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Effectual binding of gallic acid with p-sulfonatocalix[4]arene: An experimental and theoretical interpretation

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ABSTRACT

The host-guest interaction of gallic acid (GA) with p-sulfonatocalix[4]arene (p-SC4) is studied using emission and excited state lifetime techniques. The quenching effect on the emission intensity and excited state lifetime is observed upon binding. The impact of oxidation potential upon binding is studied using cyclic voltammetric technique. The structural features and the mode of binding of GA with p-SC4 is examined using ^{1}H NMR and rotating frame overhauser effect spectroscopy (ROESY) techniques. The binding of GA with p-SC4 has also been examined by means of density functional theory simulations. The calculated interaction energy of GA with p-SC4 (22.15 kcal/mol) indicates the strong binding nature.

1. Introduction

The host-guest chemistry has wide range of applications from molecular recognition, drug delivery to gas storage materials. Construction of supramolecular architectures involves different types of interactions like electrostatic, hydrophobic, van der Walls, π-π, cation-π and hydrogen bonding and depends on the nature of the guest molecules [1,2]. The calixarene chemistry is a well-established field with in the supramolecular chemistry [3,4]. These phenol interlinked molecules are represented as macrocycles with enormous opportunities for synthetic tuning due to the flexible methyl bridge and functional upper and lower rims [5,6]. The plausible functionalization at the upper and lower rims can be tuned to capture selective target molecules [7]. The introduction of acid groups such as p-sulfonato-, o-phosphonato-, o-alkylcarboxylato- groups makes calixarene platforms as water soluble so as to bind with a variety of biologically interesting molecules [8–10]. p-Sulfonatocalix[4]arene (p-SC4) is an important water soluble macrocyclic compound due to its facile synthesis and appropriate cavity size [11,12]. p-SC4 possess three-dimensional, flexible, π-electron rich cavity. The additional anchoring points provided by the sulfonato groups, endows strong binding affinities and recognition properties towards several guest molecules such as metal ions, organic cations, neutral organic molecules, dyes and bio-relevant molecules [13–20]. p-SC4 has been exploited as a carrier for numerous drug molecules, which exhibit low biological toxicity, good water solubility and also to improve the solubility of water insoluble drug molecules upon supramolecular complexation [21–25].

Gallic acid (GA) (3,4,5-trihydroxybenzoic acid) is an important class of aromatic phenolic acid that can be found in great abundance in the natural sources, especially in gallnuts, citrus fruits, cereals, green tea, berries, cherries, pomegranate, grapes, honey, red wine, and herbs [26–28]. GA is also obtained from bio-synthesis of shikimate pathway by the enzyme dihydroshikimate [27]. GA and its derivatives are used in pharmaceutical, tanning, ink dye, manufacturing of paper and food industries [29,30]. GA has wide range of biochemical properties, including antioxidant, anti-inflammatory, anti-microbial, anti-carcinogenic, anti-allergic, anti-artherogenic, scavenging of free radicals, and protection against cardiovascular diseases [31–34]. Both the pro-oxidant and the anti-oxidant properties of GA facilitates cytotoxic effect against several tumor cells such as lung cancer, breast cancer, intestinal cancer, gastric cancer, prostate cancer, cervical cancer, colon cancer and skin cancer [35–40]. The electron transfer characteristics of GA is responsible for all these biological properties, therefore the electron transfer properties of GA with enzyme models such as iron and ruthenium(II) complexes have been studied previously [26,41]. The inclusion of GA with α- and β- cyclodextrin has been studied previously by

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Rajendiran et. al.[42] In the present work, we report the inclusion of biologically important GA within p-SC4 using spectrofluorimetric, fluorescence lifetime, electrochemical and NMR techniques. To gain deeper insights into the intermolecular interaction between host and guest molecules, we performed density functional theory (DFT) simulations. The DFT calculations assist in understanding the nature and binding strength of the GA with p-SC4.

2. Experimental section

2.1. Materials

p-SC4 is synthesized by direct sulfonation of p-*tert*-butylcalix[4] arene using the literature procedure [25,43,44]. GA is procured from Avra synthesis Pvt. Ltd, Hyderabad, India. Millipore water is used as a solvent throughout the study.

2.2. Determination of binding constant from emission measurement

Fluorescence measurements are carried out using fluorescence Agilent spectrophotometer. Initially, the GA concentration is fixed at 1 $\times$ 10^{-5} M and the p-SC4 concentration is increased from 1 $\times$ 10^{-5} M to 9 $\times$ 10^{-5} M. The fluorescence intensity of GA is decreased upon addition of p-SC4. The binding constant value for this measurement is determined using modified Stern-Volmer equation [19].

$$\log[(F_0-F)/F] = n\log[H] + \log K_a \quad (1)$$

In Eq. (1), F_0 is the fluorescence intensity of GA in the absence of p-SC4, F is the fluorescence intensity of GA in the presence of p-SC4, [H] is the concentration of p-SC4, K_a is the binding constant value, n is the stoichiometric ratio of GA/p-SC4 complex. The binding ratio is determined using Job's plot method. The GA concentration is varied from 1 $\times$ 10^{-5} M to 9 $\times$ 10^{-5} M and the p-SC4 concentration is varied in the reverse order from 9 $\times$ 10^{-5} M to 1 $\times$ 10^{-5} M and the emission changes are recorded. The plot of mole fraction versus change in emission intensity gives the host-guest association for the GA with p-SC4. The quenching constant, k_q is calculated using the Stern-Volmer equation [19,45].

$$F_0/F = 1 + k_q\tau[H] \quad (2)$$

where τ is the excited state lifetime of GA.

2.3. Determination of free energy change

The free energy change, ΔG°, one of the thermodynamic functions, can be evaluated from the binding constant, K_a, values by Eq. (3).

$$\Delta G^\circ = -RT\ln K_a \quad (3)$$

In Eq. (3), ΔG° is the free energy change of the reaction, R is gas constant, T is temperature and K_a is binding constant value.

2.4. Lifetime measurement

The fluorescence lifetime of GA in the absence and in the presence of p-SC4 is recorded on HORIBA JOBIN-VYON data station using time-correlated single photon counting method (TCSPC). For this analysis, the 280 nm LED is the light source used to excite the molecule for the emission maxima of GA at 347 nm. For GA, the concentration is kept constant at 1$\times$ 10^{-4} M and the addition of varying concentration of p-SC4 is from 0.5 $\times$ 10^{-4} M to 2 $\times$ 10^{-4} M. The excited state fluorescence lifetime of GA alone and in the presence of p-SC4 were examined by plotting decay versus time using the recorded data.

2.5. Determination of binding constant from electrochemical study

The electrochemical behavior of GA and GA/p-SC4 sample solutions in aqueous medium is analyzed using cyclic voltammetry on a CHI604D electrochemical analyzer. The electrochemical cell consists of three electrode system. Glassy carbon (GC) as working electrode, silver-silver chloride as a reference electrode, and platinum as counter electrode respectively. The experiment is carried out with sample solutions without using any external electrolyte. The volume of p-SC4 is fixed at 10 ml of 10^{-3} M. The amount of GA is increased by means of incremental additions of 2 ml of 10^{-3} M of GA and vice versa. After the each 2 ml addition of host or guest, the resultant mixture was agitated for 2 min using magnetic stirrer. The binding constant value is determined using Benesi-Hildebrand equation [46,47].

$$(1/I_{HG})-I_G = 1/\Delta I + 1/K_a[GA]_0\Delta I[p-SC4]_0 \quad (4)$$

where I_G is the oxidation peak current of GA in the absence of p-SC4, I_{HG} is the oxidation peak current of the GA in the presence of p-SC4, and I_{HG} - I_G is the difference in the oxidation peak current of the GA/p-SC4 mixture and the GA alone, ΔI is the difference between the molar peak current coefficient of GA/p-SC4 complex mixture and the GA. $[GA]_0$ and $[p\text{-}SC4]_0$ are the initial concentrations of GA and p-SC4 respectively. The plot of $1/I_{HG}$ - I_G versus $1/[p\text{-}SC4]$ gives a straight line. We obtained the binding constant value from slope of the straight line. The ΔG° value is also calculated from the binding constant value K_a by using Eq. (3).

2.6. NMR technique

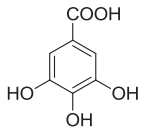
The binding of GA with p-SC4 is structurally investigated by NMR spectral titration using Bruker 500 MHz spectrometer. Deuterium oxide is used as solvent for ^{1}H NMR titration and for rotating frame nuclear Overhauser effect (ROESY) spectral techniques.

3. Results and discussion

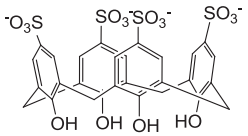
The formation of stable complex of GA with p-SC4 is studied by emission, excited state lifetime, cyclic voltammetry, NMR technique and computational studies. The chemical structures of GA and p-SC4 are shown in Chart 1.

3.1. Fluorescence measurement

The emission maximum of GA is around 352 nm upon excitation at 260 nm. The emission spectrum of GA is given in Fig. S1, whereas p-SC4 does not exhibit emission properties. Therefore the emission spectroscopy can be used to study the interaction between p-SC4 and GA. The concentration of GA is fixed and the concentration of p-SC4 is varied as described in the experimental section and the emission spectra recorded. The quenching of emission intensity is observed upon increasing the concentration of p-SC4. (Fig. 1) This observation is due to the binding of GA with p-SC4. The fluorescence quenching effect on guest upon complexation with p-SC4 follows the similar trend of



3,4,5-trihydroxybenzoic acid (or) Gallic acid (GA)



p-Sulfonatocalix[4]arene (p-SC4)

Chart 1. Structural illustration of p-sulfonatocalix[4]arene and gallic acid.