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Electroanalytical Method of Acid Blue 120 and Its Supramolecular System with Cyclodextrins

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Key words: Acid Blue 120, cyclodextrin, inclusion constants, polarography, supramolecular system

Abstract

In this paper, a simple, rapid, sensitive and accurate electroanalytical method of Acid Blue 120 (AB120) has been established by polarography. In a supporting electrolyte of 0.01 mol l^{-1} Na_2HPO_4–KH_2PO_4 (pH 7.04) solution, a sensitive first derivative reduction peak (*ip′*) of AB120 was found by Linear Sweep Voltammetry (LSV). The peak potential is −820 mV (*versus* SCE). The peak current (*ip′*) is proportional to the concentration over the range 2.0×10^{-7}–5.0×10^{-5} mol l^{-1} ($r = 0.9961$–0.9991) and the limit of detection (LOD) is 1.0×10^{-7} mol l^{-1}. The recovery of AB120 varied from 95.3 to 103.0% and the relative standard deviation (RSD) was 2.2% ($n = 8$). The method has been expected to determination of wastewater in dye industry. In addition, the supramolecular system of AB120 with cyclodextrins has been studied. It can form 1:1 inclusion complex with six CDs. The inclusion constants were calculated and the inclusion ability of different kinds of CDs was compared. Furthermore, the inclusion mechanism was also preliminarily discussed, which provided some valuable information for further application of AB120 and CDs.

Introduction

Azo dyes consist of a diazotized amine coupled to an amine or a phenol, and contain one or more azo linkages. They are the largest class (60–70%) of dyes with the greatest variety colors. Approximately 10–25% of the dyes are released into the environment during dyeing of different substrates, such as textile fibers, paper, foodstuffs or leather [1]. Even at very low concentration (10–15 mg/l) water-soluble azo dyes can cause waste streams to become highly colored. Aside from their negative aesthetic effects certain azo dyes and biotransformation products have been shown to be toxic, and in some cases these compounds are carcinogenic and mutagenic [2, 3]. Therefore, it is necessary to optimize the analytical procedures for the determination of azo dyes at low level. In recent years, several methods have been reported, including HPLC and MS [4–6], photocatalysis [7], capillary electrophoresis [8–10] and thin layer chromatography [11]. But these methods are time consuming and the price of the apparatuses used is high. The paper established the electroanalytical method of Acid blue 120 (AB120) by polarography. The method of polarography is sensitive, rapid, simple, and accurate.

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The supramolecular system of AB120 with cyclodextrins was also investigated by polarography. The formation of inclusion complexes modifies the physical and chemical characteristics of guest molecules. It can improve the retarding, migrating and leveling of dyeing. It can also enhance thermostability [12, 13]. Various methods have been used for the study of the formation of inclusion complexes of azo dyes, such as spectroscopy [14–16], and volumetry [17]. However, the papers about AB120 interaction with CDs by means of electrochemical method have been seldom found in literatures. In this paper, the interaction of eight cyclodextrins, α, β, γ-cyclodextrin (CD), hydroxypropyl-β-cyclodextrin (HP-β-CD), di-o-methyl- and tri-o-methyl-β-cyclodextrins (DM-β-CD and TM-β-CD), hydroxypropyl-α-cyclodextrin (HP-α-CD), hydroxypropyl-γ-cyclodextrin (HP-γ-CD), with AB120 has been studied. The results indicate that AB120 can form 1:1 inclusion complex with six CDs, respectively. Their inclusion constants were calculated by 'electric current method' and the inclusion capacity of different CDs was compared. The inclusive ability of γ-CD with AB120 is the strongest, yet the inclusive ability of α-CD is the weakest among the parent CDs. Modified β-CD and modified γ-CD exhibits stronger inclusive ability than their parent CDs. Therefore, the supramolecular data have provided information for the further application of cyclodextrins and AB120 (Figure 1).

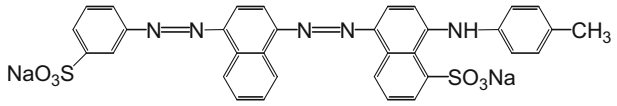

Figure 1. The structure of AB 120 (C.I.26400).

Experiment

Reagents and apparatus

AB120 was purchased from Jiangsu Gaoyou Chemical Factory, China. β-CD (YuNan Gourmet Factory, China) was purified by recrystallization in double distilled water. α-CD, γ-CD, HP-α-CD and HP-γ-CD was purchased from Aldrich. HP-β-CD (MW = 1,380), degree of substitution (DS = 0.6), DM-β-CD (MW = 1,412) TM-β-CD (MW = 1,427) were obtained from SIGMA. Other reagents used were of analytical reagent grade and distilled water was used.

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 AB120.

Method

Appropriate amounts of AB120 working solutions were added to a 10 ml volumetric flask, then 1.0 ml 0.1 mol l^{-1} Na_2HPO_4–KH_2PO_4 (pH 7.04) buffer solution was added, and the solutions were diluted to final volume with distilled water.

When the inclusion constants measured, 1.00 ml AB120 of the stock solution (1.0×10^{-3} 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} Na_2HPO_4–KH_2PO_4 (pH 7.04) buffer solution were added, then the solutions were diluted to final volume with distilled water. Shake them thoroughly and allow equilibrating at room temperature for 15 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 3.62, 5.86), ammonia–ammonium chloride buffer (pH 9.55), phosphate buffer (pH 7.04), and sodium chloride solution, was examined. The experiment results show that a reduction peak is obtained for AB120 in all the cases. However, this peak is more clear and sensitive in Na_2HPO_4–KH_2PO_4 (pH 7.04) buffer solution. So 0.01 mol l^{-1} Na_2HPO_4–KH_2PO_4 (pH 7.04) buffer solution was selected as the supporting electrolyte. In the above-given buffer, a well-defined linear sweep first derivative peak was obtained at −820 mV (*versus* SCE) (Figure 2).

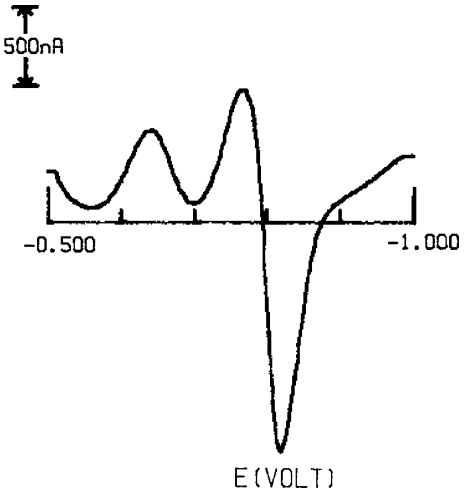

Figure 2. First derivative voltammogram of 1.0×10^{-4} mol l^{-1} AB120 in 0.01 mol l^{-1} phosphate buffer (pH 7.04).

The electroanalytical method of AB 120

In the presence of 0.01 mol l^{-1} Na_2HPO_4–KH_2PO_4 (pH 7.04) buffer solution different concentration of AB120 were added and then carried out the experiment by the above described method. The dependence of ip' on the concentration of AB120 was investigated by LSV. There is a good linear relationship between the analytical characteristics (ip') and concentration of AB120 in the range of 2.0×10^{-7}–5.0×10^{-5} mol l^{-1}. The result is shown in Table 1.

The limit of detection (LOD) is 1.0×10^{-7} mol l^{-1}. The precision of the determination of AB120 by LSV is excellent, and at a concentration of 1.0×10^{-6} mol l^{-1} the RSD was 2.2% ($n = 8$).

The content of artificial sample of AB120 was 1.0×10^{-6} mol l^{-1}, in which standard solutions of different concentration of AB120 were added and the contents were determined. The results of recovery studies are listed in Table 2. The recovery of AB120 varied from 95.3 to 103.0%. The mean recovery of AB 120 is 99.4%, which is able to meet the need of analytical work.

Supramolecular system of AB120 with cyclodextrins

Confirmation of inclusion complexes

In 0.01 mol l^{-1} Na_2HPO_4–KH_2PO_4 (pH 7.04) buffer solution, AB120 with all the six CDs gives rise to a

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

Equation	Range of concentration (mol l^{-1})	r
$ip' = -3.01 + 2.48c$	2.0×10^{-7}–1.0×10^{-6}	0.9965
$ip' = 3.375 + 20.3c$	1.0×10^{-6}–1.0×10^{-5}	0.9991
$ip' = -22.8 + 40.1c$	1.0×10^{-5}–5.0×10^{-5}	0.9961

Table 2. Recovery test of artificial sample

Component	Added (mol l^{-1})	Found (mol l^{-1})	Recovery (%)
1.0×10^{-6} mol l^{-1}	2.0×10^{-6}	1.995×10^{-6}	99.7
AB120	4.0×10^{-6}	3.811×10^{-6}	95.3
	6.0×10^{-6}	5.819×10^{-6}	97.0
	6.0×10^{-6}	6.182×10^{-6}	103.0
	8.0×10^{-6}	8.141×10^{-6}	101.8

decrease of the *ip′* and a shift of the *Ep* (Figure 3). It implies that all the six cyclodextrins can form inclusion complexes with AB120 in Na_2HPO_4–KH_2PO_4 (pH 7.04) buffer solution.

Confirmation of the diffusion current

To elucidate the electrode reaction of AB120, the effect of scan rate (v) on the peak current was investigated. When the concentration of AB120 is above 1×10^{-4} mol l^{-1}, the peak current is proportional to the square root of scan rate $v^{1/2}$. The correlation coefficients of $ip' \sim v^{1/2}$ are greater than that of $ip' \sim v$. The linear regression equation may be represented as $ip' = 0.0007c + 5.7851$ ($r = 0.9881$, $ip' \sim v$) and $ip' = 0.0266c + 5.5606$ ($r = 0.9981$, $ip' \sim v^{1/2}$), respectively. All of the above given matters indicate that in the lower concentration of AB120, the irreversible peak has adsorption behavior. However, when the concentration of AB120 is above 1×10^{-4} mol l^{-1}, the variation of *ip′* is controlled by diffusion.

Determination of 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^{-4} mol l^{-1}, were prepared and the mole ration of the AB120 changed from 0 to 1. The peak current in absence (ip_0') and presence of CDs (ip_x') were determined, respectively. A plot of $\Delta ip'$ (ip_0'–ip_x') *versus* the mole fraction of AB120 (x_A) was provided in Figure 4. It shows a maximum at $x_A = 0.5$, indicating that the AB120–CDs inclusion complex have 1:1 stoichiometry. In this mole ratio, the sharpest decrease of peak current is obtained.

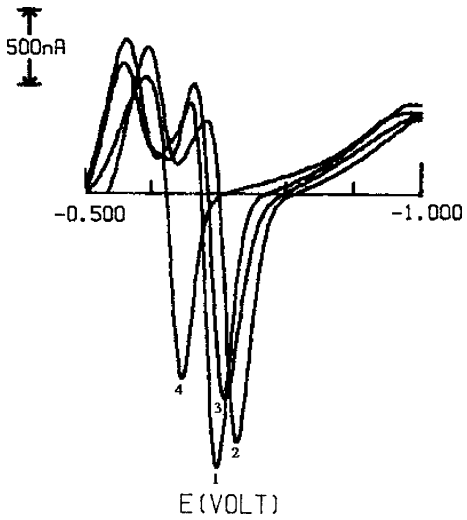

Figure 3. Linear sweep voltammogram of 1.0×10^{-4} mol l^{-1} AB120 in the absence of CDs (1) and presence of 1.0×10^{-3} mol l^{-1} CDs; (2) α-CD; (3) β-CD; (4) γ-CD.

Determination of the inclusion constant

The conformation of inclusion complexes result to the decrease of the *ip′* and the shift of the *Ep* (Figure 2). The decrease of the peak current is due to the decrease of the apparent diffusion coefficient of AB120, which has been formed the inclusion complexes with CDs. The shift of the *Ep* suggests that the reduction of the inclusion complexes at the Hg electrode needs less or more activation energy.

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

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

where ip_x is the limited diffusion current of in the absence of CDs; *ip* is the detected diffusion current of guest molecule in the presence of different concentration of CDs; $i_{px\text{-}CD}$ is the limited diffusion current of AB120 being concluded by CD; K_d is the dissociation constant. K ($1/K_d$) is the inclusion constant. Plot of ip^2 *versus* $(ip_x^2 - ip^2)/[CD]$ gives a curve in which the slope corresponds to K_d. From the reciprocal of slope, the inclusion constant can be calculated easily. Our experimental results are list in Table 3.

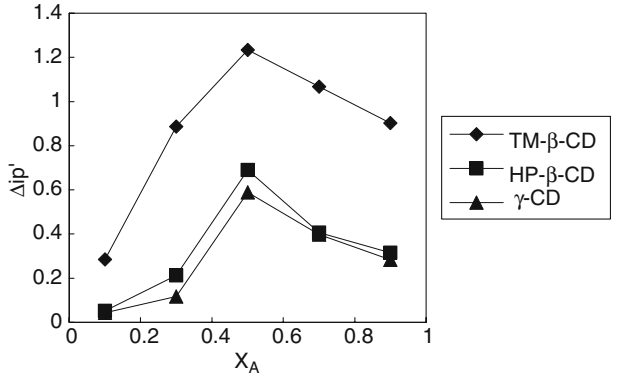

Figure 4. Continuous variation plot.

Table 3. The inclusion constants of AB120 with six CDs

CD	α-CD	β-CD	γ-CD	TM-β-CD
K(l/mol)	–	378	5.0×10^4	1.4×10^7
CD	HP-α-CD	HP-β-CD	HP-γ-CD	DM-β-CD
K(l/mol)	–	2.0×10^5	1.0×10^6	5.6×10^5

Note: – Indicate the inclusive ability is very weak.

The experimental results show that the modified β-CD (HP-β-CD, DM-β-CD, and TM-β-CD) and modified γ-CD (HP-γ-CD) exhibited stronger binding ability than the parent CDs 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 modified CDs cavity and to have bigger inclusion constants [19]. So strong inclusion complex by modified β-CD and γ-CD is supposed to be applied more extensively. The inclusive ability of γ-CD with AB120 is the strongest among the three parent CDs. This is because the cavity of γ-CD has the best size match to AB120. So that it can most effectively include AB120. However the cavity of α-CD is too small, so the inclusive ability is very weak.

Conclusion

Analytical method for AB120 was established by polarography. The reduction of AB120 in Na_2HPO_4–KH_2PO_4 (pH 7.04) buffer solution is an irreversible process. The peak current (*ip′*) is proportional to the concentration over the range 2.0×10^{-7}–5.0×10^{-5} mol l^{-1} ($r=0.9961$–0.9991) and the limit of detection is 1.0×10^{-7} mol l^{-1}. The recovery of AB120 varied from 95.3 to 103.0% and the RSD was 2.2%. The polarographic method is sensitive, rapid, simple and accurate. Polarography has demonstrated the inclusion interaction between AB120 and CDs. AB120 can form 1:1 inclusion complex with six CDs, respectively. Modified β-CD and γ-CD exhibits stronger inclusive ability than their parent CDs. The inclusive ability of γ-CD with AB120 is the strongest, yet the inclusive ability of α-CD is the weakest among the parent CDs. 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 was proved to be available, easy to perform, less time consuming for the study on the inclusion interaction of supramolecular system.

Acknowledgement

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