Journal of Inclusion Phenomena and Macrocyclic Chemistry (2006) 56: 237–241
DOI 10.1007/s10847-006-9089-y

Electrochemical Study on Reactive Red 15 and Its Interaction with Cyclodextrins

YOU-QIN LI[1,2], YU-JING GUO[1] and JING-HAO PAN[1,*]
[1]*School of Chemistry and Chemical Engineering, Shanxi University, 030006, Taiyuan, P.R. China;* [2]*Department of Chemistry, Datong University, 037009, Datong, P.R. China*

Key words: Reactive Red 15, interaction, cyclodextrin, supramolecular system, inclusion constant

Abstract

In this paper, the electrochemical behavior of the interaction of Reactive Brilliant Red K-2G (C.I. Reactive Red 15) with cyclodextrins in 0.1 $mol \cdot l^{-1}$ NaCl (pH 6.9) has been studied by polarography and voltammetry. In a supporting electrolyte of NaCl (pH 6.9), a sensitive second derivative reduction peak (i_p'') of Reactive Red 15 was found by linear sweep voltammetry (LSV). The peak potential is about −0.78 V (versus SCE). On the addition of CDs into the Reactive Red 15 solution, the reduction peak current (i_p'') of Reactive Red 15 decreases and the peak potential (E_p) shifts to a more positive potential. The study shows that Reactive Red 15 can form 1:1 inclusion complexes with nine CDs. The inclusion constants were calculated by ''electric current method''. Furthermore, the inclusion ability of different kinds of cyclodextrins was compared, which provided some elemental data for application of Reactive Red 15 and cyclodextrins.

Introduction

Cyclodextrins (CDs) are cyclic oligomers comprising six, seven, or eight (α,β, γ, respectively) glucopyranose units linked by α-1,4 bonds. CDs and derivatives of CDs have the peculiar ''interior hydrophobic, exterior hydrophilic'' structure forming a 1:1 or 1:2 inclusion complex with various guest molecules. The formation of inclusion complex changes the physical, chemical and biochemical property of guest molecules. So CDs were widely studied and used in many applied fields, such as agriculture, food, medical science, organic synthesis, and environmental protection [1]. In addition, CDs possessed extensive applied perspective in dye printing industry. The formation of inclusion complexes of cyclodextrin with dyes can modify dyes molecule's assemble state, sustain the release rate of dyes and avoid effectively hydrolysis of colors in dye bath [2]. It can improve retarding, migrating, levelling, and utilizing ratio of disperse dyes [3].

There has been a steady growth of interest in Supramolecular Chemistry. To date mainly UV spectrophotometry [4], visble spectrophotometry [5], fluorescence spectrophotometry [6], ^{1}HNMR [7], HPLC [8], phase solubility [9] and capillary electrophoresis [10] have been used for the study inclusion complexes of CDs and guest molecules.

Reactive Brilliant Red K-2G ($C_{25}H_{14}ClN_7O_{13}S_4 \cdot 4Na$) (C.I. Reactive Red 15) is one of the azo dyes, which is widely used in a variety of products, such as textile, paper, dye printing industry [11]. A number of azo dyes exhibit toxicity [12] leading to the need for sensitive analytical procedures for their determination at lower levels. H.F. Zhang *et al.* studied in detail photocatalytic degradation of Acid Red G and Reactive Red 15 by TiO_2 Photocatalyst [13, 14]. Besides, C.L.Huang *et al.* gave a discussion about inclusion complex mechanism of basic dyestuff with β-CD [15]. The structure of Reactive Red 15 is given in Figure 1.

To our knowledge, the papers about Reactive Red 15 interaction with CDs by means of polarography and voltammetry have been seldom reported in literatures. In this paper, the interactions of Reactive Red 15 with CDs were investigated by polarography and voltammetry. The interaction of Reactive Red 15 with α,β,γ-cyclodextrin (CD), hydroxypropyl-α-cyclodextrin (HP-α-CD), hydroxypropyl-β-cyclodextrin (HP-β-CD),

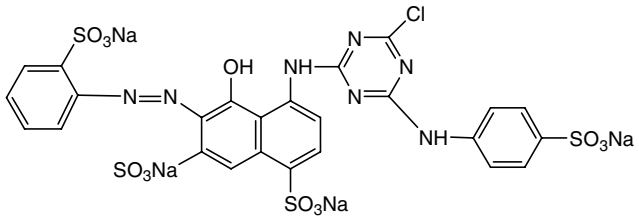


Figure 1. The structure of Reactive Brilliant Red K-2G (CI. Reactive Red 15).

* Author for Correspondence. E-mail: jhpan@sxu.edu.cn

hydroxypropyl-γ-cyclodextrin (HP-γ-CD), di- and tri-*o*-methyl-β-cyclodextrins (DM-β-CD and TM-β-CD), carboxymethyl-β-cyclodextrin (CM-β-CD) and sulfurbutylether-β-cyclodextrin (SBE-β-CD) have been studied in 0.1 mol·l^{-1} NaCl (pH 6.9).

The results indicate that Reactive Red 15 can form 1:1 inclusion complex with nine CDs, respectively. Their inclusion constants were calculated by "electric current method" and the inclusion capacity of different CDs was compared. The inclusive ability of α-CD with Reactive Red 15 is the strongest, yet the inclusive ability of β-CD is the weakest among the parent CDs. Derivatives of β-CD and γ-CD exhibits stronger inclusive ability than their parent CDs. Therefore, the supramolecular data have provided information for the further application of CDs and Reactive Red 15.

Experimental

Reagents and apparatus

Reactive Red 15 was purchased from Jiangsu Taixing Chemical Factory (China). γ-CD, HP-α-CD, HP-β-CD and HP-γ-CD was purchased from Aldrich. α-CD, β-CD, DM-β-CD, TM-β-CD were obtained from Sigma. SBE-β-CD were synthesized employing the paper written by Jacques Reuben [16]. All other reagents used were of analytical reagent grade and distilled water was used throughout.

A UV–visible spectrophotometer was used for recording absorption spectra. 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 auxiliary electrode. All voltammograms were drawn with a DMP-40 digital platter. A JP-303 polarographic analyzer with three electrodes system (Chengdu Instrument Factory, China) was used for the quantitative analysis of Reactive Red 15.

Method

Appropriate amounts of Reactive Red 15 working solutions were added to a 10 ml volumetric flask, the 1.0 ml 0.1 mol·l^{-1} NaCl (pH 6.9) solution was added, and the solutions were diluted to final volume with distilled water.

When the inclusion constants were measured, 1.00 ml Reactive Red 15 of the stock solution (1.0×10^{-4} mol·l^{-1}) were transferred into a 10 ml volumetric flask and an appropriate amount of 0.01 mol·l^{-1} CDs, 1.0 ml 0.1 mol·l^{-1} NaCl (pH 6.9) solution were added, then dilute the solutions to final volume with distilled water. Shake them thoroughly and allow equilibrating at room temperature for 10 min.

Results and discussion

Choice of supporting electrolyte

The effect of the supporting electrolyte on the peak current, e.g. acetic acid–sodium acetate buffer (pH 5.3), ammonia–ammonium chloride buffer (pH 9.5), phosphate buffer (pH 7.3), and sodium chloride solution (pH 6.9) was examined. The experiment results show that a reduction peak is obtained for Reactive Red 15 in all the cases. However, this peak is more clear and sensitive in 0.1 mol·l^{-1} NaCl (pH 6.9) buffer solution. In the presence of CDs, the peak current (i_p'') decreases and the peak potential (E_p) shifts to a more positive potential. The effect of CDs on both the i_p'' and the E_p are remarkable in this buffer than in the others. So 0.1 mol·l^{-1} NaCl (pH 6.9) solution was selected as the supporting electrolyte. In the above-given buffer, a well-defined linear-sweep second derivative peak was obtained at −0.78 V (versus SCE) (Figure 2).

Reduction peak current

To elucidate the electrode reaction of Reactive Red 15, a cyclic voltammogram at an HMDE was examined: the cathodic peak potential $Ep_c = -0.78$ V and no anodic peak. It indicates that the electrode reaction is irreversible. The effect of scan rate (v) on the peak current was investigated. When the concentration of Reactive Red 15 is 1×10^{-5} mol·l^{-1}, the peak current is proportional to the square root of scan rate $v^{1/2}$. The correlation coefficients of $i_p'' \sim v^{1/2}$ are greater than that of $i_p'' \sim v$. The linear regression equation may be represented as $i_p'' = 0.7953C + 174.2$ ($r = 0.9764$, $i_p'' \sim v$) and $i_p'' = 30.77C - 79.70$ ($r = 0.9969$, $i_p'' \sim v^{1/2}$), respectively. The first derivative curve shows that the height of up branch is greater than that of down branch, which indicates that i_p'' is diffusion current. All of the above given data indicate that when the concentration of Reactive Red 15 is 1×10^{-5} mol·l^{-1}, the variation of i_p'' is controlled by diffusion. The electro-reduction of Reactive Red 15 gives rise to a well-defined irreversible two-electron wave with the following reduction equation, which is caused by the electron uptake of the azo group.

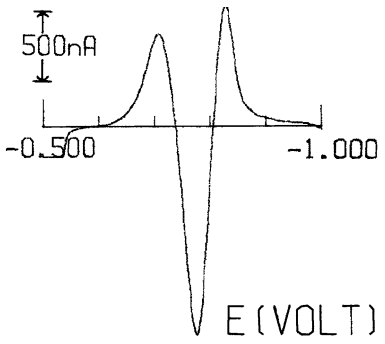
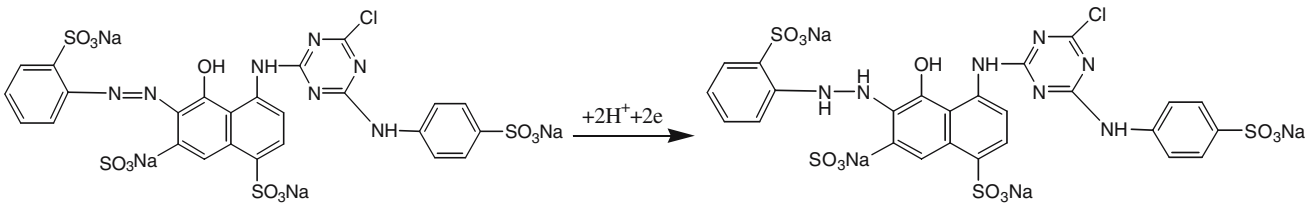


Figure 2. Linear sweep second derivative voltammogram of 1×10^{-4} mol·l^{-1} Reactive Red 15 in 0.1 mol·l^{-1} NaCl solution (pH 6.9).



In the presence of 0.1 mol·l^{-1} NaCl (pH 6.9) solution different concentration of Reactive Red 15 were added and then carried out the experiment by above method. The dependence of i_p'' on the concentration of Reactive Red 15 was investigated by LSV. There is a good linear relationship between the analytical characteristics (i_p'') and concentration of Reactive Red 15 in the range of $7.0\times10^{-8}\sim1.0\times10^{-4}$ mol·l^{-1}. The Limit of detection is 6.0×10^{-8} mol·l^{-1}. The result is shown in Table 1.

Supramolecular system of Reactive Red 15 with cyclodextrins

Confirmation of inclusion complexes

UV–vis absorption spectra. Figure 3 shows the UV–vis absorption spectra of Reactive Red 15 and its mixture with CDs at 0.1 mol·l^{-1} NaCl solution (pH 6.9), which was obtained by keeping the Reactive Red 15 concentration and pH value constant and changing the CDs concentration. In the wavelength range from 300 to 700 nm, CDs show no absorption and Reactive Red 15 has a maximum absorption at 503 nm (curve 1). On the addition of CDs, the absorbance of Reactive Red 15 at 503 nm decreased (curve 2, 3, 4). The changes of absorption spectra indicate that there are interactions between Reactive Red 15 and CDs and a new inclusion complex is formed.

Linear sweep voltammetry

In 0.1 mol·l^{-1} sodium chloride solution (pH 6.9), Reactive Red 15 with all the nine CDs gives rise to a decrease of the i_p and a shift of the E_p (Figure 4). It implies that all cyclodextrins can form inclusion complexes with Reactive Red 15.

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

Range of concentration (mol·l^{-1})	Linear regression equation	Correlation coefficient (r)
$7.0\times10^{-8}\sim1.0\times10^{-7}$	$i_p''=0.2204\ C+0.044$	0.9900
$2.0\times10^{-7}\sim1.0\times10^{-6}$	$i_p''=1.977\ C+2.058$	0.9947
$2.0\times10^{-6}\sim1.0\times10^{-5}$	$i_p''=21.99\ C-22.03$	0.9963
$2.0\times10^{-5}\sim1.0\times10^{-4}$	$i_p''=91.31\ C+603.7$	0.9893

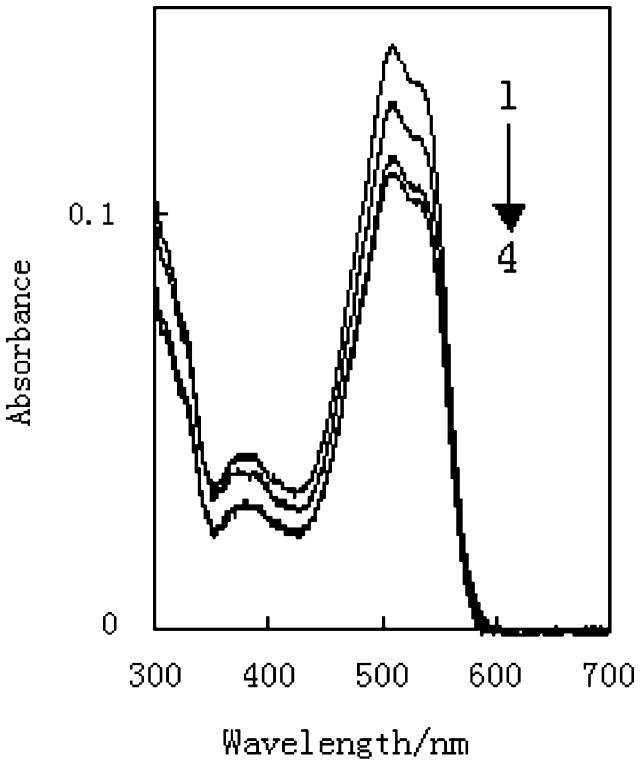


Figure 3. Absorption spectra of Reactive Red 15(1×10^{-5} mol·l^{-1}) in the absence of CDs and presence of 5×10^{-4} mol·l^{-1} CDs (2) γ-CD (3) α-CD (4)HP-γ-CD.

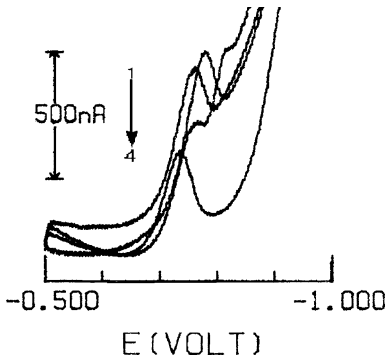


Figure 4. Linear sweep voltammogram of 1.0×10^{-5} mol·l^{-1} Reactive Red 15 in the absence of CDs (1) and presence of 2.0×10^{-4} mol·l^{-1}CDs: (2)α-CD; (3)β-CD; (4)γ-CD.

Determination of the stoichiometry

The determination of stoichiometry of the inclusion complex was performed using equimolar variation method. A series of solution, in which the total concentration is 1.0×10^{-5} mol·l^{-1}, were prepared and the mole ration of the Reactive Red 15 changed from 0 to 1.

The peak current in absence ($i_p''_0$) and presence of CDs ($i_p''_x$) were determined respectively. A plot of $\Delta i_p''$ ($i_p''_0 - i_p''_x$) versus the mole fraction of Reactive Red 15 (x_A) was provided in Figure 5. It shows a maximum at $x_A = 0.5$, indicating that the Reactive Red 15-CDs inclusion complex have 1:1 stoichiometry. In this mole ratio, the sharpest decrease of peak current is obtained.

Determination of the inclusion constant

The inclusion complexes of Reactive Red 15 with all CDs give rise to the decrease of the i_p'' and the positive shift of the E_p (Figure 4). It implies that all CDs can form inclusion complexes with Reactive Red 15 in 0.1 mol·l^{-1} sodium chloride solution (pH 6.9). The decrease of the peak current is due to the decrease of the apparent diffusion coefficient of Reactive Red 15, which has been formed the inclusion complexes with CDs. The positive shift of the peak potential suggests that the reduction of the inclusion complexes at the Hg electrode needs less activation energy [17].

The inclusion constants are calculated by "electric current method" [18] in this paper. The formula is:

$$i_p^2 = \frac{K_d}{[\mathrm{CD}]}(i_{px}^2 - i_p^2) + i_{p_{x-\mathrm{CD}}}^2$$

where i_{px} is the limited diffusion current of in the absence of CDs; i_p is the detected diffusion current of guest molecule in the presence of different concentration of CDs; $i_{px-\mathrm{CD}}$ is the limited diffusion current of Reactive Red 15 being included by CD; K_d is the dissociation constant. K ($1/K_d$) is the inclusion constant. Plot of i_p^2 versus $(i_{px}^2 - i_p^2)/[\mathrm{CD}]$ gave a curve in which the slope corresponds to K_d. From the reciprocal of slope, the inclusion constant can be calculated easily. The formation constants of Reactive Red 15 with different CDs are shown in Table 2.

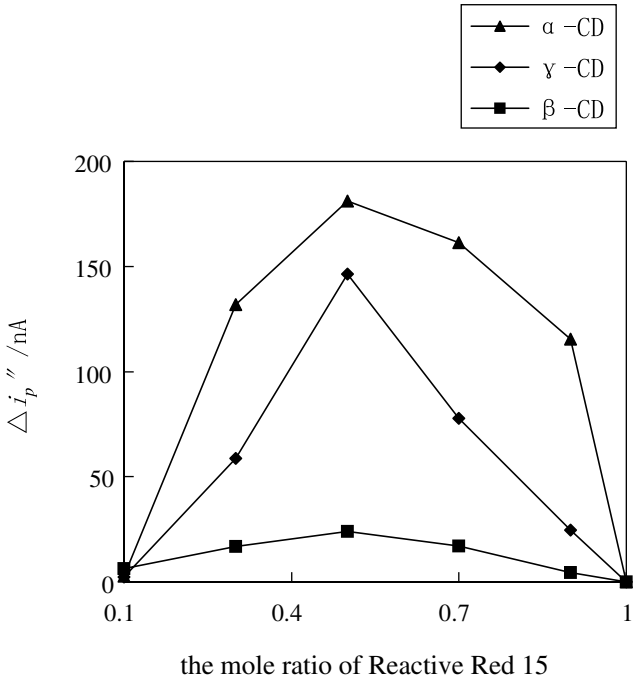


Figure 5. Continuous variation plot (Job Plot).

Table 2. The inclusion constants of Reactive Red 15 with CDs

CD	α-CD	β-CD	γ-CD	TM-β-CD	CM-β-CD
K (l/mol)	1.0×10^5	1.1×10^4	5.0×10^4	2.5×10^4	1.0×10^5
CD	HP-α-CD	HP-β-CD	HP-γ-CD	DM-β-CD	SBE-β-CD
K (l/mol)	–	1.3×10^5	1.0×10^5	1.1×10^6	1.0×10^5

Note: – Indicate the inclusive ability is very weak.

Discussion of the inclusion 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].

The experimental results show that derivatives of β-CD (DM-β-CD, HP-β-CD, SBE-β-CD, CM-β-CD and TM-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 inclusive ability can be understood that the substitution by hydroxypropyl, di-*o*-methyl, tri-*o*-methyl groups leads to the enlargement of the bigger opening of β-CD cavity and the contraction of the smaller opening and destroy the strong hydrogen bond network, which make it easier for guest molecules to gain access to derivative of CDs cavity and to have bigger inclusion constants. So strong inclusion complex of derivative of β-CD is supposed to be applied more extensively. Besides, the inclusive ability of α-CD with Reactive Red 15 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 construction unit of Reactive Red 15, which agrees with literature [20]. So that it can most effectively include Reactive Red 15. However the cavity of β-CD can't match well with the size of the benzene and naphthalene ring construction unit of Reactive Red 15, so the inclusive ability is weak. The possible structures of inclusion complexes of Reactive Red 15 with α-CD and γ-CD are shown in Figures 6 and 7.

Conclusion

Polarography and voltammetry have demonstrated the inclusion interaction between Reactive Red 15 and

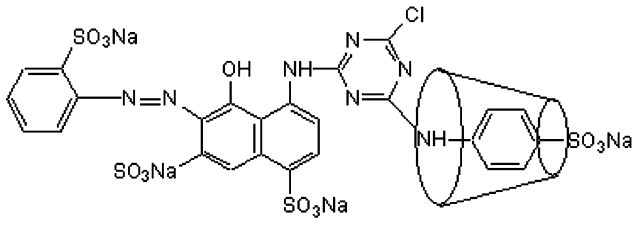


Figure 6. Structure of inclusion complex of Reactive Red 15 with. α-CD.

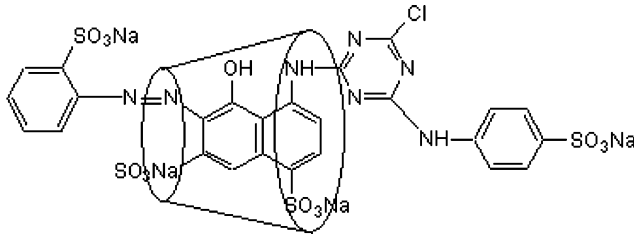


Figure 7. Structure of inclusion complex of Reactive Red 15 with. γ-CD.

different CDs. Reactive Red 15 can form 1:1 inclusion complex with nine CDs respectively. Modified β-CD such as DM-β-CD and HP-β-CD exhibits stronger inclusive ability than their parent CD. The inclusive ability of α-CD with Reactive Red 15 is the strongest, yet the inclusive ability of β-CD is the weakest among the parent CD. This is indicating the major factors affecting inclusive ability are size matching between CDs and guest and the hydrophobicity of the guest molecule. Furthermore, the polarography and voltammetry were proved to be available, easy to perform, less time consuming for the study on the inclusion interaction of supramolecular system [21].

Acknowledgement

This work was supported by the Natural Science Foundation of Shanxi province of China.

References

1. J. Gu, Y. Chang, and J.H. Pan: *Chinese J. Appl. Chem.* **13**, 5 (1996).
2. J.J. Long: *J. Text. Auxil.* **20**, 31 (2003).
3. J.J. Long and H.Z. Wang: *J. Dyes Printing* **28**, 4 (2002).
4. K.M. Tawarah and S.J. Khouri: *J. Dyes Pigments* **45**, 229 (2000).
5. C.S.P. Sastry, A.S.R.P. Tipirneni, and M.V. Suryanayana: *J. Analyst* **114**, 513 (1989).
6. G.M. Zhang, S.M Shuang, C. Dong *et al.*: *J. Spectrchimica Acta Part A* **59**, 2935 (2003).
7. L.H. Tong: *Cyclodextrins Chemistry-Based and Application*, Beijing Science Press, Beijing, China (2001), pp. 148.
8. A.N. Ahmed and S.M. El-Gizawy: *J. Chromatogr. Sci.* **25**, 424 (1987).
9. X.J. Li, J. Lian, S.M. Shuang *et al.*: *J. Anal. Sci.* **15**(5), 368 (1999).
10. X.F. Li, L. Chen, and Q.H. Wan: *J. Tianjin Inst. Technol.* **20**(1), 85 (2004).
11. H.L. He: *Dyes*, Chemical Industry Press, Beijing, China (2004), pp. 410.
12. G.Z. Qian: *Dye Chemistry* , Shanghai Jiaotong University Press, Shanghai, China (1988), pp. 77.
13. H.F. Zhang, C. Wen, and X.P. Geng: *J. Chem. Eng. Technol.* **33**(1), 33 (2004).
14. H.F. Zhang, C. Wen, and X.P. Geng: *J. Chem. Industry Time* **18**(1), 37 (2004).
15. C.L. Huang and W.B. Qi.: *J. Anal. Lab.* **9** (6), 1 (1990).
16. R.C. Jacques, T.R. Trinadha, and P. Joseph: *Carbohydr. Res.* **258**, 281 (1994).
17. P.Z. Li, M.Y. Wao, and T.T. Zhu: *Chin. J. Anal. Chem.* **22**(1), 58 (1994).
18. S.J. Dong and D.B. Zhang: *J. Acta Chimica Sinica* **46**, 335 (1988).
19. W.B. Qi and Z.H. Qi: *New Analytical Synergistic Agent*, Hangzhou University Press, Hangzhou, China (1994), pp. 152.
20. Y. Liu, C.C. You, and H.Y. Zhang: *Supramolecular Chemistry*, Nankai University Press, Tianjin, China (2001), pp. 194.
21. X.P. Wang, J.H. Pan, S.M. Shuang *et al.*: *Supramol. Chem.* **14**, 419 (2002).