



# The difference between the aggregates of short-tailed and long-tailed cationic calix[4]arene in water as detected using fluorescein dyes



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## ABSTRACT

Water-soluble cationic calixarenes readily form aggregates in water. The properties of these aggregates, however, markedly vary along with alterations in the molecular structure. In a set of our recent studies, such aggregates were examined by various methods, and first of all using acid–base indicator dyes. The latter acted in fact as monoprotic acids exhibiting one color transition, and their  $pK_a$  shifts against the values in water were relatively close for different calixarenes. In the present paper, we report the behavior of a much more complicated dye, fluorescein, and two relative compounds, in aqueous solutions of two cationic calix[4]arenes. The last named possess four choline groups on the upper rim and the sole difference is the length of the alkoxy groups at the lower rim:  $O(CH_2)_2CH_3$  and  $O(CH_2)_7CH_3$ . In water, both calixarenes form aggregates of similar size and with similar zeta-potential. However, their influence on the acid–base and tautomeric equilibria of fluorescein clearly demonstrate that the aggregates of the long-tailed calixarene resemble the common micelles of colloidal surfactants to a higher degree than those of tetrapropoxy compound.

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## 1. Introduction

Along with other macrocyclic compounds, calixarenes are given much attention as they can selectively bind different ‘guests’ [1–4]. Calixarenes can be readily functionalized to obtain different recognition sites and, as a rule, are of low toxicity that causes them to be widely used in biochemical and biomedical research [5–9]. At that point of view, the state of water-soluble calixarenes in solutions, as well as their interactions with different molecules and ions, is of special interest.

Both anionic and cationic calixarenes are known to aggregate in aqueous solutions [4,9–21]. The colloidal particles are observed not only in the case of calixarenes bearing only hydrophobic moieties [14,19], but also for the more hydrophilic ones [12,16,20,21]. The aggregate formation was widely examined by electrical conductivity [4,15,17], surface tension [10,12,16], NMR [9,11,12,15,17], dynamic light scattering [10,14,16], transmission electron microscopy [14,16,19], fluorescent probes [10,20], and other methods.

The ability of diphilic calixarenes to form aggregates is known to depend on the size of their hydrophobic portion. For instance, it was demonstrated that the methyl-substituted tetramethylenesulfonated calix[4]resorcinarene is non-aggregated in water, whereas in aqueous solutions of its pentyl-substituted analog species with aggregation number around 20 have been registered [13]. The self-aggregation of sulfonated calix[4]arenes with alkyl chains in the lower rim in aqueous

solutions becomes more pronounced on going from tetrabutyl to tetraoctyl [18].

Previously, we reported the aggregate formation of cationic calixarenes in aqueous media [21–24]. The colloidal species resemble to some extent the common micelles of cationic surfactants; in particular, they readily bind various organic ions and molecules which are present in the solution. However, it is still unclear what peculiarities of the calixarene structure may provide the influence upon the bound (solubilized) species analogous to that of surfactant micelles.

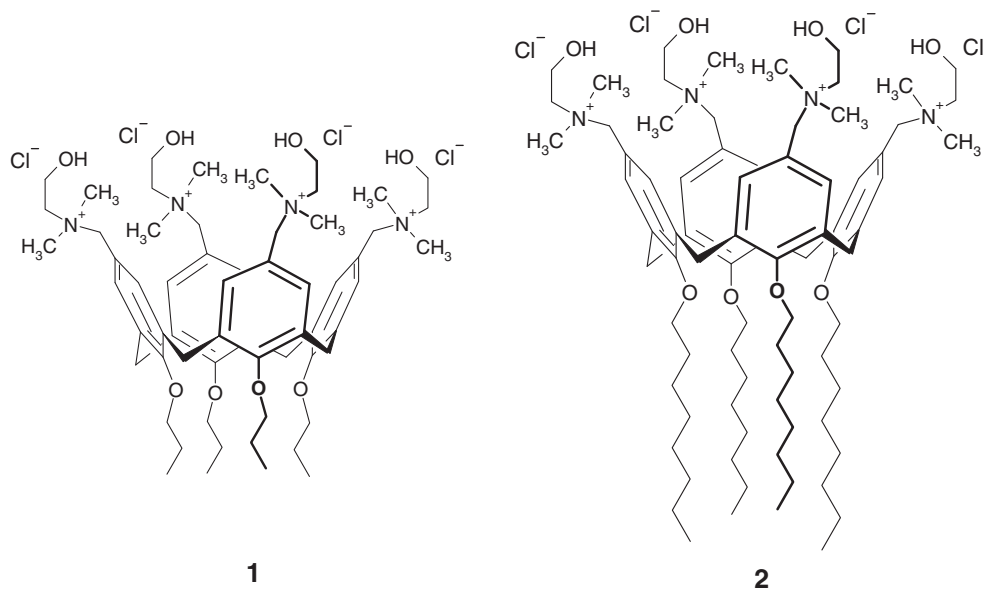
In order to shed light on this problem, it seemed to be worthwhile to perform a comparative study of two calixarenes bearing hydrocarbon tails of different lengths.

Recent studies demonstrated the possibility to examine the calixarene aggregates using acid–base indicator probes [13,21,22] analogous to the investigation of ‘traditional’ colloidal particles, such as surfactant micelles. The important parameter measured in such studies is the so-called ‘apparent’ ionization constant,  $K_a^a$ . It can be calculated from the ratio of the equilibrium concentrations of the conjugated indicator species, which is determined spectrophotometrically in the presence of colloidal particles, and pH of the bulk phase [23,24]. Up to now, only monoprotic indicator acids have been used in calixarene solutions for such purposes [21–24]. It was demonstrated that the size of the calixarene cavity does not influence strongly the properties of the indicators bound by the aggregates [21–24].

In the present study, we examined the peculiarities of aggregates of two tetrameric cationic calixarenes that bear propoxy and octyloxy groups at the lower rim (Scheme 1) and compared these aggregates to micelles of *N*-cetylpyridinium chloride.

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**Scheme 1.** Structures of calixarenes **1** and **2** (cone conformations).

As probes, fluorescein and related dyes, *n*-decylfluorescein and sulfonefluorescein, were chosen. The first named ionizes in a stepwise manner:



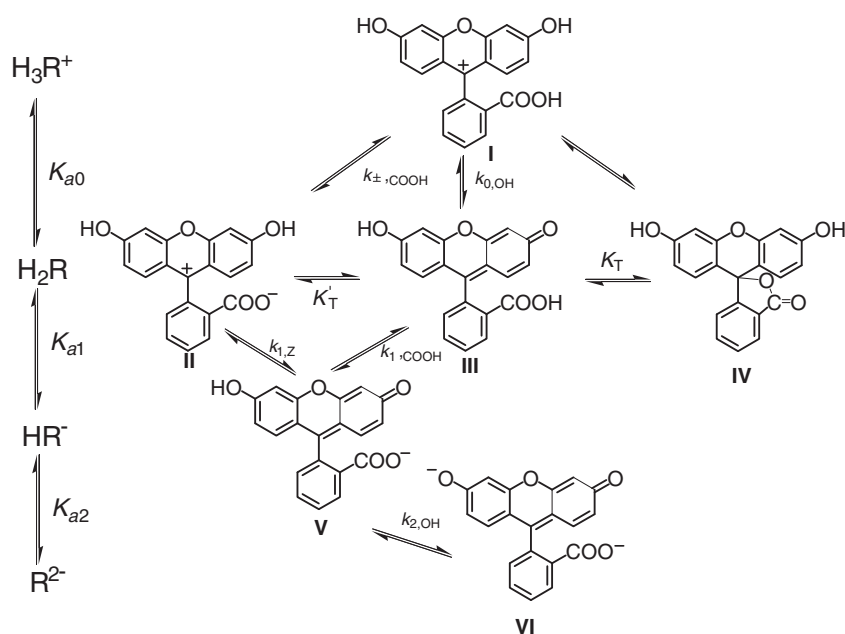
and undergoes tautomeric interconversion (Scheme 2), being sensitive to the nature of the dye microenvironment. For sulfonefluorescein, the equilibrium (1), which corresponds to the dissociation of the  $\text{SO}_3\text{H}$  group, is shifted toward strongly acidic media and, therefore, can

be excluded from consideration (Scheme 3). *n*-Decylfluorescein dissociates in two steps:



As *n*-decylfluorescein is poorly soluble in water, its transition to solution is solely due to its solubilization by colloidal particles. This makes it possible to investigate calixarenes under a condition that the dye is completely but non-covalently bound to calixarene aggregates within a wide pH range.

The equilibrium of fluorescein is much more complicated as compared with those of monoprotic indicator acids previously studied in calixarene solutions [21–24].



**Scheme 2.** Protolytic equilibrium of fluorescein.

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