_{290\,nm} = 3600$	$\varepsilon_{301\,nm} = 2000$	$\varepsilon_{325\,nm} = 1500$
CA6	$\varepsilon_{294\,nm} = 4800$	$\varepsilon_{298\,nm} = 2600$	$\varepsilon_{307\,nm} = 2000$	$\varepsilon_{321\,nm} = 1900$
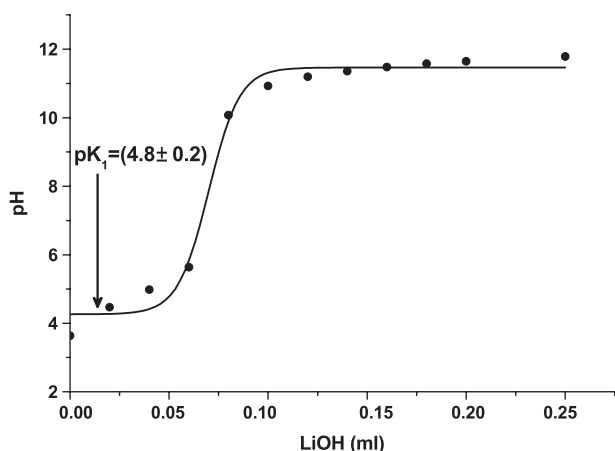
Figure 4. Potentiometric titration of **TC4** with LiOH in ethanol/water (3/1) and 25.0 °C. (The pK$_a$ informed in the plot is the average of at least three titrations (three similar plots).
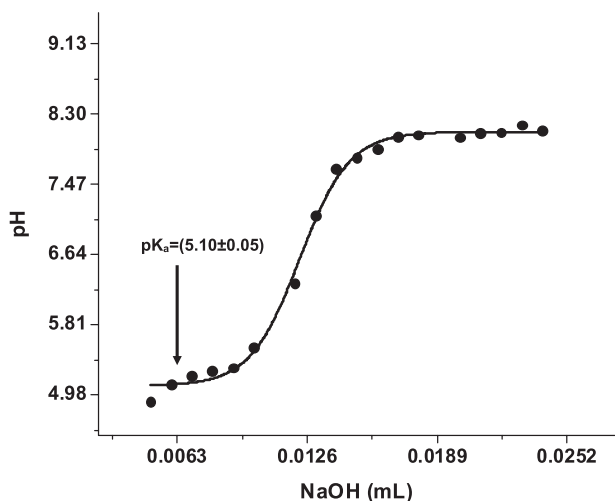
Figure 5. Potentiometric titration of **TC4** with NaOH in ethanol/water (3/1) and 25.0 °C. (The pK$_a$ informed in the plot is the average of at least three titrations (three similar plots).

3. Results and discussion

3.1. UV–vis Characteristic of the macrocycles

The changes on the spectra of **TC4**, **CA4** and **CA6** produced by the variation of the pH are shown in Figures 1–3 (these figures correspond to solutions prepared as described in 2.2.3 with HCl and NaOH and are representatives of the changes observed by the speciation of the macrocycle involved). As can be observed the spectra are characteristic for each macrocycle.

The spectra for **TC4** show little changes with the increasing of the pH, the absorbance at the maximum wavelength (301.0 nm) decreases and a weak shoulder at 325.0 nm appear.

In the case of **CA4** the maximum at 270.0 nm and the shoulder a 295.0 nm in acid media exhibits a bathochromic shift of 20 nm with a very clear difference of ratio in absorbance between then in basic media, also is evident the increase in absorbance at 290.0–315.0 nm at higher pH (see Figure 2 in basic media).

For **CA6** the wavelength of maximum absorption is 294.0 nm, showing the higher intensity at basic pH. A shoulder at 275.0 nm is observed in acid and neutral media, with a higher absorbance at acid pH. In very acid media (below pH 2.00) a tail at longer wavelengths could indicate scatter due to the incomplete solubilisation of the neutral macrocycle. In neutral and basic pH a shoulder at 300.0 nm is noticeable with higher intensity at basic media.

The molar absorptivity coefficients for the macrocycles at different λ at pH 6.00 and in the selected experimental conditions are presented in Table 1.

3.2. Potentiometric and Spectrophotometric titrations

Following the procedures described in the experimental section, the pH values were plotted vs the increasing volume of each base added (LiOH, NaOH and KOH) for each macrocycle (Figures 4–6 are representative for **TC4** with LiOH, NaOH and KOH; see Supplementary Information (SI) for the others systems). Mainly one or two pK$_a$ for each system with each base could be determined from the application of the Equation (1); these were named pK$_1$ and pK$_2$. The higher values of pK$_a$ were not clearly observed by this technique.

The spectrophotometric titrations were followed at different wavelengths in order to observe the better changes as shown for **CA6** in Figure 7 with NaOH (Figure 7 is representative, see Supplementary Information (SI) for examples with the others systems (Figure S7 for **TC4** with LiOH and Figure S8 for **CA4** with KOH. Similar behaviours (not shown) were found with the other systems). Some intervals of pH were amplified, doing the titrations with more diluted hydroxides in order to include more data for the determination of the corresponding pK$_a$ (Figure 8, for **CA6** with NaOH pH values from 6.00 to 11.00). In the case of **CA6** it was possible determined a third value of pKa (pK$_3$).

For the better comparison of the results, all the values of pK$_a$ from the two techniques are presented in Table 2. In the cases where it was possible determined a pK$_a$ by the two techniques the values were the same within experimental errors. In others cases, the magnitude of the changes
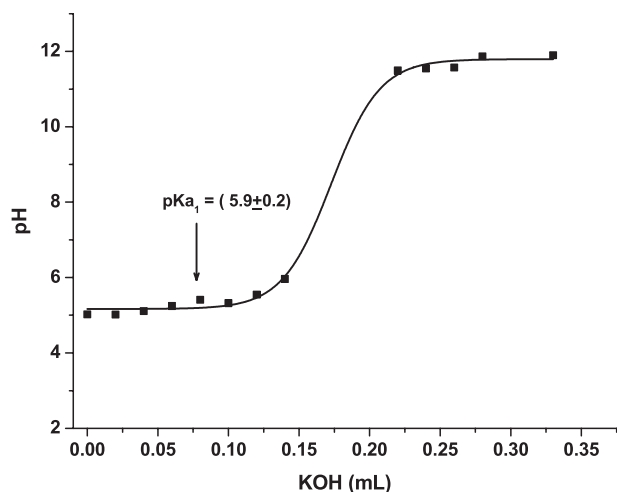
Figure 6. Potentiometric titration of **TC4** with KOH in ethanol/water (3/1) and 25.0 °C. (The pK$_a$ informed in the plot is the average of at least three titrations (three similar plots).
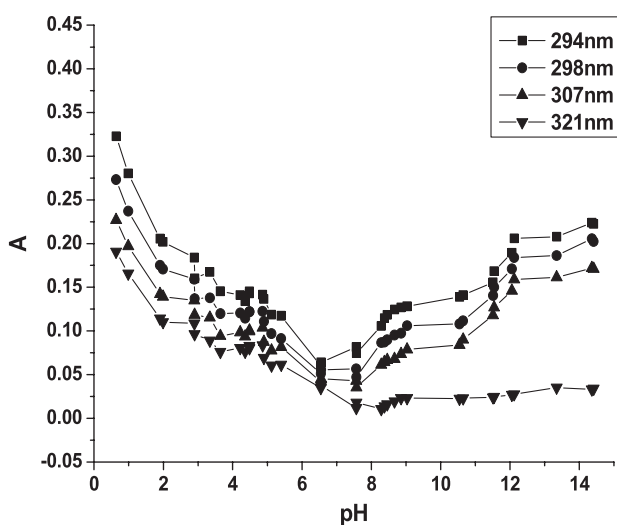

Figure 8. Amplification of the spectrophotometric titration of **CA6** with NaOH between pH 6.00–11.00 in ethanol/water (3/1) and 25.0 °C.

Figure 7. Spectrophotometric titration of **CA6** with NaOH in ethanol/water (3/1) and 25.0 °C.

in each method allowed the determination of a pK$_a$ from only one of them. Both techniques are complementary.

Although the analysis of the Table 2 indicates the dependence of the values of pK$_a$ of these macrocycles with the counter ion of the base (the metallic cation), there is not a straight correlation between the pK$_a$ values with the radius of the alkaline cations or their electronic characteristic, neither with the diameter or the number of units of the macrocycle.

For example in the case of **TC4** the pK$_1$ and pK$_2$ values for Li$^+$ and Na$^+$ are practically the same; but both of them are one unit higher for K$^+$. This was interpreted as the better interaction of the smaller ions with the narrow rim. For **CA4** a similar behaviour was observed in the value of pK$_2$ for Li$^+$ in comparison with the value obtained for K$^+$; but
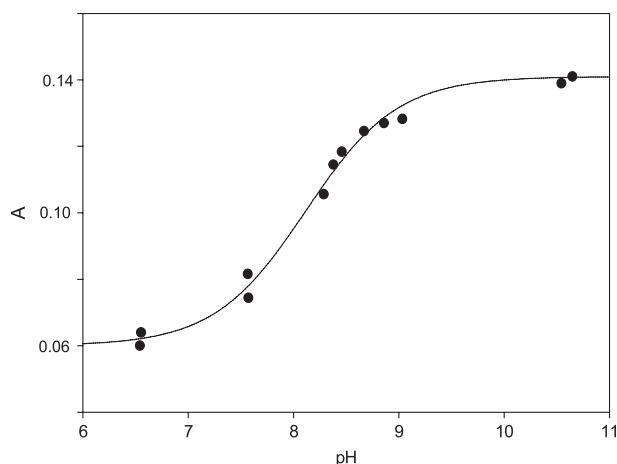
in this case the first pK$_a$ (pK$_1$) is the same, within experimental errors, for the three cations. The higher basicity of pK$_2$ for K$^+$ indicates a more effective interaction (stabilisation) between the mono-ionised **CA4** and this cation. In the case of **CA6**, the values of pK$_1$ are similar for the three cations but the pK$_2$ and the pK$_3$ values for Na$^+$ are higher and lower, respectively, than for Li$^+$ and K$^+$. The increases in basicity must be rationalised as an assistance of Na$^+$ in the stabilisation of the mono-ionised **CA6** (higher pK$_2$) and a similar effect for Li$^+$ and K$^+$ for the double-ionised **CA6** (higher pK$_3$).

Also it is possible some comparison between the three macrocycles. For example, the low acidity of **TC4** than **CA4** can be explained by the relative strength of hydrogen bonds in the stabilisation of the conjugated base, related to slight variations of the conformation of the calix. The sulfur bridge is longer than the methylene, and the consequence is an increase in the distance in the phenolic hydroxyls, as shown by the increase in stretch of the O–H bond in the infrared spectra and the lower chemical shift for hydroxyls in ^{1}H NMR (*18*).

The pK$_a$ values obtained by reverse experiments from neutral to acidic pH with HCl (assigned as pK$_1$ in Table 2) are 4.2, 3.9 and 4.9 for **TC4**, **CA4** and **CA6,** respectively. These values are slightly different to those determined in the complete titration from pH 2.00 with alkaline bases, confirming the influence of metallic cation of the base in the pK$_a$ values. We define the pK$_a$ values reported in this work by titration with alkaline bases as apparent values because they involve the proton transfer reaction from the macrocycle to the base and the complex formation of the macrocycle with the alkaline cation.

The differences in the pKa values may be also explained by the preferred approximation side of the cations to the macrocycles. The assistance and the complexation of the

Table 2. Potentiometric and Spectrophotometric pK$_a$ values for **TC4**, **CA4** and **CA6** in ethanol/water (3/1) and 25.0 °C. Influence of the metallic cation of the hydroxide.

Alkaline cation	a	TC4 P	TC4 S	CA4 P	CA4 S	CA6 P	CA6 S
Li⁺	1	4.8±0.2	4.8±0.5	2.3±0.1	2.3±0.1	2.5±0.1	2.4±0.1
	2	7.4±0.2	7.6±0.5		4.1±0.3	7.6±0.1	
	3						1 2.18±0.05
Na⁺	1	5.10±0.05		2.41±0.01	2.8±0.3	2.9±0.1	2.9±0.5
	2		7.35±0.08			8.3±0.5	8.35±0.07
	3						11.8±0.1
K⁺	1	5.9±0.2		2.56±0.08	2.5±0.3	3.3±0.2	2.8±0.2
	2		8.4±0.5		5.8±0.2	7.6±0.2	7.51±0.01
	3						12.37±0.04
HCl acid		4.2±0.6		3.9±0.3		4.9±0.2	

hard cations Li⁺ and Na⁺ for the narrow or endo rim that is the harder rim of the macrocycles (hard to hard effect). Meanwhile, the effects produced for the soft and polarisable K⁺ may be rationalised as an interaction or complexation by the wide or exo rim (soft to soft effect).

The values of the pK$_1$ are lower than for the monomer of them, *p*-terbutylphenol with pK$_a$ = 10.23 in water ([19]) and pK$_a$ = 11.25 in mixtures ethanol/water 60% ([20]), by the 'macrocycle effect' attributed to the stabilisation of the conjugated base by intramolecular hydrogen bonding as in the case of water soluble derivatives calixarenes and thiacalixarenes (nitro and sulfonate) ([21–24]). No further investigations were performed about the influence of the cation-calixarene complex formation in aqueous solution for these soluble derivatives of the macrocycles; or were interpreted as the possibility that Na⁺ and K⁺ form complexes or the same stability ([21]).

In the case of a water soluble nitro-**CA4** (one *t*-butyl group was replaced by nitro and two ones by methyl) at high concentration of alkaline hydroxides (0.5 M) an hypo and hypsochromic shift in the absorption spectra with Li⁺ than for Na⁺ and K⁺ was interpreted in terms of an a better interaction of the small cation with the calixarene anion ([22]).

The acidity in the pK$_1$ and pK$_2$ of water soluble sulfonate derivatives (*t*-butyl groups replaced by sulfonate) of **TC4** (2.18 and 8.45) compared to **CA4** (3.08 and 12.02), using NaOH as base ([23]) contrast with the results obtained in this paper for the *t*-butyl-homologues (**TC4** more basic than **CA4**). Also, the acidity in water of the nitro derivative (*t*-butyl groups replaced by nitro) of the **TC4** (2.74 and 6.48) ([24]) shows a similar value for the pK$_1$ and inclusive a lower pK$_2$ than the sulfonate-**TC4** ([23]). These results indicate the influence of the substituent (electron withdrawing, SO$_2^{-2}$ and NO$_2$; or electron donor, alkyl) on the *para* position to the hydroxyl group of the macrocycle in the stabilisation of the neutral and ionised specie ([5]).

Although the results presented in the present paper cannot provide further evidence for the conformations of the different acid–base specie formed, we consider previous literature data for it. The hydrogen bond network displays and important role for the conformational dynamics of calix[n]arenes, directing to the cone conformation for the monoanion of calix[4]arene ([25]) and 1,2,3-alternate for the dianion of calix[6]arenes ([26]). Solvents that act as hydrogen-bond acceptor disrupt the hydrogen bond array ([27]) and increase the mobility of the calix structure, whereas cations able to interact by cation-π directs for 1,3-alternated conformations of calix[4]arenes ([28,29]).

4. Conclusions

The acid–base constants for the polyprotic macrocycles **TC4**, **CA4** and **CA6** were determined in ethanol/water 3/1 by potentiometry and spectrophotometry with good agreement. The properties of these supramolecular systems in organic/aqueous media have been up to now scarcely investigated.

The influence of the metallic cations (Li⁺, Na⁺ or K⁺) of the base used for the deprotonation of the macrocycle was observed in the pK$_a$ values determined. There is not a straight correlation between the pK$_a$ values with the size or the electronic characteristic of the macrocycle or the cations.

These results were attributed as the influence of the complex formation between the macrocycle and each counter ion in stabilising the ionised receptor. The acid–base constants for the macrocycles reported in this work allow establishing their correct electronic species depending on the pH and the counter ion of the base employed, in order to interpret the interactions with substrates of different electronic characteristics in this media.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

References

(1) Zarra, S.; Wood, D.M.; Roberts, D.A.; Nitschke J.R. *Chem. Soc. Rev.* **2015**, *44*, 419–432.
(2) Rebilly, J.N.; Colasson, B.; Bistri, O.; Over, D.; Reinaud, O. *Chem. Soc. Rev.* **2015**, *44*, 467–489.
(3) Brinker, U.H.; Mieusset, J.L. *Molecular Encapsulation: Organic Reactions in Constrained Systems*; John Wiley & Sons Ltd: Chichester, 2010.
(4) Gutsche, D.C. *Calixarenes: An Introduction*, 2nd ed.; RSC, Cambridge, 2008.
(5) Sliwa, W.; Kozlowski, C. *Calixarenes and Resorcinarenes: Synthesis, Properties and Applications*; Wiley-VCH: Weinheim, 2009.
(6) Kumagai, H.; Hasegawa, M.; Miyanari, S.; Sugawa, Y.; Sato, Y.; Hori, T.; Ueda, S.; Kamiyama, H.; Miyano, S. *Tetrah. Lett.* **1997**, *38*, 3971–3972.
(7) Kumar, R.; Lee, Y.O.; Bhalla, V.; Kumar, M.; Kim, J.S. *Chem. Soc. Rev.* **2014**, *43*, 4824–4870.
(8) Miñambres, G.G.; Jaques, T.S.; Veglia, A.V.; Lazzarotto, M.; Nachtigall, F.F. *J. Incl. Phenom. Macrocycl. Chem.* **2015**, *81*, 311–319.
(9) Ghosh, I.; Nau, W.M. *Adv. Drug Deliver. Rev.* **2012**, *64*, 764–783.
(10) Davis, F.; Higson, S. *Macrocycles: Construction, Chemistry, and Nanotechnology Applications*; John Wiley & Sons Ltd: Chichester, 2011.
(11) Steed, J.W.; Atwood, J.L. *Supramolecular Chemistry*, 2nd ed.; John Wiley & Sons Ltd: Chichester, 2009.
(12) Bhalla, V.; Kumar, R.; Kumar, M.; Dhir, A. *Tetrahedron* **2007**, *63*, 11153–11159.
(13) Fontàs, C.; Anticó, E.; Vocanson, F.; Lamartine, R.; Seta, P. *Sep. Purif. Technol.* **2007**, *54*, 322–328.
(14) Agrawal, Y.K.; Pancholi, J.P. *Ind. J. Chem. Sec.* **2007**, *46A*, 1373–1382.
(15) Guo, D.S.; Liu, Y. *Acc. Chem. Res.* **2014**, *47*, 1925–1934.
(16) Scharff, J.P.; Mahjoubi, M.; Perrin, R. *New. J. Chem.* **1991**, *15*, 883–887.
(17) Strauts, C.R.N.; Gilfillan, J.H.; Wilson, H.N., Eds.; *Analytical Chemistry The working tools*; Oxford University Press: London, 1958; Vol. I, 228.
(18) Iki, N.; Kabuto, C.; Fukushima, T.; Kumagai, H.; Takeya, H.; Miyanari, S.; Miyashi, T.; Miyano, S. *Tetrahedron* **2000**, *56*, 1437–1443.
(19) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics, Internet Version 2005*; CRC Press: Boca Raton, FL, 2005. http://www.hbcpnetbase.com.
(20) Altun, Y.; Koseoglu, F. *J. Solution Chem.* **2013**, *42*, 1691–1705.
(21) Arena, G.; Cali, R.; Lombardo, G.G.; Rizzarelli, E.; Sciotto, C.; Ungaro, R.; Casnati, A. *Supramol. Chem.* **1992**, *1*, 19–24.
(22) Böhmer, V.; Schade, E.; Vogt, W. *Chem. Rapid. Commun.* **1984**, *5*, 221–224.
(23) Matsumiya, H.; Terazono, Y.; Iki, N.; Miyano, S. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1166–1172.
(24) Hu, X.; Zhu, Z.; Shen, T.; Shi, X.; Ren, J.; Sun, Q. *Can. J. Chem.* **2004**, *82*, 1266–1270.
(25) Nachtigall, F.F.; Vencato, I.; Lazzarotto, M.; Nome, F. *Acta Cryst.* **1998**, *C54*, 1007–1010.
(26) Ferreira, C.I.; Castellano, E.E.; Veglia, A.V. *J. Mol. Struct.* **1067**, *2014*, 88–93.
(27) Gutsche, C.D.; Bauer, L. *J. Am. Chem. Soc.* **1985**, *107*, 6052–6059.
(28) Assmus, R.; Harrowfield, J.M.; Ogden, M.I.; Richmond, W.R.; Skelton, B.W.; White, A.H.; Böhmer, V. *J. Chem. Soc. Dalton Trans.* **1993**, 2427–2433.
(29) Cuc, D.; Bouguet-Bonnet, S.; Morel-Desrosiers, N.; Morel, J.-P.; Mutzenhardt, P.; Canet, D. *J. Phys. Chem. B* **2009**, *113*, 3499–3503; Cuc, D.; Bouguet-Bonnet, S.; Morel-Desrosiers, N.; Morel, J.-P.; Mutzenhardt, P.; Canet, D. *J. Phys. Chem. B* **2009**, *113*, 10800–10807.