



Complexation study and spectrofluorometric determination of the binding constant for diquat and *p*-sulfonatocalix[4]arene

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ABSTRACT

The interactions between diquat (DQ) and *p*-sulfonatocalix[4]arene (C4S) were studied in an aqueous solution as a function of the ionic strength. Evidence for the formation of a complex between DQ and C4S was obtained using fluorescence measurements, while the stoichiometry of the complex was confirmed as 1:1 for DQ/C4S using UV–vis spectroscopy. The ionic strength had no influence on the stoichiometry of the complex, but exerted a significant influence on the complexation constant, K_c , decreasing with an increase in the ionic strength. The thermodynamic complexation constant, K_c' , was computed as $5.25 \pm 1.11 \times 10^7$ using the extended Debye–Hückel law. The rate constants for the heterogeneous electron transfer for the reduction of DQ at an electrode surface were evaluated as $0.150 \pm 0.010 \text{ cm s}^{-1}$ in the absence of C4S and $0.065 \pm 0.010 \text{ cm s}^{-1}$ when C4S was added to the solution in a 1:1 ratio.

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1. Introduction

Calix[*n*]arenes are macrocyclic compounds synthesised from the condensation of phenol with formaldehyde.¹ *p*-Sulfonatocalix[*n*]arenes (Fig. 1(a)), *p*-sulfonatocalix[4]arene, C4S) are an important class of calix[*n*]arene, which are water soluble and have the ability to bind with a wide range of metal cations, organic ammonium cations and neutral organic molecules.^{2,3} This diverse supramolecular chemistry has led to their application in several fields including pharmaceutical chemistry,⁴ catalysis⁵ and sensors.⁶ The ability of *p*-sulfonatocalix[*n*]arenes to bind with viologens was first reported by Kaifer et al.⁷ More recently, it has been shown that the strong electrostatic interaction of the cationic viologen with the anionic calix[*n*]arene can be enhanced by the π – π interactions

between the host cavity and the guest molecule.⁸ Viologens are an important class of redox active compounds and the formation of supramolecular architectures, based on the complexation of *p*-sulfonatocalix[*n*]arenes with viologens, has been investigated in the literature.^{9–14} Moreover, viologens are commonly used as herbicides and are potentially fatal to human health.¹⁵ Interestingly, a number of recent studies^{16,17} have investigated the potential of employing the complexation of *p*-sulfonatocalix[4]arenes with viologens as a therapeutic agent for methylviologen poisoning. The likelihood of medicinal applications of *p*-sulfonatocalix[4]arenes has increased as preliminary studies would indicate that C4S has a low toxicity.^{18–20}

Diquat (DQ), Fig. 1(b), is a generally used herbicide, which is also toxic to humans.²¹ Work by Wang et al.¹⁷ have shown that DQ forms an inclusion complex with C4S. The complexation constants, determined using isothermal calorimetry, were $5.40 \times 10^5 \text{ M}^{-1}$ and $7.95 \times 10^5 \text{ M}^{-1}$ at pH 2.0 and 7.2, respectively.¹⁷ In addition, from the magnitude of the shift changes in the ¹H NMR signals of DQ upon complexation, it was reported that DQ binds with C4S in a sloping orientation. However, no study on the role and influence of ionic strength on the complexation was carried out. It is well recognised that host–guest complexation based on electrostatic interactions will decrease by increasing the ionic strength of the surrounding solution.²²

In this paper the influence of ionic strength on the interaction of C4S with diquat (1,1'-ethylene-2,2'-bipyridinium) is assessed. The thermodynamic constant (K_c') for the complexation of diquat by *p*-sulfonatocalix[4]arene was determined using the extended Debye–Hückel equation. In addition, the reduction of diquat to its

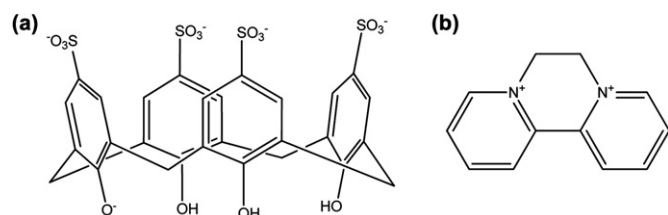


Fig. 1. (a) *p*-Sulfonatocalix[4]arene (C4S), which exists in the pentaionic form at pH 6.7 and (b) diquat (DQ).

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radical cation was investigated in the presence and absence of the C4S. This study is important as it is known that the formation of the radical cation is an important intermediate in the biochemical mechanism of viologen toxicity.²³

2. Results and discussion

2.1. Stoichiometry of the DQ·C4S complex in solutions of low and high ionic strength

The work by Wang et al.¹⁷ showed that the stoichiometry of the DQ·C4S complex was 1:1 at an ionic strength of 0.17 M at a pH of 7.2. In the present study, the stoichiometry between DQ and C4S (Fig. 1) was evaluated using the continuous variation method²⁴ at two ionic strengths of $I=4.24\times 10^{-3}$ and $I=0.30$ M. The ionic strength was maintained constant by the addition of Na_2SO_4 . Fig. 2(a) and (b)

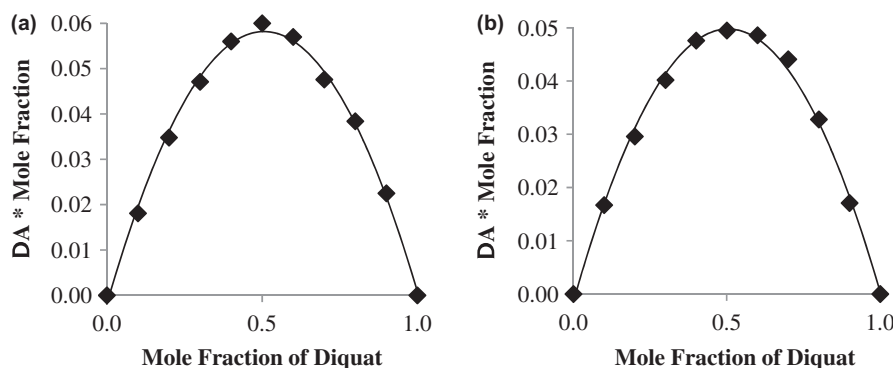


Fig. 2. Job's Plot of DQ and C4S carried out using UV–vis spectroscopy at an ionic strength of (a) 4.24×10^{-3} M and (b) 0.30 M, which was maintained constant using Na_2SO_4 . The pH for these solutions was 6.7.

shows the bell-shaped curves constructed from the data obtained using UV–vis spectroscopy. It is evident from both Fig. 2(a) and (b) that the maximum of each curve is centred at 0.5, indicating the formation of a 1:1 complex in both solutions, with the ionic strength having little or no influence on the stoichiometry of the complex.

2.2. ^1H NMR investigation of the interaction of DQ with C4S

^1H NMR spectra were recorded at a fixed concentration of DQ (4.86×10^{-3} M) in a KCl solution ($I=0.1$ M) of D_2O as a function of adding C4S up to a mole ratio of DQ/C4S of 1:5 and these data are presented in Fig. 3. As previously reported by Wang et al.,¹⁷ upon addition of the C4S there was a strikingly large upfield shift in the signals for the protons on the heterocyclic rings. For example, the signal for H_c shifted from 8.87 to 6.88 ppm. On the basis of the observed changes in chemical shifts, Wang et al.¹⁷ proposed that the geometry of the DQ·C4S complex is as shown in Fig. 4. The partial inclusion is consistent with the observation that the free and bound DQ undergoes fast exchange on the NMR timescale as only one resonance signal was observed for each of the equivalent protons in all the spectra recorded. It is likely that these large shifts were predominantly due to the close proximity of the protons on

the DQ molecule with the anionic sulfonate groups on the C4S. In addition, the interaction of the guest protons with the ring current of the aromatic nuclei of the host may also have contributed to the shift changes. A further striking observation from the spectra shown in Fig. 3 was the significant broadening of the proton signals

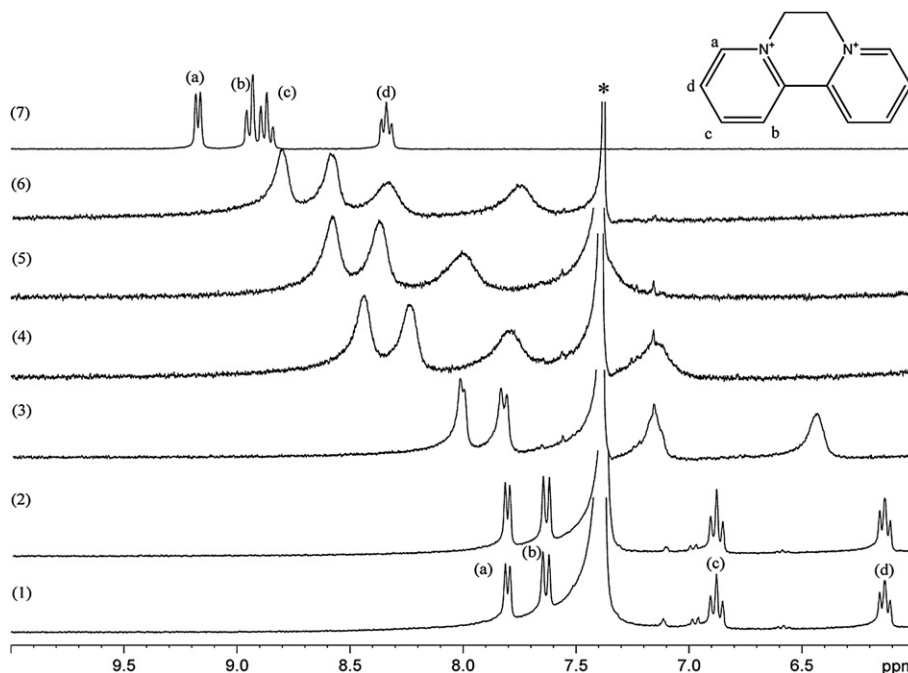


Fig. 3. ^1H NMR spectra of 4.86×10^{-3} M DQ with the following equivalents of C4S: (1) 5.00, (2) 3.10, (3) 1.00, (4) 0.63, (5) 0.50, (6) 0.31 and (7) 0.00. All solutions were prepared in D_2O and the ionic strength of all solutions was maintained constant at 0.10 M using KCl. The pH of these solutions was 6.5. The titration was carried out at 25 °C. The peak at 7.40 ppm arises from the aromatic hydrogen atoms on the *p*-sulfanocalix[4]arene.

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