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Inclusion Complexation of Diphenylamine-4-diazonium Chloride and *p*-Sulfonatocalix[4]arene

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Inclusion complexation of *p*-sulfonatocalix[4]arene (SC4A) and diphenylamine-4-diazonium chloride (DDC) in aqueous solution was investigated in this study. The inclusion of DDC in the cavity of SC4A leads to ^{1}H NMR chemical shifts of DDC moving towards higher magnetic field. The complexation of SC4A also results in a bathochromic shift and a decrease in optic intensity of the absorption spectrum of DDC. In the presence of SC4A, the thermal stability of DDC in aqueous solution increases significantly while its photosensitivity still remains high.

Keywords: Calixarene; Diazo compounds; Inclusion complexation

Calixarenes, cyclic oligomers from phenol and formaldehyde, play a key role in host–guest chemistry and have attracted much attention in the past two decades [1,2]. The water-soluble *p*-sulfonatocalix[4]arene (SC4A), which adopts a "cone" conformation in aqueous solution [3], was first synthesized by S. Shinkai *et al.* [4]. It was found to be able to form complexes with a variety of organic compounds and inorganic ions in water [5]. Crystallographic studies show that the solid state complexes of SC4A usually present a bilayer structure similar to that of clays [6–9]. SC4A complexes in solution were also studied using NMR and UV-vis spectroscopy [3,10–14]. Shinkai *et al.* [3,11,12] determined the association constants of some quaternary ammoniums with SC4A. Recently its interaction with lysine and arginine in aqueous solution was studied by Coleman *et al.* [13,14]. It is believed that hydrophobic interaction, electrostatic force [12] and the so-called "cation–π" interaction [15] are important for the formation of SC4A complexes. Up to now most of the cationic guests are ammonium ions. Here, we demonstrate that diphenylamine-4-diazonium chloride (DDC), a diazonium salt, can form a complex with SC4A in water as a guest. This is of interest because the diazonium salt is an important cation in organic chemistry, whereas DDC is important in the dye industry and its formaldehyde resin is the most important photosensitive agent of the negative presensitized plates.

SC4A was synthesized according to S. Shinkai *et al.*'s method [4]. A commercial DDC (1/2 $ZnCl_2$ complex) was used in this study. It was purified by two precipitations from ether into ethanol, followed by drying in dark at room temperature. Absorption spectra were recorded on a Shimadzu UV 2101 spectrophotometer. A Varian 500 MHz instrument was employed for ^{1}H NMR spectroscopy measurements. DSS was used as internal standard and phosphate buffer was used to keep the pD of the solution at 5.

The chemical structures of DDC and SC4A are illustrated in Scheme 1. We first examined ^{1}H NMR spectra of DDC in the absence and presence of SC4A. Changes in chemical shifts ($\Delta\delta$) as a function of [SC4A]/[DDC] are shown in Fig. 1. We can see that all peaks of DDC shift to higher magnetic field ($\Delta\delta <$ 0) in the presence of SC4A. This indicates that DDC is included in the cavity of SC4A and affected by the ring current of the aromatic component [3,11,12] (see Scheme 2). The formation of a 1:1 complex can be assumed, since the changes in chemical shifts start to saturate at [SC4A]/[DDC] = 1 [3]. The change of chemical shifts increases in the order of $\Delta\delta_e > \Delta\delta_d > \Delta\delta_c \approx \Delta\delta_a > \Delta\delta_b$. This suggests that

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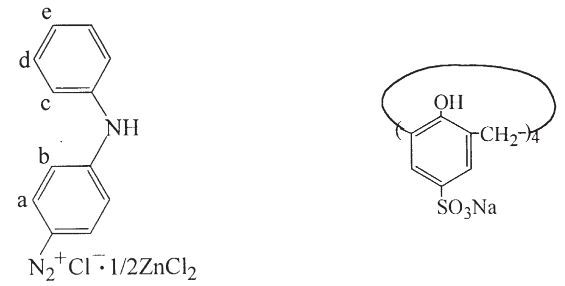


SCHEME 1 Structure of diphenylamine-4- diazonium chloride(DDC) and *P*-sulfonatocalix[4]arene(SC4A).

the inclusion of DDC into the cavity of SC4A does not give a single complex structure specifically, but rather various time-averaged structures as described earlier [3,12]. Such structures may include (1) and (2), as shown in Scheme 2, with structure (1) being more stable than (2). With the assumption of a 1:1 complex, the association equilibrium constant K_a was determined as 1.67×10^4 using nonlinear least-squares procedure.

The complexation process was also monitored by means of UV-vis spectrophotometric titration. As shown in Fig. 2, the addition of SC4A to the solution of DDC results in a bathochromic shift of the wavelength of maximum absorption and a decrease of intensity of the absorption band. The λ_{max} of pure DDC in water was measured to be 377 nm. It shifts to 383 nm when the molar ratio of [SC4A]/[DDC] reaches 15, which agrees with the studies on phenol blue and *p*-sulfonatocalix[*n*]arene ($n = 4,6,8$) [16]. This can also be explained by the resonance theory: the charge-separated structure b (see Scheme 3b) contributes more to the excited state and can be stabilized by complexing with SC4A, so the excitation energy decreases. The smaller difference between the energy of the ground and excited state causes the red-shift in absorption band [16].

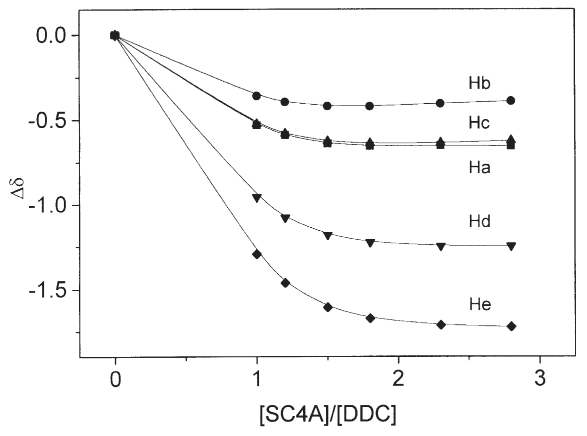
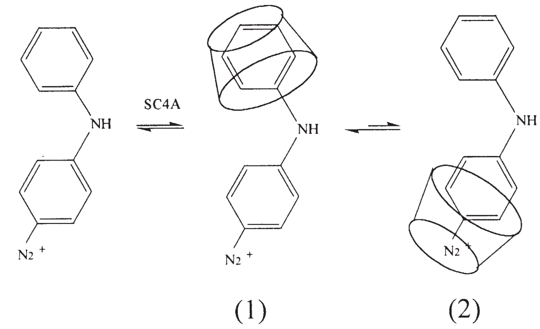


FIGURE 1 Changes in ^1H NMR chemical shifts (Δδ) of DDC at various concentrations of SC4A.



SCHEME 2 The schemetic illustration of inclusion of DDC in the cavity of SC4A. (1) and (2) are two representatives of time-averaged structures.

The clear isosbestic point of the DDC absorption spectra with SC4A at different concentrations indicates the formation of single SC4A-DDC complex [16]. The association equilibrium constant K_a can be obtained according to the Benesi–Hildebrand equation [17] which was deduced on condition of $[SC4A]_t \gg [DDC]_t$:

$$\frac{1}{\Delta A} = \frac{1}{K_a \cdot \Delta\varepsilon \cdot [DDC]_t \cdot [SC4A]_t} + \frac{1}{\Delta\varepsilon \cdot [DDC]_t}$$

where $[SC4A]_t$ and $[DDC]_t$ represent the total concentrations of SC4A and DDC in solution, and ΔA and $\Delta\varepsilon$ represent the change in absorbance and the difference between the molar extinction coefficients of complexed and free DDC, respectively. The double reciprocal plot (the inset plot of Fig. 2.) exhibits the linear feature fairly, and K_a was calculated to be $2.34 \times 10^4 M^{-1}$ which is in accord with the NMR titration result.

We also found that the rate of the thermal decomposition of DDC decreases obviously in the presence of SC4A. It was confirmed that it follows first order reaction kinetics. The thermal decomposition constant k_d at 70°C was measured at various [SC4A]/[DDC]. As evidenced in Fig. 3, the thermal

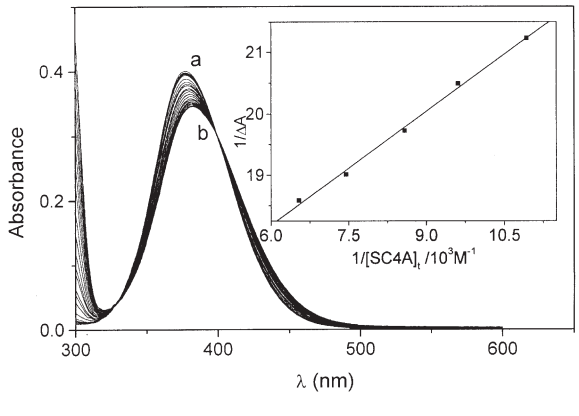
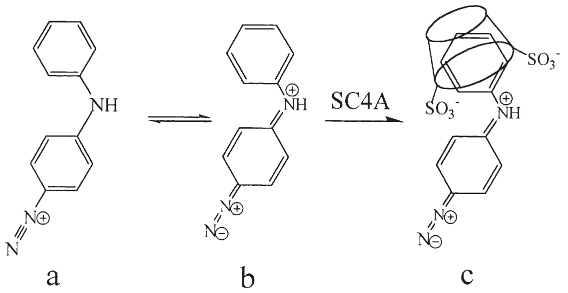


FIGURE 2 Absorption spectra of DDC in aqueous solution at various concentrations of SC4A (a to b, [SC4A = 0 to 0.15 mM) at 20°C([DDC] = 1×10^{-5} M). Inset: double reciprocal plot.



SCHEME 2 Resonant structure of DDC and its inclusion in the cavity of SC4A.

decomposition of DDC significantly slows down when adding SC4A. For instance, the k_d value at [SC4A]/[DDC]=9 becomes approximately 1/9 of that when in the absence of SC4A.

The photo-decomposition of DDC under UV irradiation is also a first-order reaction. The photo-decomposition rate constant k_p in the absence of SC4A was determined as $0.061\,s^{-1}$ with irradiation intensity of $1.0 \times 10^3\,\mu W\,cm^{-2}$. Under the same experimental condition, slightly decreased k_p values were found at various concentrations of SC4A (e.g. $k_p = 0.054\,s^{-1}$ for [SC4A]/[DDC] = 2). This reveals that the inclusion complex of the DDC-SC4A still remains highly sensitive towards UV-light.

In conclusion, SC4A and DDC can form an inclusion complex in aqueous solution, which results in a significant change in ^1H NMR chemical shifts of DDC, a bathochromic shift in wavelength and a decrease in intensity of the absorption spectrum of DDC. In addition, the thermal stability of DDC in aqueous solution increases significantly in the presence of SC4A while the photosensitivity remains high.

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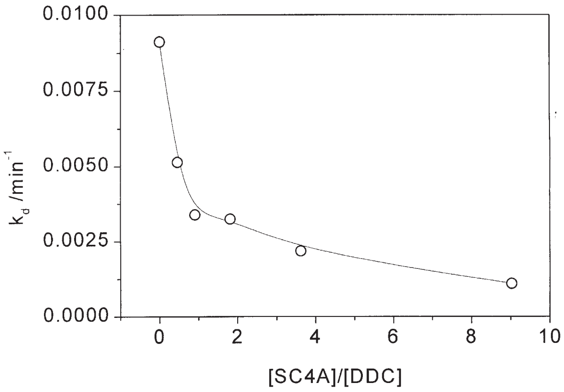

FIGURE 3 Plot of the decomposition constants k_d (at 70°C) of DDC as a function of [SC4A]/[DDC]([DDC]=1×10^{-5}M) in aqueous solution.

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