

Determination of the acid dissociation constants of the p-sulphonato-calix[4]arene

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Abstract

The acid dissociation constants of the hydroxyl groups in 25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetrasulphonic-calix[4]arene (SC₄) were determined at 25°C by a combination of potentiometric and spectrophotometric titration method. The first and second acid dissociation constants (pK_{a1}, pK_{a2}) were found to be 3.19 and 12.1, which demonstrated pK_a shift due to intramolecular hydrogen bonding interactions among hydroxyl groups in SC₄.

Keywords: p-sulfonatocalix[4]arene; acid-base properties ; acid dissociation constant

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1. Introduction

Calix[n]arenes are cyclic oligomers made up of phenol units linked by methylene. These compounds are considerably stronger acids than their monomeric phenolic counterparts, but the accurate measurement of their pK_a values has created some difficulties [1]. The acid dissociation of the phenolic OH groups in calixarenes, which induces the change of electron density in the aromatic π-system, plays one of the key roles in the inclusion process of guest molecules into the calixarene cavity. So the knowledge of the proton dissociation behavior of calixarene is indispensable to understand the chemistry of calixarene. So far, a few appeared literatures [2-5] have simply estimated the pK_a of several calixarene derivatives such as p-sulfonatocalix[4]arene and p-nitrocalix[4]arene with spectroscopic or potentiometric titration. Bohmer et al. [2] synthesized calixarenes containing a p-nitrophenol unit and estimated the pK_a by a spectroscopic method. They concluded that the p-nitrophenol unit in calix[4]arene shows nearly the same pK_a as in the acyclic analogues. Using both potentiometric and spectrophotometric methods, Reinhoudt and Shinkai [6] measured the pK_a values of calix[4]arenes carrying SO₂N(CH₂CH₂OH), or NO₂ groups in the p-positions. They compared these values with those of the analogous monomers and trimers. It is interesting to note that the pK_a values for the linear trimers fall between those of the calix[4]arenes and

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the monomers and, in the case of the *p*-nitro series, quite close to the former. Determination of the Calix[*n*]arenes are cyclic oligomers made up of phenol units linked by methylene. These compounds are considerably stronger acids than their monomeric phenolic counterparts, but the accurate measurement of their pK_a values has created some difficulties¹. The acid dissociation of the phenolic OH groups in calixarenes, which induces the change of electron density in the aromatic π -system, plays one of the key roles in the inclusion process of guest molecules into the calixarene cavity. So the knowledge of the proton dissociation behavior of calixarene is indispensable to understand the chemistry of calixarene. So far, a few appeared literatures [2-5] have simply estimated the pK_a of several calixarene derivatives such as *p*-sulfonatocalix[4]arene and *p*-nitrocalix[4]arene with spectroscopic or potentiometric titration. Bohmer et al. [2] synthesized calixarenes containing a *p*-nitrophenol unit and estimated the pK_a by a spectroscopic method. They concluded that the *p*-nitrophenol unit in calix[4]arene shows nearly the same pK_a as in the acyclic analogues. Using both potentiometric and spectrophotometric methods, Reinhoudt and Shinkai [6] measured the pK_a values of calix[4]arenes carrying $SO_2N(CH_2CH_2OH)$, or NO_2 groups in the *p*-positions. They compared these values with those of the analogous monomers and trimers. It is interesting to note that the pK_a values for the linear trimers fall between those of the calix[4]arenes and the monomers and, in the case of the *p*-nitro series, quite close to the former. Determination of the pK_a values for the water soluble *p*-sulfonatocalixarenes has been a particularly complicated problem because of the difficulty in distinguishing between the strongly acidic calixarene OH and SO_3H groups. For instance, the first and second pK_a values for the phenolic OH groups of *p*-sulfonatocalixarenes were reported to be 3.26 and 11.8, respectively, which significantly deviate from the pK_a value (8.9) of the corresponding monomer, *p*-hydroxybenzenesulfonate⁷. It has been established that the phenolic hydroxyl groups appended on the lower rim from strong intermolecular hydrogen bonds which serve as the main driving force for the stabilization of the cone conformation [8,9]. In this work we carried out the potentiometric and spectrophotometric titration of 25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetrasulphonic-calix[4]arene (SC_4) (Fig. 1) and succeeded to determine two first acidic dissociation constants of SC_4 .

2. Experimental

2.1. Chemicals

25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetrasulphonic-calix[4]arene (SC_4) was obtained from Acros Organics and used without further purification. The ionic strength was maintained on 0.1 mol dm^{-3} with sodium perchlorate. Sodium hydroxide from Merck was used. The pH of the solutions was adjusted with HCl 0.1 mol dm^{-3} and doubly distilled water was used throughout this study.

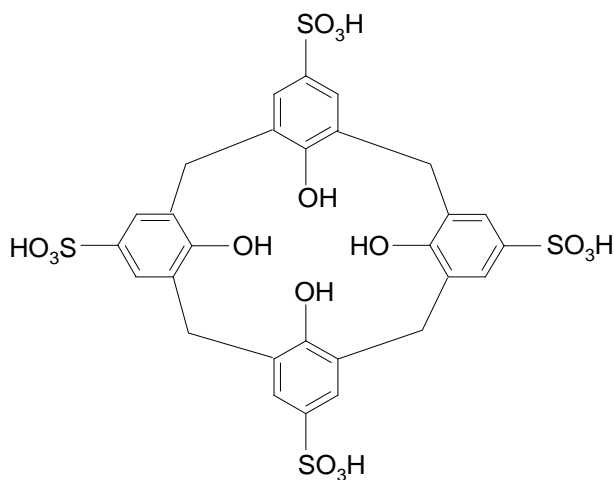


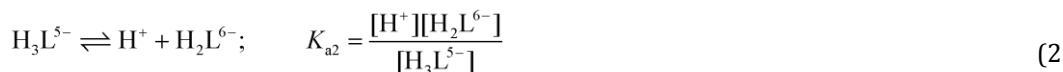
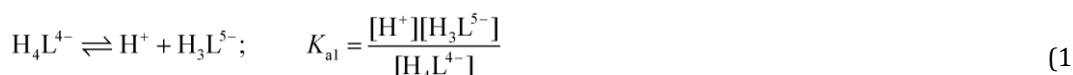
Fig. 1. The structure of *p*-sulphonato-calix[4]arene

2.2. Measurements

A Metrohm research pH-meter was used for the pH measurements. The hydrogen ion concentration was measured with a Metrohm combination electrode. The pH-meter was calibrated with Metrohm pH 4.0 and 7.0 buffers leading to pH estimate error of ± 0.001 pH units. Spectrophotometric measurements were performed using a UV-Vis Cecil-7200 spectrophotometer with a Pentium 4 computer using 10 mm quartz cells. The system was thermostated at 25 °C by circulating water from an isothermal bath. The ionic strength was maintained on 0.1 mol dm^{-3} with sodium perchlorate. The procedure is as follows: 30 cm^3 acidic solution of calixarene $0.0002 \text{ mol dm}^{-3}$ was titrated with NaOH solution 0.1 mol dm^{-3} both of the same ionic strength. The $-\log[\text{H}^+]$ and absorbance were measured after addition of few drops of titrant, and this procedure was extended up to the required $-\log[\text{H}^+]$. In all cases, the procedure was repeated at least three times.

3. Results and Discussion

p-sulphonato-calix[4]arenes have four phenolic OH groups within one molecule. Therefore, four-step acid dissociations of the phenolic OH groups will occur in aqueous solution. The first to fourth acid dissociation constants, $K_{a,n}$ ($n = 1-4$), are then defined by below equations, where L^{8-} denotes the completely deprotonated form of the calix[4]arene.



In order to evaluate the acidity of the SC_4 , a combination of potentiometric and spectrophotometric techniques was carried out under the conditions of 25 °C and $I = 0.1 \text{ M}$ with NaClO_4 , where I is the ionic strength of the solutions. The UV absorption spectra of the SC_4 at various pH conditions are shown in Fig. 2. The absorptivity over the entire wavelength region increased with the acid dissociations of the phenolic OH, as previously reported by Yoshida et al [7]. p-sulphonato-calix[4]arene has two absorption peaks at 276 and 284 nm in an acidic solution. The absorption peak at 276 nm first disappeared at acidic pH, and then the peak at 284 nm disappeared at basic region. Such changes in UV absorption are attributed to proton dissociation from the phenol groups.

The change in absorbance at 290 nm as a function of pH is given in Fig. 3. At $\text{pH} < 2$ the absorbance is small and constant. Then, an increase of absorbance is observed in the region $2 < \text{pH} < 5$ which shows that an acid dissociation takes place in an acidic solution. At $\text{pH} > 10$ the absorbance increases obviously with an increase in the pH. Therefore a second acid dissociation is likely to occur at this pH. Then the absorbance still increases, showing that the other acid dissociation take places near this region.

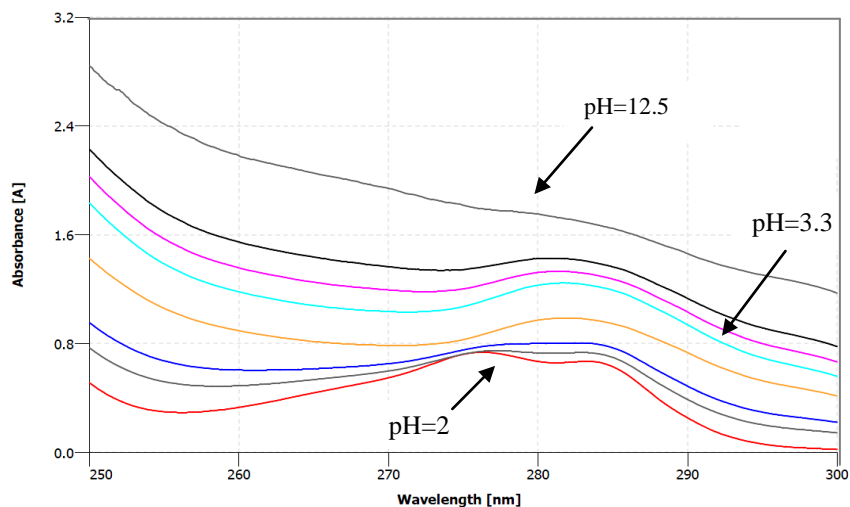


Fig. 2. UV absorption spectra of SC_4 as a function of the solution pH at $25^\circ C$ and $I = 0.1 \text{ mol dm}^{-3}$.

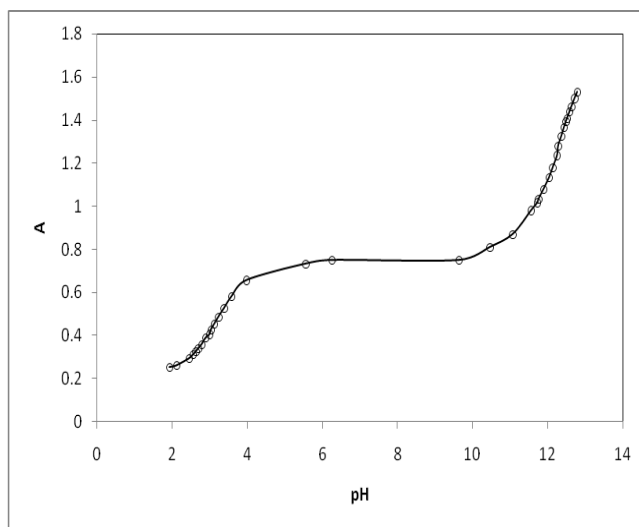


Fig. 3. Variation of the absorbance at 290 nm as a function of the pH at $25^\circ C$

Based on these results, the pK_a values of SC_4 were determined from the photometric titration data (for details, see the experimental section). The first and second pK_a values of SC_4 were calculated by computer program Squad [10]. Determination of the dissociation constant was employed using the method described before [11,12]. The obtained result revealed that the first pK_a values are far lower than the subsequent pK_a values (Table1). This indicates that the first acid dissociation of the phenolic OH groups occurs quite easily, whereas the further acid dissociations are strongly inhibited. These can be ascribed chiefly to the stabilization of the monophenolate species through the strong intramolecular hydrogen bonding between the phenolate O^- and OH groups, which are in turn stabilized by a hydrogen bonding with the fourth OH group, whereas the second acid dissociation occurs in a basic pH region. Computational studies by Grootenhuis et al. [8] also indicate that the hydrogen bonding effects still contribute to suppress the further acid dissociations although unfavourable intramolecular electrostatic repulsion seems to become the dominant factor with further acid dissociations. In this study we succeeded to determine two first acidic dissociation constants of SC_4 .

Table 1. pKa values determined for SC4 at 25°C and I = 0.1 mol dm⁻³(NaClO₄)

pK _{a1}	pK _{a2}	pK _{a3}	pK _{a4}	Ref
3.19	12.1	-	-	This work
3.26	11.3	12.8	14	7
3.34	11.5	-	-	5

4. Conclusion

The present study establishes that, as expected on the basis of previous reports [5,7], the dissociation of the first proton in calix[4]arene-sulphonated takes place at unusually low pH, whereas the remaining acid dissociation occur in a basic pH region. The remarkable differences between pK_{a1} and pK_{a2} is ascribed to the formation of strong intramolecular hydrogen bonds among phenolate O- and OH groups and the stability produced by that.

References

- [1] (a) Gutsche, C. D. Calixarenes: An Introduction; Royal Society of Chemistry: Cambridge, (2008); (b) Calixarenes 2001; Asfari, Z., Bohmer, V., Harrowfield, J., Vicens, J., Eds.; Kluwer Academic: Dordrecht, (2001)
- [2] V. Böhmer, E. Schade, W. Vogt, Makromol. Chem., Rapid Commun. 5 (1984) 221.
- [3] S. Shinkai, K. Araki, H. Koreoshi, T. Tsubaki, O. Manabe, Chem. Lett. (1986) 1351.
- [4] S. Shinkai, K. Araki, J. Shibata, D. Tsugawa, O. Manabe, Chem. Lett. (1989) 931.
- [5] G. Arena, R. Cali, G. G. Lombardo, E. Rizzarelli, D. Sciotto, R. Ungaro and A. Casnati, Supramol. Chem. (1992), 1, 19.
- [6] S. Shinkai, K. Araki, P. D. J. Grootenhuys and D. N. Reinhoudt, J. Chem. Soc. Perkin Trans.2 (1991), 1883.
- [7] I. Yoshida, N. Yamamoto, F. Sagara, D. Ishii, K. Ueno and S. Shinkai, *Bull. Chem. Soc. Jpn.*, (1992), 65, 1012.
- [8] P. D. J. Grootenhuys, P. A. Kollman, I. C. Groenen, D. N. Reinhoudt, G. J. van Hummel, F. Ugozzoli and G. D Andreetti, *J. Am. Chem. Soc.* (1990), 112, 4165.9
- [9] S. Shinkai, K. Araki, H. Koreishi, T. Tsubaki and O. Manabe, *Chem. Lett.*, (1986), 1351.
- [10] M. Meloun, M. Javůrek, J. Havel, *Talanta* 33 (1986) 513
- [11] F. Gharib, M. Shakarami, S. Taghvaei-Ganjali, *Acta Chim. Slov.* 55 (2008) 570.
- [12] F. Gharib, M. Hajmalek, R. A. Alamoti, A. Farajtabar, *J. Mol. Liq.* 159, (2011) 161