ORIGINAL ARTICLE

Study on the inclusion interaction of ethyl violet with cyclodextrins by MWNTs/Nafion modified glassy carbon electrode

Jin-Ping Song · Yu-Jing Guo · Shao-Min Shuang · Chuan Dong

Abstract The interactions of ethyl violet (EV) with cyclodextrins (CDs) were investigated by Multi-wall carbon nanotubes/Nafion composite film modified glassy carbon electrode (MWNTs/Nafion/GCE). It was found that the MWNTs/Nafion composite film can effectively catalyze the electrode reaction of EV. The variation of the electrochemical behavior of EV upon the addition of CDs indicated the formation of the inclusion complexes of EV with β-CD, heptakis (2,3,6-tri-O-methyl)-β-CD (TM-β-CD), heptakis (2,6-di-O-methyl)-β-CD (DM-β-CD), hydroxypropyl-β-CD (HP-β-CD), and carboxymethyl-β-CD (CM-β-CD). The stoichiometry ratios of EV and the above five CDs were found to be 1:1. The inclusion ability obeyed the order: CM-β-CD > HP-β-CD > TM-β-CD > DM-β-CD > β-CD. The results showed that the modified β-CDs exhibited stronger binding ability than native β-CD, especially the charged CM-β-CD, which implied that the inclusion capacity depends on not only size matching and hydrophobicity but also electrostatic interaction. ^{1}HNMR spectra and molecule mechanics calculations suggested that EV was included into the cavity of β-CD from the wider side.

Introduction

Ethyl violet (EV) is a triphenylmethane dye, which has been widely used in a variety of products, such as textile, paper, and dye printing industry. Over the past decades, some triphenylmethane dyes still keep commercial value because they can supply the whole color range, but unfortunately the intensity of the primary dye fades with time and exposure to light [1, 2]. A number of studies have showed that the formation of inclusion complexes between cyclodextrins (CDs) and dyes can modify the physical and chemical characteristics of dyes, improve the retarding, migrating, leveling of dyeing and enhance thermostability [3–6]. Current methods for the inclusion research of guests with CDs have been focused on UV–Vis, fluorescence spectrophotometry, ^{1}HNMR and circular dichroism, as well as electrochemical methods [7–12]. Compared with other methods, considerable attention has been given to the electrochemical evaluation of the CD complexes with electroactive species [13]. Cyclic voltammetry [14, 15] and polarography [16–18] are particular useful in the study of guest molecules which are not amenable to other methods but which has a suitable electroactivity. However, the electrochemical studies of the inclusion interaction of guest with CDs by traditional dropping mercury electrode and other unmodified electrode are limited for those substances which possess weak electrochemical activity. So it is

J.-P. Song · Y.-J. Guo (✉) · S.-M. Shuang (✉) · C. Dong
Research Center for Environmental Science and Engineering, Department of Chemistry, Shanxi University, Taiyuan 030006, China
e-mail: guoyj@sxu.edu.cn

S.-M. Shuang
e-mail: smshuang@sxu.edu.cn

J.-P. Song
College of Chemistry and Chemical Engineering, Shanxi Datong University, Datong 037009, Shanxi, China

necessary to introduce new electrode materials to improve the electrochemical activity of guests.

CNTs have been widely applied to modify the electrodes due to its subtle electronic properties, excellent conductivity, and high surface activity [19–23]. But a major barrier for developing such CNT-based devices is the insolubility of CNT in all solvents [24]. Fortunately, solubilizing CNT has been improved through their covalent modification [25] or noncovalent functionalization [26]. In particular, "wrapping" of CNT in polymeric chains was a useful method for improving their solubility but without impairing their physical, chemical and electrochemical properties [27–30]. In our work, Nafion, an ion-exchange polymer, is served as a binder to improve dispersion of CNTs in ethanol and to enhance redox activity of EV at CNT/Nafion-coated glassy carbon electrodes.

In this paper, MWNTs/Nafion film coated GCE was used to study the electrochemical behavior of EV and its interaction with five kinds of CDs (β-CD, HP-β-CD, DM-β-CD, TM-β-CD, and CM-β-CD) by cyclic voltammetry and differential pulse voltammetry, respectively. The inclusion capacity of different CDs was compared and the factors affecting the inclusion capacity was discussed. The possible inclusion mechanism was proposed by ^{1}HNMR spectroscopy and molecule mechanics calculations.

Experimental

Reagents

Multi-wall carbon nanotubes (MWNTs) were purchased from Shenzhen Bill Technology developing CO., LTD, and were purified according to the reference [31]. Nafion was purchased from Aldrich, and 0.1% ethanol solution was prepared. 1.0×10^{-3} M stock solution of EV (Shanghai Chemical Reagent Plant) was prepared in double-distilled water. β-CD was purchased from Shanghai Chemical Reagent Plant of China Pharmaceutical Group Corporation. TM-β-CD, DM-β-CD, and CM-β-CD were purchased from Sigma. HP-β-CD was purchased from Aldrich. 1.0×10^{-2} M stock solutions of CDs were prepared in double-distilled water. 6.7×10^{-2} M Na$_2$HPO$_4$–KH$_2$PO$_4$ buffer (pH 6.2) was used as the supporting electrolytes. Other reagents were of analytical reagent grade, and double-distilled water was used in all experiments.

Apparatus

The cycle voltammetry and differential pulse voltammetry were carried on a CHI 660C electrochemical workstation (Shanghai CH Instrument Company, China). A bare glassy carbon electrode (GCE, 3 mm diameter), Nafion modified GCE (Nafion/GCE) or MWNTs/Nafion modified GCE (MWNTs/Nafion/GCE) were used as a working electrode, a platinum wire and a saturated calomel electrode (SCE) were used as a counter and reference electrodes, respectively. Absorbance spectra were measured on a TU-1901 spectrophotometer (Beijing Puxi Instrument Limited Co., China). The measurement of ^{1}HNMR was performed on DKX-300 MHz (Bruker, Switzerland).

Preparation of the MWNTs/Nafion modified GCE

The surface of the working electrode was polished with 0.3 and 0.05 μm alumina/water slurries, washed with double-distilled water, and finally ultrasonicated for 5 min before use. 1 mg of purified MWNTs were dispersed in 10 mL 0.1% Nafion ethanol solution with the aid of ultrosonication to form a 0.1 mg mL^{-1} MWNTs/Nafion black solution. Then, the MWNTs/Nafion modified GCE was fabricated by casting 5 μL of the suspension on the surface of the treated GCE and dried at room temperature. The modified GCE was activated by using cyclic voltammetry between −0.8 and 0.6 V at a scan rate of 100 mV s^{-1} in the supporting electrolytes until a stable cyclic voltammetric profile was obtained.

Procedure

0.2 mL stock solution (1.0×10^{-3} M) of EV was transferred into a 10 mL volumetric flask. 1 mL supporting electrolyte was added and the solution was diluted to 10 mL with double-distilled water. Shake thoroughly at room temperature. Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1}. If the inclusion constants were measured, an appropriate amount of 1.0×10^{-2} M different CDs were added to the system, and diluted to final volume with double-distilled water. Differential pulse voltammograms were measured after reaction for 10 min at room temperature. To confirm the formation of inclusion complexes, the UV–Vis spectroscopy and ^{1}HNMR were employed.

Results and discussion

Electrochemical behavior of EV

The cyclic voltammetric behaviors of EV at the bare GCE, Nafion/GCE, and MWNTs/Nafion/GCE were shown in Fig. 1. It can be seen that the cyclic voltammetric response of EV at the bare GCE was very weak (Fig. 1, curve a). On Nafion/GCE, EV gave a pair of cathodic ($E_{pc} = 141$ mV) and anodic ($E_{pa} = 233$ mV) peak with the potential difference (ΔE_p) of 92 mV (Fig. 1, curve b). The peak
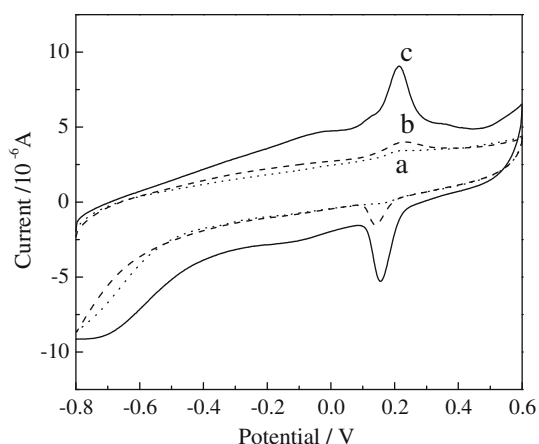
Fig. 1 Cyclic voltammograms of 2.0×10^{-5} M EV in 6.7×10^{-2} M Na$_2$HPO$_4$–KH$_2$PO$_4$ buffer (pH 6.2) at (a) bare GCE, (b) Nafion modified GCE, (c) MWNTs/Nafion modified GCE. *Scan rate* 100 mV s^{-1}

currents were obviously improved, indicating that the Nafion film modified GCE can improve the electrochemical response of EV. This can be explained as follows: as a cation-exchange, Nafion can incorporate positive charged ions and reject the anionic species. EV which possesses positive charge in acidic medium can be absorbed on polyanionic structure surface of Nafion to generate ion exchange and give an enhanced peak current, so the cathodic peak current apparently increased. Furthermore, an interesting phenomenon was noticed. The cathodic peak current of EV at the Nafion/GCE was higher than the anodic peak. This may be due to the ion exchange property of Nafion toward EV with positive charge is stronger than that of the neutral reduction product. On MWNTs/Nafion/GCE, EV showed a pair of well-defined redox peaks with the cathodic (E_{pc}) and anodic (E_{pa}) peak potential of 165 and 204 mV, respectively (Fig. 1, curve c). The potential difference was 39 mV. And the peak currents were dramatically enhanced comparing with that of Nafion/GCE and bare GCE. The decrease of potential difference and the increase of peak current suggested that electrocatalytic activity of the MWNTs/Nafion composite film is much higher than that of the Nafion film. The improvement of the electrochemical response is attributed to the excellent electrocatalysis ability of MWNTs, ion exchange of Nafion, and the synergistic characteristics of Nafion and MWNTs.

In order to investigate the reaction mechanism of EV at the MWNTs/Nafion/GCE, the cyclic voltammograms of EV in Na$_2$HPO$_4$–KH$_2$PO$_4$ buffer (pH 6.2) at the different scan rates were investigated. The peak currents and potential differences of EV increased with increase of the scan rates. And the E_{pa} of EV shifted to more positive and E_{pc} shifted to more negative. The electron transfer numbers

can be determined, according to the following equation [32],

$$E_p = B - \frac{RT}{\alpha nF} \ln v \tag{1}$$

where B is a constant, n is the number of electron, α is the transfer coefficient, v is the scan rate, and other terms have their usual meanings. The linear relationships of E_{pc} and $\ln v$ of EV could be expressed as $E_{pc} = 0.1216 - 0.02024 \ln v$ ($r = 0.9917$) (see Fig. S1 of supporting information). Therefore, the electron transfer numbers of EV was calculated to be 2. In addition, the good linear relationships of peak currents i_p with v in the range of 125–300 mV s^{-1} (Fig. S2), indicating that the electrode reaction is an absorption controlled process.

The effect of pH was investigated over the range of interest from pH 5.0 to 9.2. The peak potential of the cathodic peak and anodic peak were found to shift to more negative potential with increasing pH. The linear relationship of peak potential versus pH was obtained by the following equation [33]:

$$E_p = E^{0'} - 2.303(mRT/\alpha nF)\text{pH} \tag{2}$$

where $E^{0'}$ is the formal potential, m is the number of the protons involved in the reaction, n is the number of electron and α is the transfer coefficient. Based on the measured data, the linear regression equation of E_{pc} versus pH is expressed as $E_{pc} = 0.4965 - \frac{0.0528m}{n}\text{pH}$ ($r = 0.9921$) (Fig. S3). A slope of 52.8 mV is close to that predicted by the Nernst equation for a redox process involving the transfer of an equal number of protons and electrons. So, the redox reaction of EV is likely to involve two protons and two electrons, and the redox mechanism is proposed in Fig. 2.

The inclusion interaction of EV with CDs

Figure 3 showed the differential pulse voltammograms of EV at the MWNTs/Nafion/GCE in the absence and presence of different concentrations of β-CD. It was observed that the anodic peak current of EV gradually decreased upon the addition of β-CD, and the peak potential shifted to more positive value. The variation of the electrochemical behavior indicated the formation of the inclusion complex of EV with β-CD. The anodic peak shifted to more positive potentials by 4 mV, revealing that EV molecules were difficult to be oxidized while they were included into the cavity of β-CD to form the inclusion complex [34]. The decrease of peak current was attributed to the reduction of the diffusion coefficient of EV with the formation of inclusion complexes. The differential pulse voltammograms of the inclusion complexes between EV and other four CDs (CM-β-CD, HP-β-CD, TM-β-CD, and DM-β-

Fig. 2 The redox mechanism of EV
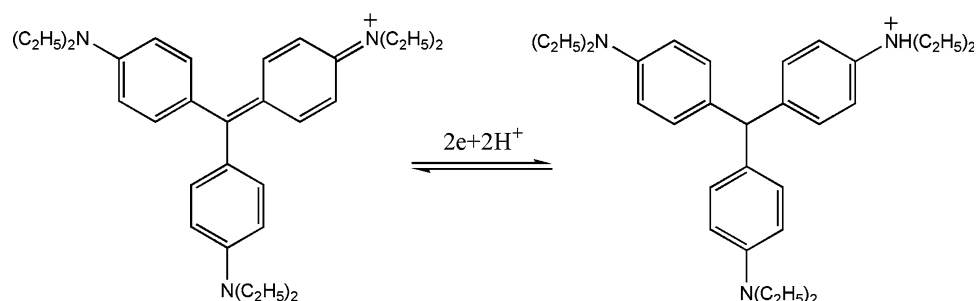
CD) are similar to each other in forms. The other vol-tammograms are not given. These illustrated that the inclusion complexes were formed between the five CDs and EV.
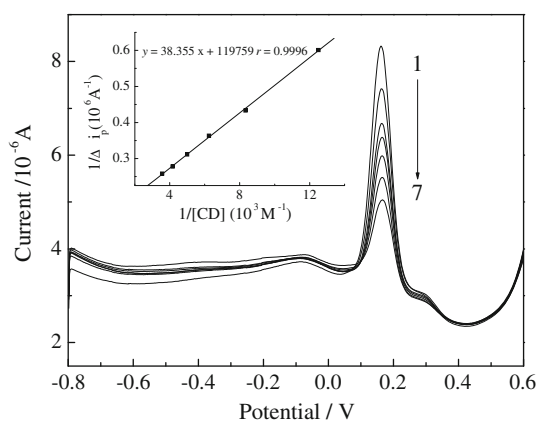
The decrease of peak currents with the increase of CDs concentration can be used to evaluate the inclusion con-stant and binding ratio. According to references [35, 36], if dye molecular and CDs only form a complex D-CD$_m$, and inclusion complex is electrochemically active, where D, m and D-CD$_m$ represent the dye, binding ratio, and inclusion complex, respectively. The inclusion complexation of the dye guest with the host CDs is expressed by Eq. 3, and the inclusion constant (K) is given by Eq. 4

$$D + mCD \overset{K}{\rightleftarrows} D\text{-}CD_m \tag{3}$$

$$K = \frac{[D-CD_m]}{[D][CD]^m} \tag{4}$$

If the decrease of peak current is proportional to the concentration of inclusion complex, the inclusion constant K can be expressed by Eq. 5

$$\frac{1}{\Delta i_p} = \frac{1}{\Delta i_{max}} + \frac{1}{\Delta i_{max} K [CD]^m} \tag{5}$$

where Δi_p signifies the variation of peak current after adding CDs, Δi_{max} represent the peak current in case of complete inclusion; [CD] is the concentration of the CDs. When m is 1, 2, 3… respectively, the plots of $1/\Delta i_p$ versus $1/[CD]^m$ can give some curves (see the inset in Fig. 3, and Fig. S4 of supporting information), the value of m corre-sponding a straight line is the binding ratio of guest with host, the value of K is intercept divided by slope. In our studies, EV can form 1:1 complexes with five CDs. The inclusion constants are listed in Table 1.

In addition, UV–Vis absorption spectra of EV were measured to testify the formation of the inclusion complex. The changes of the absorption spectra with addition of β-CD were shown in Fig. 4. It was found that the maxi-mum absorption wavelength of EV at 593 nm shifted to 596 nm, and the absorbance decreased gradually with addition of β-CD. This phenomenon showed that the inclusion complexes of EV with β-CD were formed. The inclusion constant (K) can be obtained by the following equation [37],

$$\frac{1}{\Delta A} = \frac{1}{\alpha} + \frac{1}{\alpha K [CD]^m} \tag{6}$$

Fig. 3 Differential pulse voltammograms of 2.0×10^{-5} M EV contain different concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 8.0×10^{-5}, (3) 1.2×10^{-4}, (4) 1.6×10^{-4}, (5) 2.0×10^{-4}, (6) 2.4×10^{-4}, (7) 2.8×10^{-4} (M). *Inset* the plots of $1/\Delta i_p$ versus $1/[CD]$

Table 1 Complex stability constant (K) for 1:1 inclusion complex-ation of various triphenylmethane dyes with β-CD and its derivatives in aqueous solutions

Host	Guest	K	Log$K$	Method	Ref.
β-CD	Crystal violet	1870	3.27	UV	[39]
β-CD	Crystal violet	1870 ± 50	3.27	UV	[40]
β-CD	Brilliant green	2187 ± 100	3.34	UV	[40]
β-CD	Brilliant green	2190	3.34	UV	[8, 39]
β-CD	Ethyl violet	3.22×10^3	3.51	UV	This work
β-CD	Ethyl violet	3.12×10^3	3.49	DPV*	This work
DM-β-CD	Ethyl violet	3.33×10^3	3.52	DPV	This work
TM-β-CD	Ethyl violet	3.80×10^3	3.60	DPV	This work
HP-β-CD	Ethyl violet	5.20×10^3	3.72	DPV	This work
CM-β-CD	Ethyl violet	5.82×10^3	3.76	DPV	This work

* *DPV* differential pulse voltammetry
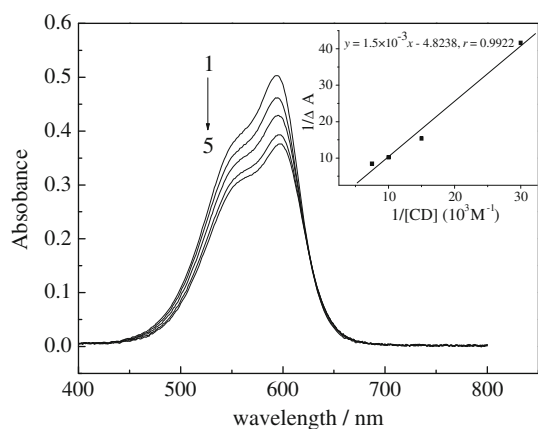
Fig. 4 Absorption spectra of 2.0×10^{-5} M EV contain different concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 3.3×10^{-5}, (3) 6.7×10^{-5}, (4) 1.0×10^{-4}, (5) 1.3×10^{-4} (M). *Inset* the plots of $1/\Delta A$ versus $1/[CD]$

where ΔA denote the difference of absorption of guest molecule in the presence and absence of CDs. α is a constant, and $[CD]$ signifies the concentration of CDs. The plot of $1/\Delta A$ vs. $1/[CD]$ exhibited good linearity (see the inset in Fig. 4). From the slope and y-intercept of the equation, the inclusion constant (K) obtained was 3.22×10^3 M^{-1}, which is consistent with that obtained from the differential pulse voltammetry.

As can be seen from the Table 1, the inclusion constant for native β-CD and modified β-CD with dye guests are affected by the substituent group of the native β-CD and the size of the guest. The inclusion constants of EV and

CDs increase as the following order: CM-β-CD > HP-β-CD > TM-β-CD > DM-β-CD > β-CD. The modified β-CD exhibited stronger binding ability than the native β-CD implying that the cavity of the modified CDs provided a better protective microenvironment. Strong inclusion ability can be understood that the substitution by hydroxypropyl, dimethyl and trimethyl groups lead to the enlargement of the bigger opening of CDs cavity and the contraction of the smaller opening of CDs cavity, which make it easier for the guest molecules to gain access to the modified CDs cavity and to have bigger inclusion constants [38]. However, it was noted that CM-β-CD exhibited a stronger binding ability than the native β-CD and other derivatives. The reason is that the carboxylic groups of CM-β-CD (pK_a <4) are deprotonated at pH >5, resulting in a negative charge on the CDs. So, additional electrostatic interactions contributed to the increase of the inclusion ability.

EV exhibited stronger binding ability than crystal violet and brilliant green with the native β-CD (Table 1), although they possess high structural similarity. It was due to the rigidity of the CDs cavity and the strict size/shape fit concept. In addition, the lack of dialkylamino group on one of the phenyls in brilliant green inevitably reduces the hydrophobic interactions upon complexation with the native β-CD, leading to the poor binding of brilliant green with the native β-CD. All results indicate that the major factors affecting inclusion ability between guest and CDs are hydrophobicity, size matching together with electrostatic interaction.

Fig. 5 ^{1}HNMR spectra (300 MHz, D$_2$O) of EV (*a*), β-CD (*b*) and the inclusion complex of EV with β-CD (*c*)
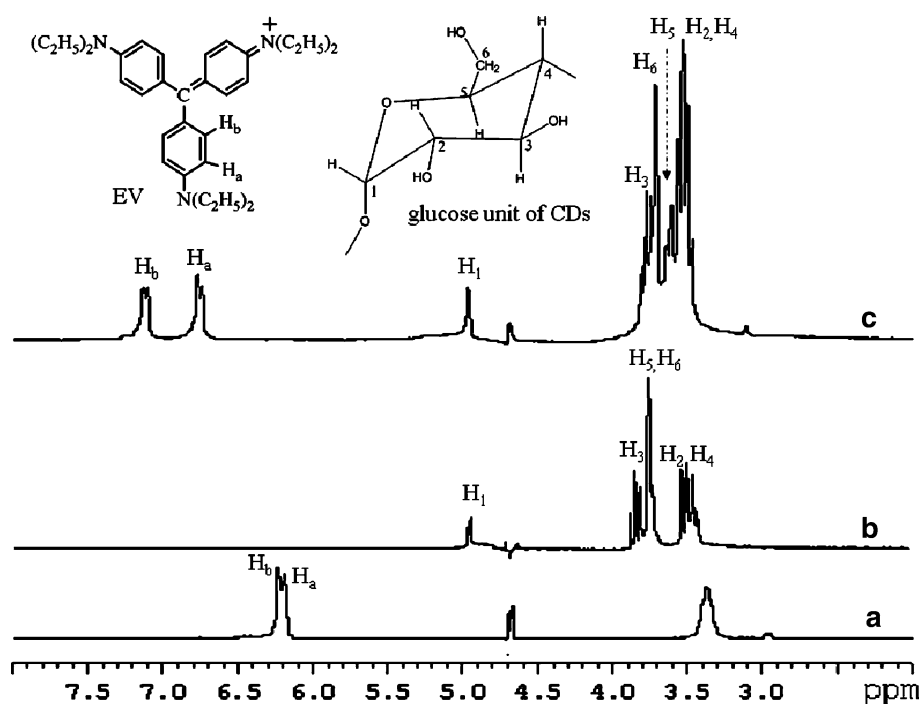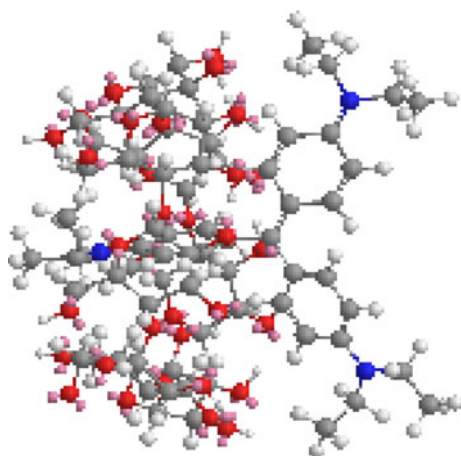
Fig. 6 The energy-minimized structures of EV-β-CD

Binding mode

To establish the real binding mode of the inclusion complex of EV with β-CD, the ^{1}HNMR spectra were recorded in the absence and presence of EV, as shown in Fig. 5. It could be seen that 3-H and 5-H showed up-field shifts due to anisotropic shielding by the guest. On the contrary, the shifts of 2-H and 4-H protons were relatively small. The dramatic shifts of H-5 and H-3 indicated that the guest molecule entered the cavity of β-CD from the wider side. On the other hand, signals for the guest protons (H_a and H_b) also showed down-field shifts due to the deshielding effect of the electron-rich cavity of β-CD, which implied the aromatic ring of guest was included into the hydrophobic cavity of β-CD. In addition, molecule mechanics calculations were carried out to obtain the dimensions and geometry of EV by using MM2 technique. Through the comparison of the spatial size between the cavity of β-CD and dye molecule, we can see that the aromatic ring may be partial included into the cavity. This conclusion is in accordance with ^{1}HNMR. The energy-minimized structure of inclusion complex is shown in Fig. 6.

Conclusions

In this paper, the inclusion interaction of EV with CDs was researched by differential pulse voltammetry and UV–Vis absorption spectroscopy. The results demonstrated that EV can form inclusion complexes with CDs. The inclusion constants of EV with β-CD obtained from the differential pulse voltammetry and UV–Vis absorption were consistent. The modified β-CD exhibited stronger binding ability than the native β-CD, implying that the cavity of the modified CDs provided a better protective microenvironment. It

further confirmed that the size/shape-fit and hydrophobic played an important role in the inclusive process. Furthermore, CM-β-CD exhibited stronger inclusion ability than native β-CD and other derivatives, suggesting electrostatic interactions contributed to the inclusion process. ^{1}HNMR spectra and molecule mechanics calculations indicated that EV molecule is included into the cavity of β-CD from the wider side. This study demonstrates that investigating inclusion interaction based on modified electrode is more accurate, sensitive and simple to operate automatically.

References

1. He, H.L.: Dyes. Chemical Industry Press, Beijing (2004)
2. Sirés, I., Guivarch, E., Oturan, N., Oturan, M.A.: Efficient removal of triphenylmethane dyes from aqueous medium by in situ electrogenerated Fenton's reagent at carbon-felt cathode. Chemosphere **72**, 592–600 (2008)
3. Savarino, P., Parlati, S., Buscaino, R., Piccinini, P., Barolo, C., Montoneri, E.: Effects of additives on the dyeing of polyamide fibres. Part II: Methyl-β-cyclodextrin. Dyes Pigm. **69**, 7–12 (2006)
4. Vonĉina, B., Vivod, V., Jauŝovec, D.: β-Cyclodextrin as retarding reagent in polyacrylonitrile dyeing. Dyes Pigm. **74**, 642–646 (2007)
5. Jenkins, D.W., El-Tahlawy, K., El-Shafei, A., Freeman, H.S., Hudson, S.M.: Use of γ-cyclodextrin/epichlorohydrin copolymer in merging fabric formation and coloration processes. Color. Technol. **122**, 345–349 (2006)
6. Cireli, A., Yurdakul, B.: Application of cyclodextrin to the textile dyeing and washing processes. J. Appl. Polym. Sci. **100**, 208–218 (2006)
7. Steed, J.W., Atwood, J.L.: Supramolecular Chemistry, pp. 11–17. Wiley, New York (2009)
8. Liu, Y., Li, L., Zhang, H.Y., Liang, P., Wang, H.: Inclusion complexation behavior of dyestuff guest molecules by a bridged bis(cyclomaltoheptaose)[bis(β-cyclodextrin)] with a pyromellitic acid diamide tether. Carbohydr. Res. **338**, 1751–1757 (2003)
9. Buschmann, H.J., Schollmeyer, E.: Cucurbituril and β-cyclodextrin as hosts for the complexation of organic dyes. J. Inclusion Phenom. Mol. Recognit. Chem. **29**, 167–174 (1997)
10. Iijima, T., Karube, Y.: The interaction of acid azo dyes with chemically modified β-cyclodextrins. Dyes Pigm. **36**, 305–311 (1998)
11. Isaacs, N.S., Young, D.J.: A volumetric study of molecular inclusion by α-cyclodextrin. Tetrahedron Lett. **40**, 3953–3956 (1999)
12. Suzuki, M., Ohmori, H., Kajtar, M., Szejtli, J., Vikmon, M.: The association of inclusion complexes of cyclodextrins with azo dyes. J. Inclusion Phenom. Mol. Recognit. Chem. **18**, 255–264 (1994)
13. Osella, D., Carretta, A., Nervi, C., Ravera, M., Gobetto, R.: Inclusion complexes of ferrocenes and β-cyclodextrins. Critical appraisal of the electrochemical evaluation of formation constants. Organometallics **19**, 2791–2797 (2000)
14. Zhao, G.C., Zhu, J.J., Zhang, J.J., Chen, H.Y.: Voltammetric studies of the interaction of methylene blue with DNA by means of β-cyclodextrin. Anal. Chim. Acta **394**, 337–344 (1999)

15. Matsue, T., Evans, E.H., Osa, T., Kobayashi, N.: Electron-transfer reactions associated with host-guest complexation. Oxidation of ferrocenecarboxylic acid in the presence of β-cyclodextrin. J. Am. Chem. Soc. **107**, 3411–3417 (1985)

16. Yuan, Z.B., Zhu, M., Han, S.B.: Supramolecular inclusion complex formation and application of β-cyclodextrin with heteroanthracene ring cationic dyes. Anal. Chim. Acta **389**, 291–298 (1999)

17. Guo, Y.J., Pan, J.H., Li, X.M., Lu, F., Li, Y.Q.: Electroanalytical method of Acid Blue 120 and its supramolecular system with cyclodextrins. J. Incl. Phenom. Macrocycl. Chem. **56**, 243–246 (2006)

18. Caballero, J., Zamora, C., Aguayo, D., Yaňez, C., González-Nilo, F.D.: Study of the interaction between progesterone and β-cyclodextrin by electrochemical techniques and steered molecular dynamics. J. Phys. Chem. B **112**, 10194–10201 (2008)

19. Zhou, O., Shimoda, H., Gao, B., Oh, S., Fleming, L., Yue, G.Z.: Materials science of carbon nanotubes: fabrication, integration, and properties of macroscopic structures of carbon nanotubes. Acc. Chem. Res. **35**, 1045–1053 (2002)

20. Tasis, D., Tagmatarchis, N., Bianco, A., Prato, M.: Chemistry of carbon nanotubes. Chem. Rev. **106**, 1105–1136 (2006)

21. Zhu, Y.H., Zhang, Zh.L., Zhao, W., Pang, D.W.: Voltammetric behavior and determination of phenylephrine at a glassy carbon electrode modified with multi-wall carbon nanotubes. Sens. Actuators B **119**, 308–314 (2006)

22. Wang, J.X., Li, M.X., Shi, Z.J., Li, N.Q., Gu, Z.N.: Direct electrochemistry of cytochrome c at a glassy carbon electrode modified with single-wall carbon nanotubes. Anal. Chem. **74**, 1993–1997 (2002)

23. Zeng, J.X., Wei, W.Z., Wu, L., Liu, X.Y., Liu, K., Li, Y.: Fabrication of poly (toluidine blue O)/carbon nanotube composite nanowires and its stable low-potential detection of NADH. J. Electroanal. Chem. **595**, 152–160 (2006)

24. Shobha Jeykumari, D.R., Ramaprabhu, S., Sriman Nrayanan, S.: A thionine functionalized multiwalled carbon nanotube modified electrode for the determination of hydrogen peroxide. Carbon **45**, 1340–1353 (2007)

25. Hazani, M., Naaman, R., Hennrich, F., Kappes, M.M.: Confocal fluorescence imaging of DNA-functionalized carbon nanotubes. Nano. Lett. **3**, 153–155 (2003)

26. Liu, Y.T., Zhao, W., Huang, Z.Y., Gao, Y.F., Xie, X.M., Wang, X.H., Ye, X.Y.: Noncovalent surface modification of carbon nanotubes for solubility in organic solvents. Carbon **44**, 1613–1616 (2006)

27. O'Connell, M.J., Boul, P., Ericson, L.M., Huffman, C., Wang, Y., Haroz, E., Kuper, C., Tour, J., Ausman, K.D., Smalley, R.E.: Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping. Chem. Phys. Lett. **342**, 265–271 (2001)

28. Kim, J.H., Sharma, A.K., Lee, Y.S.: Synthesis of polypyrrole and carbon nano-fiber composite for the electrode of electrochemical capacitors. Mater. Lett. **60**, 1697–1701 (2006)

29. Cochet, M., Maser, W.K., Benito, A.M., Callejas, M.A., Martinez, M.T., Benoit, J.M., Schreiber, J., Chauvet, O.: Synthesis of a new polyaniline/nanotube composite: in situ polymerization and charge transfer through site-selective interaction. Chem. Commun. **1**, 1450–1451 (2001)

30. Du, P., Liu, S.N., Wu, P., Cai, C.X.: Single-walled carbon nanobubes functionalized with poly (nile blue A) and their application to dehydrogenase-based biosensors. Electrochim. Acta **53**, 1811–1823 (2007)

31. Tsang, S.C., Chen, Y.K., Harris, P.J.F., Green, M.L.H.: A simple chemical method of opening and filling carbon nanotubes. Nature **372**, 159–162 (1994)

32. Bard, A.J., Faulkner, L.R.: Electrochemical Methods Fundamentals and Applications, p. 222. Wiley, New York (1980)

33. Bond, A.M.: Modern Polarographic Methods in Analytical Chemistry, p. 27. Marcel Dekker, New York (1980)

34. Tong, L.H., Shen, B.J.: Physical Methods in Supramolecular Chemistry Research. Science Press, Beijing (2004)

35. Li, N.Q., Gao, X.X.: Polarographic catalytic wave study of vanadium-I. Chin. J. Anal. Chem. **1**, 40–48 (1973)

36. Li, N.Q., Gao, X.X.: Polarographic catalytic wave study of vanadium-II. Chin. J. Anal. Chem. **2**, 459–461 (1974)

37. Benesi, H.A., Hildebrand, J.H.: A spectrophotometric investigation of the interaction of iodine with aromatic hydrocarbons. J. Am. Chem. Soc. **71**, 2703–2707 (1949)

38. Qi, W.B., Qi, Z.H.: New Analytical Synergistic Agent. Hangzhou University Press, Hangzhou (1994)

39. Liu, Y., Li, B., You, C.C., Wada, T., Inoue, Y.: Molecular recognition studies on supramolecular systems. Molecular recognition of dyes by organoselenium-bridged bis(β-cyclodextrin)s. J. Org. Chem. **66**, 225–232 (2001)

40. Liu, Y., Chen, Y., Li, L., Huang, G., You, C.C., Zhang, H.Y., Wada, T., Inoue, Y.: Cooperative multiple recognition by novel calix[4]arene-tethered β-cyclodextrin and calix[4]arene-bridged bis(β-cyclodextrin). J. Org. Chem. **66**, 7209–7215 (2001)