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A ^{1}H NMR study on the complexation of tetraalkylammonium cations, mono and diprotonated amines, and amino acids with a derivatized cyclotetrachromotropylene in an aqueous solution

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Abstract—The derivatized cyclotetrachromotropylene host forms complexes of 1:1 host to guest stoichiometry with tetraalkylammonium cations and amino acids whereas complexes of 1:2 host to guest stoichiometry are formed with mono and diprotonated amines in an aqueous solution. Both electrostatic and hydrophobic interactions are involved in the complexation.

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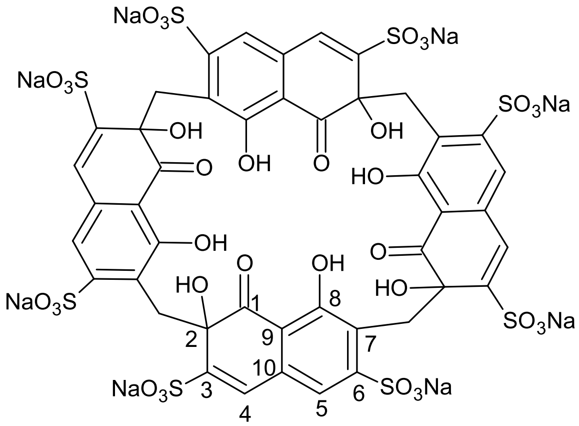
1. Introduction

The study of host–guest complexation in an aqueous medium is of great importance because it provides an understanding of the chemistry in the biological system. Organic cations as guests have received extensive attention[1–13] in the last decade, especially after the report that acetylcholine can be bound to acetylcholine esterase through interaction with aromatic residues present in the enzyme.[14] Several reviews on the complexation of organic cations have also been published.[15–19] Depending on the kind of host used, the non-covalent forces involved in the binding of the organic cations could be hydrogen bonding, π–π, CH–π, cation–π or cation–anion interactions. Until now only a few host molecules capable of binding organic cations in an aqueous medium have been reported and they are mainly from the sulfonatocalixarenes.

The water-soluble derivative of cyclotetrachromotropylene (**1**) that we have synthesized recently, appeared to be a good host for organic cations. It has a rigid shallow bowl structure with exposed π surfaces for hydrophobic interaction and eight adjacent sulfonic anions on the upper rim for electrostatic interaction (CPK molecular models shown in **1a–1c**). We were interested to gain an understanding of the interactions involved in the complexation of organic cations with **1**. This paper reports our study on the complexation of four tetraalkylammonium cations, four monoprotonated amines, three diprotonated amines and four amino acids with **1** in an aqueous medium at 25 °C using ^{1}H NMR spectroscopy.



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Keywords: Complexation; Stability constant; Tetraalkylammonium cations; Protonated amines; Amino acids; Derivatized cyclotetrachromotropylene.

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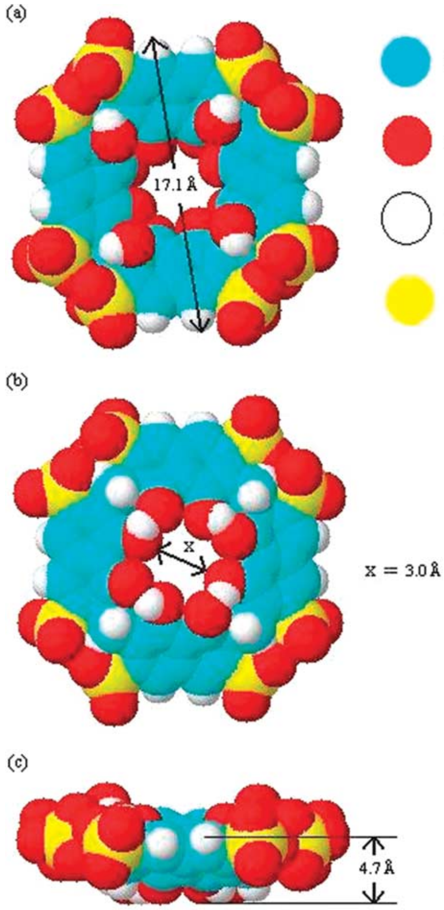
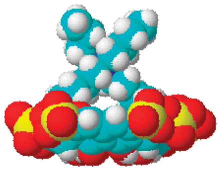


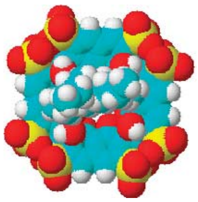
2. Results and discussion

2.1. Complexation of tetraalkylammonium cations

Four quaternary ammonium cations (tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium) were studied. Their proton chemical shifts in D_2O are shifted upfield and the resonance peaks broadened in the presence of **1** as shown in Figure 1, indicating that they are included in the cavity of **1**. All the proton chemical shift titration curves show two tangents meeting at a point where the molar ratio of host to guest is unity (Fig. 2), indicating that the complexes are of 1:1 host to guest stoichiometry. CPK molecular models of the complexes indicate that of the four alkyl chains of the spherical guest cations, at any given time two are pointing inside the host cavity and the other two pointing away from the cavity (see **2** for an illustration of the 1:1 complex of tetrabutylammonium cation and **1**). The average position of each guest proton determines the magnitude of the induced chemical shift change. For a short alkyl chain like ethyl, the induced chemical shift of H_1 is larger than that of H_2 (the subscript in H indicates the carbon bonded to the proton, the carbon atom attached to N is numbered 1). As the alkyl chain becomes longer, the differences in the induced chemical shifts of the various alkyl protons diminish (Table 1).



2 (Side view)



2 (Top view)

The stability constant K of each 1:1 host to guest complex was obtained by a non-linear regression fitting procedure.[20] A representative calculated titration curve together with the experimental chemical shifts is shown in Figure 3 for the tetramethylammonium cation. The K values obtained from different protons of the same tetraalkylammonium cation are in good agreement with one another (Table 1). The trend

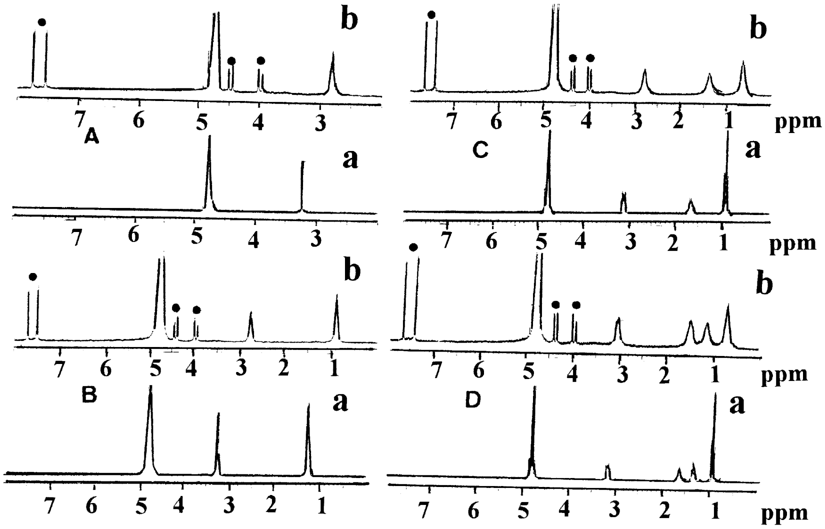


Figure 1. 400 MHz ^1H NMR spectra in D_2O at 25 °C of (A) 1.16×10^{-3} M of tetramethylammonium chloride: (a) no host; (b) in the presence of 1.23×10^{-3} M of **1**; (B) 1.17×10^{-3} M of tetraethylammonium chloride: (a) no host; (b) in the presence of 1.29×10^{-3} M of **1**; (C) 1.15×10^{-3} M of tetrapropylammonium bromide: (a) no host; (b) in the presence of 1.14×10^{-3} M of **1**; (D) 1.14×10^{-3} M of tetrabutylammonium iodide: (a) no host; (b) in the presence of 1.11×10^{-3} M of **1**. Solvent peak at 4.70 ppm used as internal reference. Peaks marked with ● are host peaks.