



Complexation of Paraquat Dication with Disodium 1,8-Disulfonato-3,4,5,6-Acridinetetracarboxylic Acid in Water

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Abstract. Disodium 1,8-disulfonato-3,4,5,6-acridinetetracarboxylic acid forms a complex of 1 : 1 stoichiometry with paraquat dication in water. The stability constant of the complex is $1.2 \times 10^4 \text{ M}^{-1}$ at 25 °C.

Key words: stability constant, paraquat dication, complexation, electrostatic interaction, π - π interaction.

1. Introduction

The paraquat dication (**1**), because of its electron relaying efficiency, is a very potent herbicide and a popular choice as an electron relay in the study of photochemically produced solar energy. The possibility of improving the electron relaying efficiency of paraquat dication by complexing it within a host molecule has attracted the attention of some researchers [1–4]. These studies have revealed that a good host is one that can provide strong electrostatic interactions with paraquat dication. Since disodium 1,8-disulfonato-3,4,5,6-acridinetetracarboxylic acid (**2**) appears to be a potential host (its dimeric form in an aqueous solution encloses a hydrophobic cavity [5, 6] and the negative charges of the sulfonic groups can provide electrostatic interactions with the paraquat dication), we undertook to study its complexation with **1** in water, using proton NMR and ultraviolet (UV) spectroscopic methods. This paper reports our results.

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2. Experimental

2.1. MATERIALS

Compound **1** was a commercial sample and compound **2** was prepared as reported earlier [7].

2.2. PROTON NMR SPECTRA

Proton NMR spectra in D₂O at 25 °C were recorded with a 300 MHz Bruker AC300 Superconducting NMR spectrometer. The solvent peak (unaffected by the concentration variation of **1** and **2**) at 4.80 ppm was used as the internal reference. Proton NMR titrations were carried out by varying the concentration of **2** for a fixed concentration of **1** (5.72×10^{-4} M) as well as by varying the concentration of **1** for a fixed concentration of **2** (1.34×10^{-3} M).

2.3. ULTRAVIOLET SPECTRA

Ultraviolet spectra of **2** in water (8.78×10^{-5} M) in the presence of various concentrations of **1** were recorded with a Hitachi U-2000 spectrophotometer.

2.4. STABILITY CONSTANT K

Calculations of the stability constant K of the 1 : 1 complex using the nonlinear regression fitting of the proton NMR chemical shift titration curves and the UV absorbance titration curves were carried out as reported earlier [4].

3. Results and Discussion

Complexation between **1** and **2** in an aqueous medium is indicated by (1) the upfield shift of their proton chemical shifts in the presence of each other (an example is shown in Figure 1) and (2) the change in the UV spectrum of **2** upon the addition of **1** (Figure 2). Proton NMR titrations were carried out by varying the concentration of **2** for a fixed concentration of **1** as well as by varying the concentration of **1** for a fixed concentration of **2**. All the NMR titration curves have their tangents intersecting at the molar ratio $R = 1$, indicating that the complex is of 1 : 1 host to guest stoichiometry (a representative plot shown in Figure 3). The same complex stoichiometry is also obtained from the UV absorbance titration curve of **2** (Figure 4).

The stability constant K of the 1 : 1 complex was obtained by a nonlinear regression fitting procedure [4]. The K values obtained from NMR titrations of different protons are in good agreement with one another (Table I) and with that obtained from the more accurate UV absorbance titration (Table II). The large K value (1.1×10^4 M⁻¹) is indicative of strong electrostatic interactions between **1** and **2**. Its

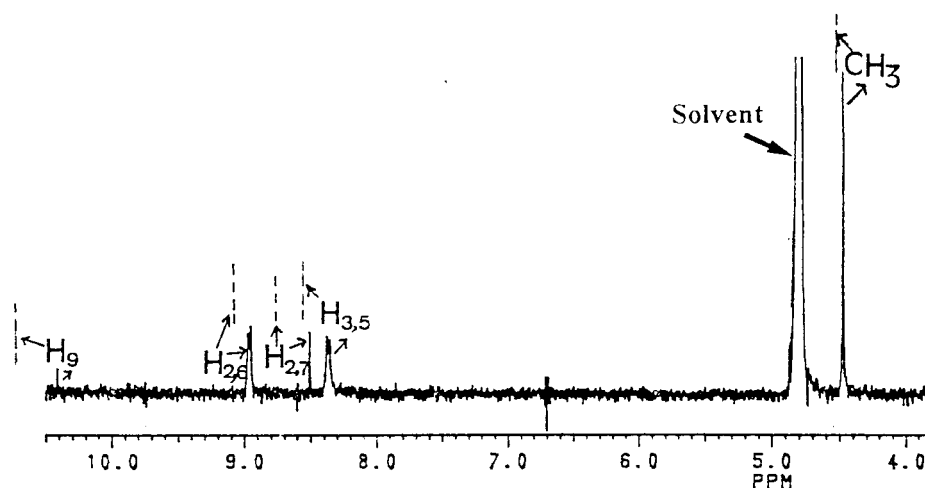


Figure 1. 300 MHz proton NMR spectra in D_2O at $25\text{ }^\circ\text{C}$ of a mixture of **1** (5.72×10^{-4} M) and **2** (4.88×10^{-4} M) (solvent peak at 4.80 ppm as internal reference; the dotted lines indicate the chemical shifts for the uncomplexed **1** and **2**).

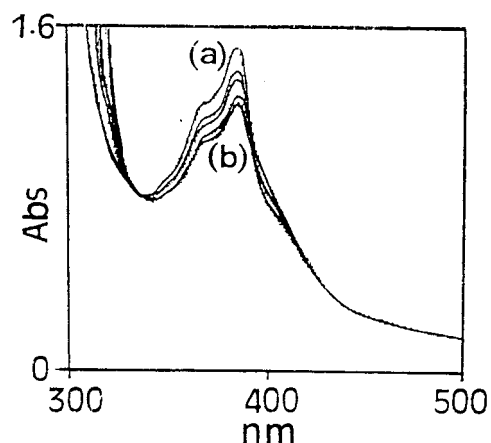


Figure 2. Ultraviolet spectra of **2** in water at $30\text{ }^\circ\text{C}$ in the presence of various concentrations of **1**; $[2] = 8.78 \times 10^{-5}$ M; $[1] = 0$ (a) to 4.98×10^{-4} M (b).

magnitude is comparable to those obtained from the complexation of **1** with macrocycles which provide electrostatic interactions [3, 4]. Hydrophobic interactions alone are expected to give a K value of only about 100 M^{-1} , as indicated by the K value of 100 M^{-1} for the 1 : 1 complex of **2** with biphenyl (a close analog of **1**, but without the positive charges), determined by the transport method [5, 8].

The K values, obtained by the UV spectroscopic method, are practically temperature independent, giving $\sim 0\text{ Kcal mol}^{-1}$ for the enthalpy and $18.7\text{ cal mol}^{-1}\text{ deg}^{-1}$ for the entropy. The large positive entropy change shows that the driving force for the complexation comes from the gain in entropy. This gain in entropy

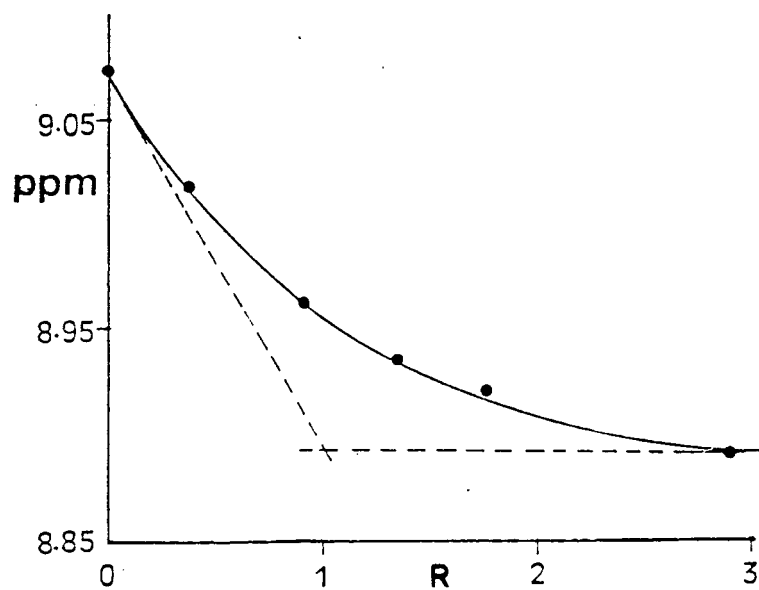


Figure 3. Variation of the chemical shift of $H_{2,6}$ of **1** (5.72×10^{-4} M) with the molar ratio R of [2] to [1] in D_2O at $25^\circ C$.

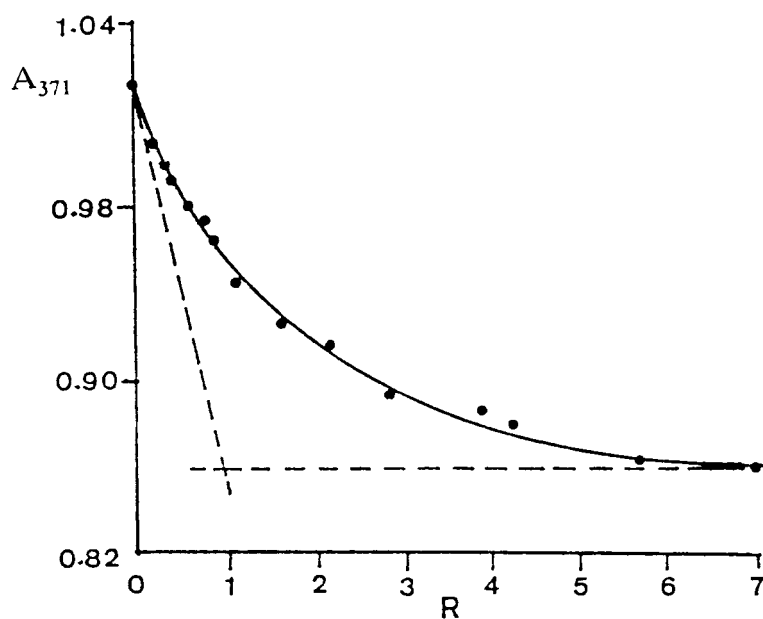


Figure 4. Variation of the absorbance at 371 nm of **2** (8.78×10^{-5} M) at $30^\circ C$ in water with the molar ratio R of [1] to [2].

Table I. Proton chemical shifts δ (ppm) and stability constant K of the 1 : 1 complex of **1** and **2** in D_2O at 25 °C

1	H _{2,6}	H _{3,5}	CH ₃
Free, δ	9.07	8.55	4.52
Complexed, δ	8.89	8.25	4.44
$K, M^{-1} (\pm 0.1 \times 10^4)$	1.0×10^4	1.0×10^4	1.0×10^4
2	H _{2,7}	H ₉	
Free, δ	8.74	10.74	
Complexed, δ	8.60	10.55	
$K, M^{-1} (\pm 0.1 \times 10^4)$	1.1×10^4	1.1×10^4	

Table II. Stability constant K of the 1 : 1 complex of **1** and **2** in water at various temperatures obtained by the UV spectroscopic method

Temperature, °C	$K, M^{-1} (\pm 0.1 \times 10^4)$
30	1.1×10^4
35	1.1×10^4
40	1.1×10^4
45	1.1×10^4

comes from the changes in solvations of **1** and **2** on complexation, analogous to the complexation of **1** with cyclotetrachromotrolylene [4].

The 1 : 1 stoichiometry of the complex indicates that each acridine ring of **2** in its dimeric form is complexed to a molecule of **1**. That the dimeric form of **2** is retained after complexation of **1** is supported by the absence of complexation between the monomeric form of **2** with polyaromatic hydrocarbons [6]. A possible structure of the complex is shown in Figure 5 (for clarity only half the dimer is shown and **1** is shown as a rectangular box). In this structure, the two positive charges of **1** lie directly below the two negative sulfonic groups of **2**, and the resulting strong electrostatic interactions account for the large K value. This structure with only partial aromatic π - π interactions between **1** and **2** is also consistent with the relatively small induced chemical shifts (about 0.2 ppm compared with about 1 ppm for large aromatic π - π interactions [4]) and the trend in the upfield shifts of the protons of **1**, $H_{3,5} > H_{2,6} > CH_3$ (Table I).

The structure of the complex in water, as shown in Figure 5, differs from that in the solid state which also has a 1 : 1 stoichiometry [9]. In the solid state, there

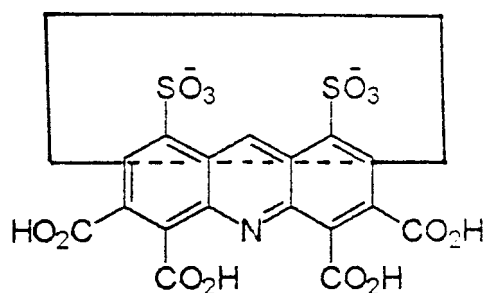


Figure 5. Partial structure of the 1 : 1 complex of **1** and **2** in water (**1** shown as a rectangular box).

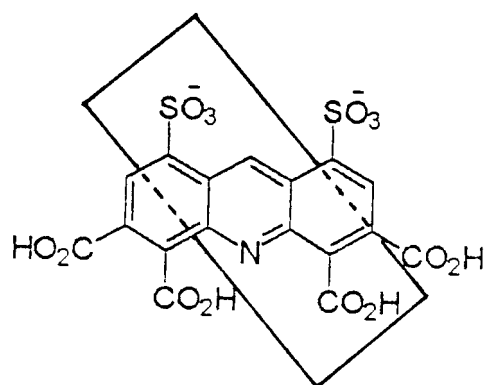


Figure 6. Partial structure of the 1 : 1 complex of **1** and **2** in the solid state (**1** shown as a rectangular box).

is an infinite array of acridine rings of **2** stacked up antiparallel to one another. A molecule of **1** is diagonally sandwiched between each pair of antiparallel acridine moieties so that one positive charge of **1** is near a negative sulfonic group of **2** and the other positive charge of the same molecule of **1** is near a negative sulfonic group of the second unit of **2** (Figure 6, for clarity the second unit of **2** is not shown and the molecule of **1** is represented as a rectangular box). This geometry gives favourable electrostatic interactions as well as large aromatic π - π interactions.

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