Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 74 (2007) 67–72
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Electrochemical studies of determination of Basic Brown G and its interaction with cyclodextrins

You-Qin Li [a,b], Yu-Jing Guo [a], Xiu-Fang Li [a], Jing-Hao Pan [a,*]

[a] *Department of Chemistry, School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, China*
[b] *Department of Chemistry, Datong University, Datong 037009, China*

Received 6 July 2005; received in revised form 17 August 2005; accepted 6 January 2006
Available online 20 March 2006

Abstract

In this paper, a simple, rapid, sensitive and accurate electroanalytical method of Basic Brown G (BBG) has been established by polarography and voltammetry. In ammonia–ammonium chloride (pH 9.1), a sensitive second derivative reduction peak (i_p'') of BBG was found by Linear Sweep Voltammetry (LSV). The peak potential (E_p) is about −0.67 V (versus SCE). The peak current (i_p'') is proportional to the concentration of BBG over the range 3.0×10^{-8}–1.0×10^{-4} mol L^{-1} ($r = 0.9935$–0.9987) and the limit of detection (LOD) is 9.0×10^{-9} mol L^{-1}. The recovery of BBG varied from 95.3 to 102% and the relative standard deviation (RSD) was 2.4% ($n = 10$). The method has been expected to achieve the determination of the concentration of remnants of dyes of wastewater in dye industry. In addition, the supramolecular system of BBG with cyclodextrins (CDs) has been studied. BBG can form 1:2 (BBG:CD) inclusion complex with α-CD and HP-α-CD, respectively, and 1:1 inclusion complex with other six CDs. The inclusion constants were calculated and the inclusion ability of different kinds of CDs was compared, furthermore, the inclusion mechanism is also preliminarily discussed, which provided some valuable information for further application of BBG and CDs.

Keywords: Polarography; Voltammetry; Basic Brown G; Supramolecular system; Cyclodextrin

1. Introduction

Basic Brown G (BBG) (C.I. Basic Brown 1) is one of the azo dyes and is widely used in dye-printing and textile industry, which is becoming extensively scattered throughout the environment around manufacturing plants. A number of azo dyes exhibit genotoxicity and ecotoxicity [1,2] leading to the need for optimize analytical procedures for their determination at lower levels. In recent years, several methods [3–5] have been reported for this purpose, but these methods need expensive equipment or long experimental procedures for the sample clean up. Polarography and voltammetry are particularly suitable for this object not only because of their applicability over an unusually wide concentration range, their low investment and low running costs but also their rapidity, simplicity, accuracy and high sensitivity.

There has been a steady growth of interest in supramolecular chemistry. CDs have the peculiar ''interior hydrophobic, exterior hydrophilic'' structure forming a 1:1 or 1:2 inclusion complex with guest molecules, thus the physical, chemical and biochemical characteristics of guest molecules were modified [6–8]. To date mainly various methods [9–15] have been used for the study of inclusion complexes of CDs and guest molecules. However, based on our knowledge, no electrochemical report on the determination of BBG and supramolecular system of BBG with CDs has appeared in the literature.

In this paper, polarography and voltammetry have been proved to be very convenient techniques for determining the azo dye at nanomolar levels. The electroanalytical method of BBG has been established. In 0.1 mol L^{-1} NH_3–NH_4Cl (pH 9.1), a sensitive reduction peak of BBG was found by LSV. The peak potential is about −0.67 V (versus SCE). The peak

* Corresponding author. Tel.: +86 351 7011 333; fax: +86 351 7011 668.
E-mail address: jhpan@sxu.edu.cn (J.-H. Pan).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.01.012

current is proportional to the concentration over the range 3.0×10^{-8}–1.0×10^{-4} mol L^{-1} ($r = 0.9935$–0.9987) and LOD is 9.0×10^{-9} mol L^{-1}. The recovery of BBG varied from 95.3 to 102% and RSD was 2.4%, which is fit for the need of analytical application.

In our research, the interaction of BBG with CDs was investigated by polarography and voltammetry. The interaction of BBG with α, β and γ-cyclodextrins (α, β and γ-CD), hydroxypropyl-α-cyclodextrin (HP-α-CD), hydroxypropyl-β-cyclodextrin (HP-β-CD), hydroxypropyl-γ-cyclodextrin (HP-γ-CD), tri-*o*-methyl-β-cyclodextrin (TM-β-CD) and carboxymethyl-β-cyclodextrin (CM-β-CD) has been studied.

The results indicate that BBG can form 1:2 inclusion complexes with α-CD and HP-α-CD, respectively, and 1:1 inclusion complexes with other six CDs. Their inclusion constants were calculated according to the literature [16–18] and the inclusion capacity of different CDs was compared. The inclusive ability of α-CD with BBG is the strongest, yet the inclusive ability of γ-CD is the weakest among the parent CDs. Modified α, β and γ-CDs exhibit stronger inclusive ability than their parent CDs. Therefore, the supramolecular data have provided information for the further application of CDs and BBG.

2. Experimental

2.1. Reagents and apparatus

Basic Brown G was purchased from Jinzhou of Hebei Province Chemical dyes Factory in China. Stock solution of 1.0×10^{-3} mol L^{-1} BBG was prepared by dissolving BBG directly in doubly distilled water. α-CD, β-CD and TM-β-CD (MW = 1427) were obtained from Sigma Chem. Co. γ-CD, HP-α-CD (MW = 1180), HP-β-CD (MW = 1380) and HP-γ-CD (MW = 1580) were purchased from Aldrich Chem. Co. CM-β-CD was synthesized. All the CDs were accepted for use without further purification and 1.0×10^{-2} mol L^{-1} CDs were prepared. Other reagents used were of analytical reagent grade and distilled water was used throughout.

A BAS-100A electrochemical analyzer (USA) with a PAR 303 electrode system (USA) serving as the working electrode was used. A saturated calomel electrode was used as reference electrode and a platinum wire as an auxiliary electrode. All the voltammograms were drawn with a DMP-40 digital platter. A JP-303 polarographic analyzer with three-electrode system (Chengdu Instrument Factory, China) was used for the quantitative analysis of BBG.

2.2. General procedure

To a dry10-ml volumetric flask, 1.0 ml of 0.1 mol L^{-1} NH_3–NH_4Cl (pH 9.1) buffer solution was added. Appropriate amounts of BBG working solutions were added and the solutions were diluted to final volume with distilled water.

If the inclusion constants were measured, solutions were added in the following order: 1.0 ml of 0.1 mol L^{-1} NH_3–NH_4Cl (pH 9.1) buffer solution, 1.0 ml of 1.0×10^{-3} mol L^{-1} BBG and an appropriate amount of 0.01 mol L^{-1} CDs, then dilute the solutions to final volume with distilled water shake them thoroughly and allow equilibrating at room temperature for 40 min.

The peak current (i_p'') was recorded in the potential range from −0.4 to −1.0 V (versus SCE). Under the same conditions, the peak current (i_{p_0}'') of the blank solution with CD was obtained and then the difference in peak current $\left(\Delta i_p'' = i_{p_0}'' - i_p''\right)$ was used to study the inclusion complex of BBG and CDs.

3. Results and discussion

3.1. Eelectroanalytical method of BBG

3.1.1. Choice of supporting electrolyte

The effect of the supporting electrolyte on the peak current, e.g. acetic acid–sodium acetate buffer (pH 5.0), sodium chloride solution (pH 7.0), phosphate buffer (pH 7.26), and ammonia–ammonium chloride buffer (pH 8–10.7), was examined. The experimental results show that a reduction peak is obtained for BBG in all the cases. However, this peak is more clear and sensitive in 0.1 mol L^{-1} ammonia–ammonium chloride buffer solution, so 0.1 mol L^{-1} NH_3–NH_4Cl buffer solution was selected as the supporting electrolyte. In the above-given buffer, a well-defined linear-sweep second derivative peak was obtained at −0.67 V (versus SCE) (Fig. 1).

3.1.2. Characteristic of reduction peak current of BBG

The effect of scan rate (v) on the peak current (i_p'') was investigated to elucidate the electrode reaction of BBG. When the concentrations of BBG are 5.0×10^{-6}, 1.0×10^{-5} and 1.0×10^{-4} mol L^{-1}, respectively, the peak current is proportional to the square root of scan rate $v^{1/2}$. The correlation coefficients of i_p''–$v^{1/2}$ are greater than those of i_p''–v, indicating that the peak current of BBG is controlled by diffusion.

In addition, a repetitive cyclic voltammogram of BBG in NH_3–NH_4Cl (pH 9.1) solution at an HMDE was examined: the cathodic peak potential $E_{p_c} = -0.67$ V and no anodic

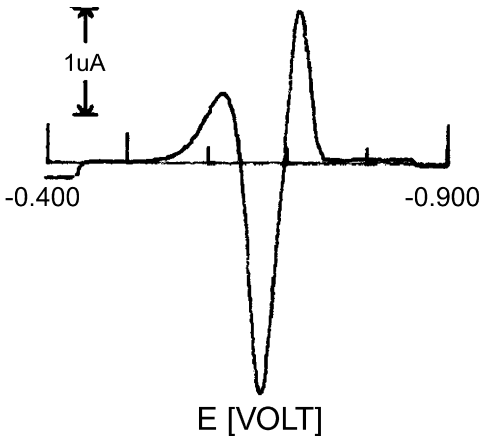

Fig. 1. Linear sweep second derivative voltammogram of 1.0×10^{-4} mol L^{-1}BBG in 0.1 mol $L^{-1}$$NH_3$–$NH_4Cl$ buffer solution (pH 9.1).

peak. It demonstrates that the reduction of BBG is an irreversible process. The repetitive cyclic voltammogram shows that the cathodic peak current decreases in the second cycle and reaches a constant value, which means that the peak current has adsorption behavior. The first derivative curve shows that the height of down branch is greater than that of up branch, which also means that the peak current has adsorption behavior. All of the above given matter indicates that the peak current of BBG not only is controlled by diffusion but also has adsorption behavior in the experiment.

3.1.3. Analytical application of BBG

In the presence of 0.1 mol L^{-1} NH_3–NH_4Cl (pH 9.1) buffer solution different concentrations of BBG were added and then carried out the experiment by method 2.2. The dependence of i_p'' on the concentration of BBG was investigated by LSV. There is a good linear relationship between the second derivative reduction peak height and concentration of BBG in the range of 3.0×10^{-8}–1.0×10^{-4} mol L^{-1}. The result is shown in Table 1.

The LOD is 9.0×10^{-9} mol L^{-1}. The precision of the determination of BBG is excellent, and at a concentration of 2.0×10^{-6} mol L^{-1}, the RSD was 2.4% ($n = 10$).

The content of artificial synthesis sample of BBG was 5.0×10^{-5} mol L^{-1}, in which standard solutions of different concentrations of BBG were added and the contents were determined by method 2.2. The results of recovery studies are listed in Table 2. The recovery of BBG varied from 95.3 to 102%. The mean recovery of BBG is 98.5%. It can be seen that BBG in synthesis samples can be determined with satisfactory results.

The interference of 16 foreign substances such as acid dyes, basic dyes and reactive dyes was tested with 1.0×10^{-4} mol L^{-1} BBG. It is found that small amount of dyes have little effect on the determination of BBG. Only few dye interfere with the assay of BBG.

3.2. Supramolecular system of Basic Brown G with cyclodextrins

3.2.1. Optimization of experimental conditions

3.2.1.1. Effects of pH value and buffer. The pH of buffer greatly affects the formation of complex between BBG and CDs. The concentrations of BBG and CD were fixed at 1.0×10^{-4} mol L^{-1} and 2.0×10^{-3} mol L^{-1}, respectively. The NH_3–NH_4Cl buffer solutions of different pH values were selected as supporting electrolyte to determine the formation of supramolecular complex. The result shows $\Delta i_p''$ primarily increased and then decreased with the increasing of pH value and it reached its maximum at pH 9.1, so pH 9.1 was chosen as the optimal pH.

Table 1
The relationship between i_p'' and concentration in different quantity grades

Range of concentration (mol L^{-1})	Linear equation	r
3.0×10^{-8}–1.0×10^{-7}	$i_p'' = 0.2974\ C + 1.027$	0.9985
1.0×10^{-7}–1.0×10^{-6}	$i_p'' = 3.764\ C + 1.002$	0.9980
1.0×10^{-6}–1.0×10^{-5}	$i_p'' = 42.28\ C + 42.47$	0.9987
1.0×10^{-5}–1.0×10^{-4}	$i_p'' = 217.2\ C + 141.7$	0.9935

Table 2
Determination results of recovery test of artificial synthesis sample

Samples	Added (mol L^{-1})	Found (mol L^{-1})	Recovery (%)
1	2.0×10^{-5}	1.93×10^{-5}	96.5
2	3.0×10^{-5}	2.86×10^{-5}	95.3
3	4.0×10^{-5}	3.93×10^{-5}	98.3
4	5.0×10^{-5}	5.01×10^{-5}	100.2
5	6.0×10^{-5}	6.12×10^{-5}	102

Experiments indicate that different buffers also have effect on the system. Among the tested buffers, such as NH_3–NH_4Cl, Na_2HPO_4–KH_2PO_4, NaCl and HAc–NaAc, NH_3–NH_4Cl buffer is suitable for the study of supramolecular system.

In the final 10 ml solution, different amounts of buffer solution, which were varied from 0.5 to 3.0 ml, also had effects on the system. $\Delta i_p''$ gave maximum when adding 1.5 ml buffer solution, so 1.5 ml NH_3–NH_4Cl is selected as the reaction buffer.

3.2.1.2. Effect of BBG concentration. The BBG concentration varied from 5.0×10^{-5} mol L^{-1} to 5.0×10^{-4} mol L^{-1}. The effect was studied with 2.0×10^{-3} mol L^{-1} CD and the result shows that $\Delta i_p''$ reached maximum at 4.5×10^{-4} mol L^{-1} and remains constant with increasing concentration of BBG. When BBG concentration is more than 2.0×10^{-4} mol L^{-1}, the reduction peak had a split for the sake of adsorption behavior at Hg electrode. Therefore, 1.0×10^{-4} mol L^{-1} BBG was employed for further experiment.

3.2.1.3. Reaction time and stability. The reaction between BBG and CDs occurs rapidly at room temperature within 35 min and remains constant for 2 h at least. Therefore, the

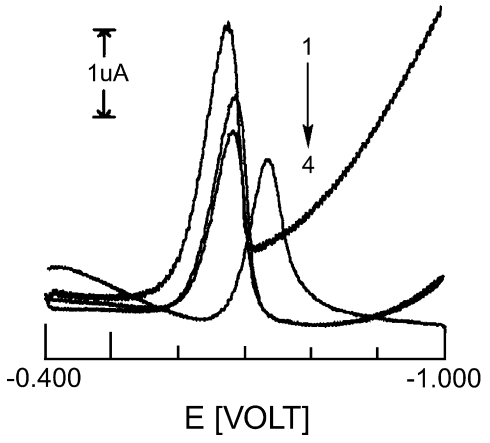

Fig. 2. Linear sweep voltammogram of 1.0×10^{-4} mol L^{-1}BBG in the absence of CDs (1) and presence of 2.0×10^{-3} mol L^{-1}CDs: (2) HP-α-CD; (3) HP-β-CD; (4) HP-γ-CD.

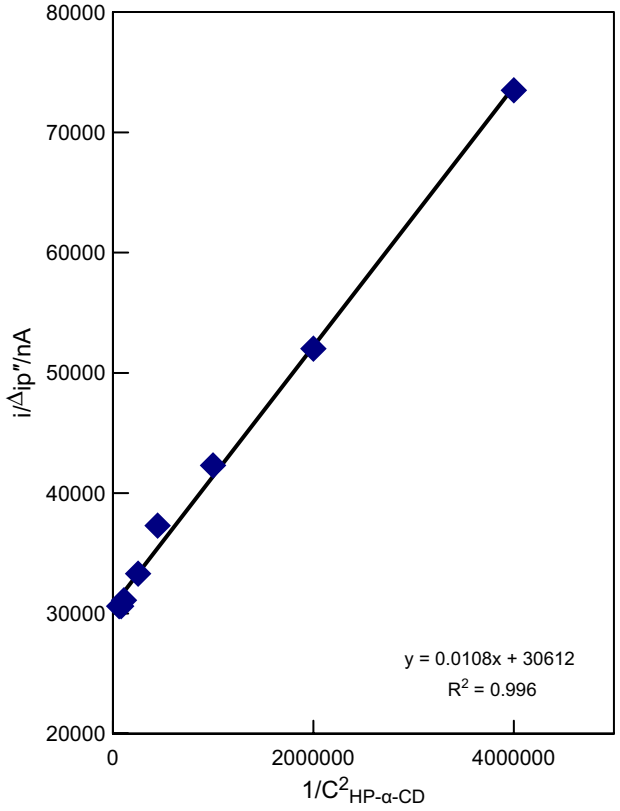

Fig. 3. The plot $1/i_p''$ versus $1/C^2_{[HP\text{-}\alpha\text{-}CD]}$.

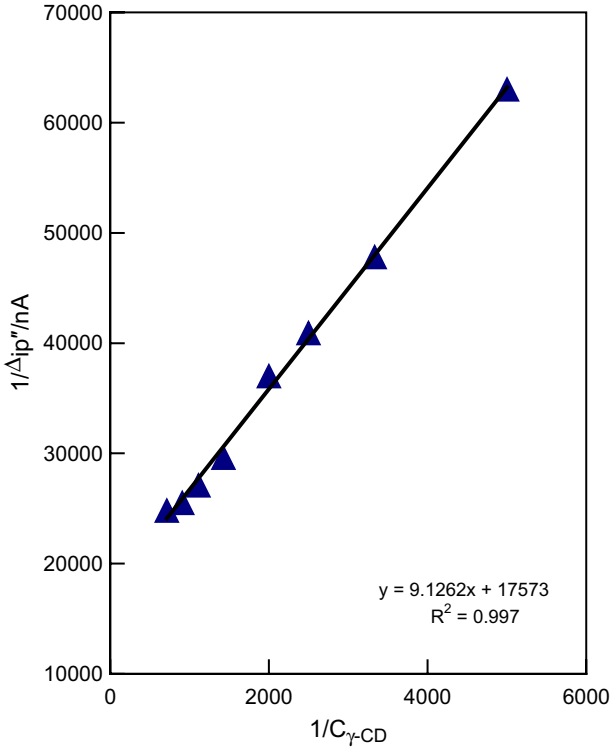

Fig. 4. The plot $1/i_p''$ versus $1/C^1_{[\gamma\text{-}CD]}$.

system allowed to equilibrate for 40 min gives ample time to measure the samples.

3.2.1.4. Optimization of instrument conditions. The scan rate and the dropping mercury static period of the instrument were studied in the paper. The peak current of the supramolecular was increased with the increase of scan rate in the range from 100 to 800 mV s^{-1} and reached maximum and stability at 400 mV s^{-1}. The dropping mercury static period was also optimized and selected at 11 s.

3.2.2. Electrochemistry behavior of BBG–CD inclusion complexes

Under the optimized condition, upon addition of different CDs to an aqueous BBG in 0.1 mol L^{-1} NH_3–NH_4Cl (pH 9.1) buffer solution (Fig. 2) a decrease in the peak current and negative shift in the peak potential are observed for BBG. The remarkable changes mean that electrochemically non-active complex BBG–CD is formed. The negative shift in the peak potential shows that the reduced form of the dye molecule is more strongly bound in the cavity of CD than in the oxidized form. The decreasing peak current is attributed to the formation of BBG–CD inclusion, which results in the decrease of equilibrium concentration of BBG in solution. The plots of i_p versus $v^{1/2}$ are linear both in the absence and presence of CD, indicating that the electron transfer process involves diffusing species.

3.2.3. Determination of stoichiometry and inclusion constant

The conformation of inclusion complexes results the decrease of the i_p and the negative shift of the E_p (Fig. 2). The change in peak currents and shift in peak potentials as the concentration of CD increases can be used to evaluate the inclusion constants if the formation and dissociation of the inclusion complex are fast enough to maintain equilibrium.

The stoichiometry and inclusion constants are estimated using the formula reported by Li and coworkers [16–18] in this paper. If BBG–CD_n is not electrochemically active, it is assumed that the decreasing value of the peak current is proportional to the concentration of BBG–CD_n inclusion complexes: according to the formula given by Refs. [16–18], $1/\Delta i_p = 1/\Delta i_{max} + 1/\{\beta \Delta i_{max} \times 1/[CD]^n\}$, where Δi_p stands for the peak current of BBG–CD supramolecule, $\Delta i_{p_{max}}$ is the peak

Table 3
The inclusion constants of BBG with eight CDs

CDs	α-CD	HP-α-CD	β-CD	HP-β-CD	TM-β-CD	CM-β-CD	γ-CD	HP-γ-CD
n	1:2	1:2	1:1	1:1	1:1	1:1	1:1	1:1
β (L mol^{-1})	8.2×10^5	2.8×10^6	2.1×10^3	1.8×10^4	5.2×10^3	1.3×10^3	1.9×10^3	9.5×10^4

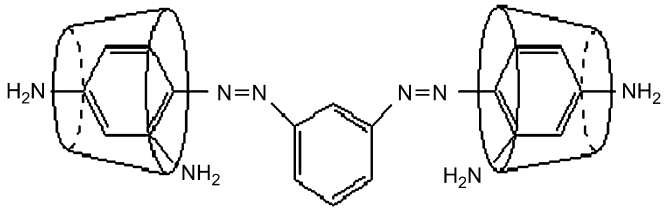

Fig. 5. The structure of inclusion complex BBG with α-CD or HP-α-CD.

current in case of complete BBG complexing, [CD] is the concentration of the CD, β is the condition formation constant and n is the inclusion ratio.

If BBG and CD form a complex BBG–CD_n, then let i_p'' replaces i_p and that is to say, when n is 1, 2, 3,…, respectively, the plots of $1/\Delta i_p''$ versus $1/[CD]^n$ give some curves. The value of n is the inclusion ratio when the curve becomes straight line and the value of β is intercept versus slope. From above formula, the slope equals to $1/\beta\Delta i_{max}$ and y-intercept equals to $1/\Delta i_{max}$ and β was obtained from the ratio of the y-intercept to the slope.

In our study, 1:2 complexes are formed between BBG and α-CD, HP-α-CD, respectively. The plot of $1/\Delta i_p''$ versus $1/[CD]^2$ of α-CD and HP-α-CD exhibited good linearity (Fig. 3) which verifies the 1:2 complexation stoichiometry. Plot of $1/\Delta i_p''$ versus $1/[CD]^1$ and other six CDs gave good linearity which verifies the 1:1 complexation stoichiometry (Fig. 4). Our experimental results are listed in Table 3.

3.2.4. Discussion of interaction mechanism

It is generally believed that dipole–dipole, electrostatic, van der Waals forces, hydrogen bond, hydrophobic interaction and the release of distortion energy of CD ring upon guest binding cooperatively govern the stability of inclusion complex [19].

From Table 3, it can be seen that modified α, β and γ-CDs exhibit stronger inclusive ability than their parent CDs implying that the cavity of the modified CDs provide a better protective microenvironment. Strong inclusive ability can be understood from the fact that the substitution by hydroxypropyl and tri-methyl groups leads to the enlargement of the bigger opening of parent CD cavity and the contraction of the smaller opening, and destroys the strong hydrogen bond network, which makes it easier for guest molecules to gain access to modified CDs cavity and to have bigger inclusion constants. It was in good agreement with the results obtained in the Ref. [19], so strong inclusion complex by modified β-CD is supposed to be applied more extensively.

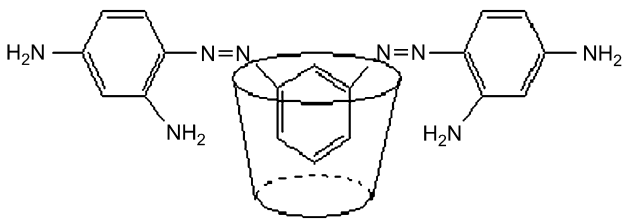

Fig. 6. The structure of inclusion complex BBG with β-CD or γ-CD.

The inclusive ability of α-CD with BBG is the strongest among the three parent CDs. This is because the cavity of α-CD has the best size match to the benzene ring of BBG, which is consistent with the Ref. [20], so that it can most effectively include BBG molecule. However, the cavity of β-CD and γ-CD is too big and couldn't match to the size of benzene ring, so the inclusive ability is weak. This is indicating that major factors affecting inclusive ability are size matching between CDs and guest and the hydrophobicity of the guest molecule.

Through the research of inclusion complex of BBG with α-CD or HP-α-CD, it can be estimated that the benzene ring part with group $-NH_2$ of BBG molecule entered the hydrophobic cavity of α-CD or HP-α-CD and hydrophilic group $-NH_2$ should be out of the cavity. While according to the stoichiometry of the inclusion complex of BBG with β-CD and γ-CD, the benzene ring part no substitute group with BBG molecule should enter the hydrophobic cavity of β-CD or γ-CD. The possible inclusion complexes could be seen from Figs. 5 and 6.

4. Conclusion

An electroanalytical method has been established for the determination of BBG at lower level. The experimental results have shown that this method could be used for the BBG analysis, which is sensitive, rapid, simple and accurate. Polarography and voltammetry have demonstrated the inclusion interaction between BBG and CDs. BBG can form inclusion complex with eight CDs. Modified α, β and γ-CDs exhibit stronger inclusive ability than their parent CDs. The inclusive ability of α-CD with BBG is the strongest, yet the inclusive ability of γ-CD is the weakest among the parent CDs. Furthermore, the application of polarography and voltammetry for the study on the inclusion interaction of supramolecular system was proved to be available, easy to perform and less time consuming.

Acknowledgement

This work was supported by the Natural Science Foundation of Shanxi Province of China and by the National Natural Science Foundation of China.

References

[1] Tonogai Y, Ito Y, Iwaida M, Tati M, Cse Y, Sato T, et al. The Journal of Toxicological Sciences 1979;4:211–9.
[2] Qian GZ. Dye chemistry. Shanghai, China: Shanghai Jiaotong University Press; 1988. p. 77.
[3] Bruins AP, Weidolf LOG, Henion JD, Budde WL. Analytical Chemistry 1987;59(22):2647–52.
[4] Fuh MR, Chia KJ. Talanta 2002;56:663–71.
[5] Perez-Urquiza M, Faerrer R, Beltran JL. Journal of Chromatography A 2000;883(1–2):277–83.
[6] Long JJ. Textile Auxiliaries 2003;20:31.
[7] Long JJ, Wang HZ. Dyes Printing 2002;28:4–5.
[8] Szejtli J. Cyclodextrin technology. Dordrecht: Kluver Academic; 1988.
[9] Tawarah KM, Khouri SJ. Dyes and Pigments 2000;45:229–33.

[10] Sastry CSP, Tipirneni ASRP, Suryanayana MV. Analyst 1989;114:513.
[11] Zhang GM, Shuang SM, Dong C, Pan JH. Spectrochimica Acta Part A 2003;59:2935–41.
[12] Tong LH. Cyclodextrins chemistry-based and application. Beijing: Science Press; 2001. p. 148–155.
[13] Li XJ, Lian J, Shuang SM, Pan JH. Journal of Analytical Science 1999;15(5):368–71.
[14] Li XF, Chen L, Wan QH. Journal of Tianjin Institute of Technology 2004;20(1):85–8.
[15] Wang XM, Chen HY. Spectrochimica Acta 1995;51(3):333–9.
[16] Yao XR, Zhang LQ. Polarographic catalytic wave atlas. Bejing: Geology Publishing House; 1988. p. 16–20.
[17] Li NQ, Gao XX. Chinese Journal of Analytical Chemistry 1971;1(4):40–8. 1974;2(6):459–461.
[18] Gao XX, Yao XR. Polarographic catalytic wave of the element of group Pt. Bejing, China: Science Press; 1977. p. 120–7.
[19] Qi WB, Qi ZH. New analytical synergistic agent. Hangzhou, China: Hangzhou University Press; 1994. p. 152.
[20] Liu Y, You CC, Zhang HY. Supramolecular chemistry. Tianjin: Nankai University Press; 2001. p. 194.