Study on the Inclusion Behavior of Cucurbit [n] Uril with Azo Dye Reactive Brilliant Red X-3B

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Abstract: Cucurbit[n]uril as one of the supramolecular complexes have many potential values because of the unique structure and properties. In this paper, the characteristics of host-guest complexes between cucurbit[n]uril and the reactive brilliant red X-3B were investigated by UV - visible absorption spectroscopy in acetate buffer solution at room temperature. It was found that the UV - visible absorption increased steadily with dropping the high concentration of cucurbit [6] uril (CB [6]) and cucurbit [8] uril (CB [8]) in the reactive brilliant red X-3B solution which indicates that that CB [8] has adsorption to reactive brilliant red X-3B dye and CB [8] can form host-guest complexes with reactive brilliant red X-3B dye. This work may extend the range of the application cucurbit [n] uril in the textile industry and pollution water treatment.

Keywords: supramolecular chemistry; cucurbit[n]uril; reactive brilliant red X-3B; host-guest complexes; pollution water treatment

1. Introduction

Cucurbit[n]uril (CB) is a novel macrocyclic host comprising different glycoluril units which is bridged by methylene in supramolecular chemistry [1] that based on the theory of non-covalent bonds has received much attention in recent years not only because it is across-subject of chemistry life science and molecular electronics and material science but also because of their unique structures and unusual properties different from those of conventional covalent polymers. With its unique hydrophobic cavity in which guest molecule can be included through hydrophobic interaction and the ureido polar carbonyl groups at the portals that can linked with organic molecules or bind metal ions through ion-dipolar [2] interaction or hydrogen bonds, cucurbit[n]uril became another ideal supramolecular host compound, and is important in molecular recognition and molecular self-assembly and so on [3-6].

Since Bhrend [7] synthesized cucurbit[n]uril (CB [n]) in 1905, scientists have shown great interest in these compounds, whose structural formula was shown in Figure 1.cucurbit [6]uril (CB[6]), which is macrocycle comprising glycoluril units interconnected with twelve methylene bridges and has a hydrophobic cavity that is accessible through two identical carbonyl-fringed portals. Cucurbit [8]uril (CB[8]) also has a similar structure and properties and they have been attracting much attention not only be cause of easy synthesis from glycoluril and formaldehyde, high symmetric structure and high chemical and thermal stability but also because of the polar carbonyl groups at the portals and hydrophobic cavity allow it to form stable host-guest complexes with small molecules such as all kind of azo dyestuffs.

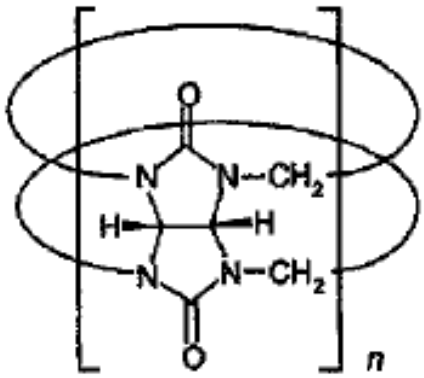

Figure 1. Structural formula of cucurbit[n]uril

At the beginning of nineties, cucurbit[n]uril has aroused attention of scientists and a great deal of basic research was investigated as a new sewage treatment technology [8, 9].

Buschmann et al the used cucurbit[n]uril to settlement of the textile dye in the treatment of dying and print manufacturing wastewater, then compared the effect of the adsorption to dyes between cucurbit[n]uril powder and cucurbit[n]uril that fixed on silica surface [10-15]. Dantz et al [16] had researched cucurbit[n]uril to remove the benzene, phenol and its derivatives in the waste water with satisfactory results. Karcher et al [17-19] studied the solubility of cucurbit[n]uril in the water and the adsorption of dye via cucurbit[n]uril. The results indicated that a certain concentration of calcium ions is conducive to the adsorption of dye and in the larger concentration of calcium ions or other metal ions in solution, due to increased solubility of cucurbit[n]uril while adsorption efficiency decreased. So the industrial automation of wastewater treatment was designed by cucurbit[n]uril

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bonding the solid material. In recent years, Karcher et al had researched the effect on the inclusion behavior of cucurbit [n] uril with dye molecules by the type of wastewater and concentration of salt and pH value.

Azo dyestuff is one typical chemical product, wastewater of which is trouble industrial wastewater due to its deep color, high COD, complicated organic components, huge amounts, poison and poor biodegradability, as well as its difficult degradation by classic biodegradation, biochemical degradation and physicochemical degradation [20]. Azo dyestuff, which is the most complete spectrum, most widely applied and lower price, is widely applied in textile industry, print, dyeing and leather industry. Azo dyes wastewater is not only high chromatic, strong noxious, but also difficult to degrade and easy decompose to carcinogenic aromatic amine under deoxidization condition. Extensive research is underway to develop non-conventional and advanced technologies for treatment of azo dyestuff wastewater.

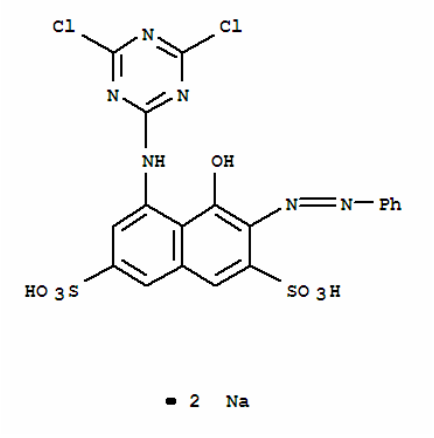

Figure 2. Structural formula of reactive brilliant red X-3B

In this paper, the reactive brilliant red X-3B whose structural formula was shown in Figure 2 which had azo dyes structure[21] was studied for research the behavior of include between cucurbit[n]uril and the brilliant red X-3B by UV-Vis absorption spectroscopy in acetate buffer solution at room temperature. At the same time because of the reactive brilliant red X-3B dye owning superior optical properties, there is a direct and practical significance to investigate the action mechanism of cucurbit[n]uril and the reactive brilliant red X-3B dye are detail. These studies provide a theoretical guidance for the wide range of applications about cucurbit[n]uril in the pollution water treatment.

2. Experimental

2.1. Chemicals

Cucurbit [6]uril (CB[6]) and Cucurbit[8]uril (CB[8]) were prepared by ^{1}H NMR, IR (infrared spectrum) and elemental analysis in accordance with the literature [13-15]. NaAc-HAc buffer solution (pH= 5.70, 0.05 mol/L^{-1}) was regulated the pH value of reaction system. The reactive brilliant red X-3B dye solution was obtained by dissolving 0.8g reactive brilliant red X-3B dye (biochemical reagents, the third factory of Shanghai Reagent, Shanghai， China) in 50 ml the distilled water and stirring the solution to dissolve the reactive brilliant red X-3B completely. All the other reagents were of analytical-reagent grade and the distilled water was used throughout.

2.2. Apparatus

Tu-1901double-beamUV-visible spectrophotometer（Tongyong Instrument Co., Ltd. Beijing, China）was used to measure the strength of the absorption of sample. PHS-3C pH meter (Shanghai Precision &Scientific Instrument Co., Ltd. Shanghai，China) was used for pH measurements.

2.3. Procedure

The above reactive brilliant red X-3B dye solution diluting with the distilled water divided equally into three beakers A, B, C. A small amount of CB [6] and CB [8] were added in the beaker A and B respectively, then mixed and stayed for some time. The phenomenon was shown that CB [6] had been dissolved in the beaker A, but the solution color had no different from the color of beaker C in the solution. While the CB [8] did not dissolve in beaker B, however, white powder of CB [8] changed into the purple powder and the color of the solution lightened significantly comparing with the solution of beaker C. Then the purple solid of the beaker B was filtered and washed with the distilled water to colorless and then placed them in a vacuum drying oven.

Specific sample of measuring the absorbance of cucurbit [8] uril and the reactive brilliant red X-3B dye solution are as follows: firstly, the dried compounds were dissolved in the above NaAc-HAc buffer solution. The 3.5ml of cucurbit [8] uril - reactive brilliant red X-3B dye solution was pipette accurately in the quartz absorption cell comparing to the buffer solution what were identified by UV-Vis spectrum after full equilibrium.

3. Results and discussion

The reactive brilliant red X-3B dye has superior solution properties, so solubility of cucurbit [6] uril increased significantly when cucurbit [6] uril were added into the reactive brilliant red X-3B dye solution. There are two possibilities: one is considered that the salt of the dye could help the CB [6] to dissolution. Another there may be formed supramolecular complexes between the CB [6] and the reactive brilliant red X-3B

dye. So the related research is in progress.

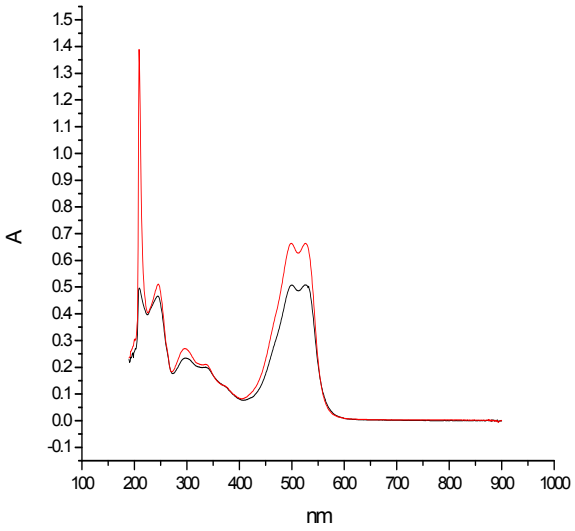

Figure 3. UV-Vis absorption spectra of host-guest complexes between cucurbit [8]uril and the reactive brilliant red X-3B

However, the color of the reactive brilliant red X-3B dye solution faded when CB [8] was joined into, indicating that CB [8] had a strong adsorption to the reactive brilliant red X-3B dye. CB [8] and the dye molecules formed the new host-guest complexes could be indicated by which the color of CB [8] changed into a red powder from white and did not bleaching by washing. UV-Vis absorption spectra of host-guest complexes between cucurbit [8] uril and the reactive brilliant red X-3B that was shown in Figure 3,which can full dictated the new host-guest complexes formed between them. Because UV-visible spectrum of the red solid samples owned the similar with the UV-visible spectrum of the reactive brilliant red X-3B dye and the characteristic peaks of cucurbit[n]uril was shown at the 209nm in the figure3. However, the concrete structure of complex was also needed further study.

4. Conclusions

The result of study on the inclusion behavior of cucurbit [n] uril with the reactive brilliant red X-3B dye show that CB [8] had a strong adsorption to the reactive brilliant red X-3B dye and the new host-guest complexes can be formed by CB [8] and the dye molecules.

Cucurbit[n]uril known as the new fourth generation supramolecule, after crown either, cyclodextrin and calixarene, is a kind of neotype host.1t can recognize guests including metal ions and organic dyestuff molecules and so on. It has great application potentiality in the molecular recognition，molecular self-assembly，molecular catalysis，pollution water treatment，mimic enzyme and drug pilot carrier .So, the new kind of host is arousing more and more researchers' considerable interest. It is believed that cucurbit[n]uril will became another ideal supramolecular host compound and have many potential values in the lots of aspects of practical application especially in the treatment of dying and print manufacturing wastewater.

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