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# Electroanalytical method of Acid red 1 and its supramolecular system with cyclodextrins

Yu-Jing Guo *, Jing-Hao Pan, Xiao-Men Li, Fei Lu

*School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, China*

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**Abstract**

In this paper, electroanalytical method of Acid red 1 (AR 1) has been established and the supramolecular system of AR 1 with cyclodextrins has been studied by polarography and voltammetry. In a supporting electrolyte of 0.1 mol $l^{-1}$ NaCl solution, a sensitive second derivative reduction peak ($i_p''$) of AR 1 was found by Linear Sweep Voltammetry (LSV). The potential peak is −830 mV (vs. SCE). The peak current ($i_p''$) is proportional to the concentration over the range $5.0 \times 10^{-7}$–$2.0 \times 10^{-3}$ mol $l^{-1}$ ($r = 0.9961$–$0.9986$) and the limit of detection (LOD) is $2.0 \times 10^{-7}$ mol $l^{-1}$. The recovery of AR 1 varied from 99.19% to 102.9% and the relative standard deviation (RSD) was 1.8%. AR 1 can form 1:1 inclusion complex with 10 CDs. The inclusion constants were calculated by "electric current method". Furthermore, the inclusion ability of different kind of cyclodextrins was compared, which provided some elemental data for application of AR 1 and cyclodextrins.


*Keywords:* Polarography; Acid red 1; Cyclodextrin; Supramolecular system; Inclusion constants

## 1. Introduction

Azo dyes, which are widely used in a variety of products, such as textile, paper, foodstuffs or leather and form the largest group of organic dyes, constitute more than 35% of the world production of all dyes and thus are becoming extensively scattered throughout the environment around manufacturing plants. A number of azo dyes exhibits genotoxic and ecotoxic [1,2] leading to the need for sensitive analytical methods for their determination. In recent years, several methods have been reported, including HPLC and MS [3–6], 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 method of polarography is sensitive, rapid, simple, and accurate. In this paper, electroanalytical method of Acid red 1 (AR 1) has been established.

The supramolecular system of AR 1 with cyclodextrins was also investigated by polarography and voltammetry. 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 [12–14]. Various methods have been used for the study of the formation of inclusion complexes of azo dyes, such as spectroscopy [15–17], and volumetry [18]. However, the papers about AR 1 interaction with CDs by means of electrochemical method have been seldom found in literatures.

In this paper, the interaction of ten cyclodextrins, α, β, γ-cyclodextrin (CD), hydroxypropyl-β-cyclodextrin (HP-β-CD), di- and tri-methyl-β-cyclodextrins (DM-β-CD and TM-β-CD), carboxymethyl-β-CD (CM-β-CD), sulfurbutylether-β-cyclodextrin (SBE-β-CD), hydroxypropyl-α-cyclodextrin (HP-α-CD), hydroxypropyl-γ-cyclodextrin (HP-γ-CD), with AR 1 has been studied.

* Corresponding author. Fax: +86 351 7011688.
*E-mail address:* jhpan@sxu.edu.cn (Y.-J. Guo).

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The results indicate that AR 1 can form 1:1 inclusion complex with 10 CDs, respectively. Their inclusion constants are calculated by 'electric current method' and the inclusion capacity of different CDs was compared. Modified α-CD, γ-CD and β-CD (HP-β-CD, DM-β-CD and TM-β-CD) exhibit stronger inclusive ability than their parent CDs. However, the charged-β-CD (CM-β-CD and SBE-β-CD) shows weaker inclusive ability. The inclusive ability of γ-CD with AR 1 is the strongest, yet the inclusive ability of α-CD is the weakest among the parent CDs. Therefore, the supramolecular data have provided information for the further application of cyclodextrins and AR 1 (Fig. 1).

## 2. Experiment

### 2.1. Reagents and apparatus

AR 1 was purchased from Schmid Gmbh. Co. β-CD (YuNan Gourmet Factory) was purified by recrystallization in double distilled water. α-CD, γ-CD, HP-α-CD and HP-γ-CD were purchased from Aldrich. HP-β-CD (MW = 1380), degree of substitution (DS = 0.6), DM-β-CD (MW = 1412) and TM-β-CD (MW = 1427) were obtained from SIGMA. CM-β-CD and SBE-β-CD were synthesized employing the paper written by Jacques Reuben [19]. 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 electrode system (Chengdu Instrument Factory, China) was used for the quantitative analysis of AR 1.

### 2.2. Method

Appropriate amounts of AR 1 working solutions were added to a 10 ml volumetric flask, then 1 ml of 0.1 mol $l^{-1}$ NaCl solution was added, and the solutions were diluted to final volume with distilled water.

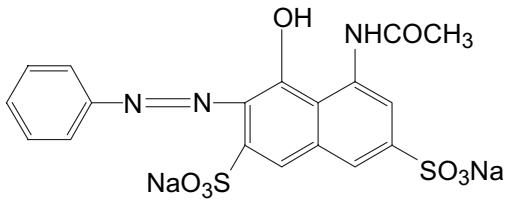


Fig. 1. The structure of AR 1 (C.I. 18050).

When the inclusion constants were measured, 1 ml AR 1 of the stock solution ($1.0 \times 10^{-3}$ mol $l^{-1}$) was transferred into a 10 ml volumetric flask and an appropriate amount of 0.01 mol $l^{-1}$ CDs, 1 ml of 0.1 mol $l^{-1}$ sodium chloride 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.

## 3. Results and discussion

### 3.1. 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 7.09), and sodium chloride solution, was examined. The experimental results show that a reduction peak is obtained for AR 1 in all the cases. However, this peak is more clear and sensitive in sodium chloride solution. So, 0.1 mol $l^{-1}$ sodium chloride solution was selected as the supporting electrolyte. In the above given buffer, a well-defined linear sweep peak was obtained at −830 mV (vs. SCE) (see Fig. 2).

### 3.2. The electroanalytical method of AR 1

In the presence of 0.1 mol $l^{-1}$ sodium chloride solution different concentrations of AR 1 were added and then the experiment was carried out by the method described in Section 2.2. The dependence of $i_p''$ on the concentration of AR 1 was investigated by LSV. There is a good linear relationship between the analytical characteristics ($i_p''$) and concentration of AR 1 in the range of $5.0 \times 10^{-7}$–$2.0 \times 10^{-3}$ mol $l^{-1}$. The result is shown in Table 1.

The LOD is $2.0 \times 10^{-7}$ mol $l^{-1}$. The precision of the determination of AR 1 by LSV is excellent, and at

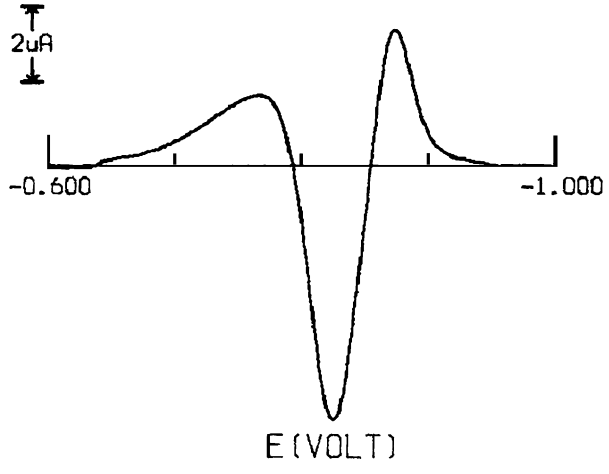


Fig. 2. Second derivative voltammogram of $1 \times 10^{-4}$ mol $l^{-1}$ AR 1 in 0.1 mol $l^{-1}$ sodium chloride solution.

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

| Equation | Range of concentration (mol l$^{-1}$) | $r$ |
|---|---|---|
| $i_p'' = -1.92 + 1.75c$ | $5.0 \times 10^{-7}$–$1.0 \times 10^{-6}$ | 0.9966 |
| $i_p'' = 2.28 + 4.32c$ | $1.0 \times 10^{-6}$–$1.0 \times 10^{-5}$ | 0.9986 |
| $i_p'' = 6.07 + 1.88c$ | $1.0 \times 10^{-5}$–$1.0 \times 10^{-4}$ | 0.9963 |
| $i_p'' = 2.22 + 3.81c$ | $1.0 \times 10^{-4}$–$2.0 \times 10^{-3}$ | 0.9961 |

a concentration of $2 \times 10^{-5}$ mol l$^{-1}$ the RSD was 1.8% ($n = 8$).

The content of artificial sample of AR 1 was $1 \times 10^{-6}$ mol l$^{-1}$, in which standard solutions of different concentration of AR 1 were added and the contents were determined by the method described in Section 2.2. The results of recovery studies are listed in Table 2. The recovery of AR 1 varied from 99.19% to 102.9%. The mean recovery of AR 1 is 100.7%, which is able to meet the need of analytical work.

### 3.3. Supramolecular system of AR 1 with cyclodextrins

#### 3.3.1. Confirmation of inclusion complexes

In 0.1 mol l$^{-1}$ sodium chloride solution, AR 1 with all the 10 CDs gives rise to a decrease of the $i_p''$ and a shift of the $E_p$ (Fig. 3). It was implied that all the ten cyclodextrins can form inclusion complexes with AR 1 in sodium chloride solution.

#### 3.3.2. Confirmation of the diffusion current

To elucidate the electrode reaction of AR 1, the effect of scan rate ($v$) on the peak current was investigated. When the concentration of AR 1 is above $1 \times 10^{-4}$ 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 $i_p = 0.0028c + 1.6203$ ($r = 0.9831$, $i_p \sim v$) and $i_p = 0.0984c + 0.8019$ ($r = 0.9983$, $i_p \sim v^{1/2}$), respectively. The first derivative curve shows that the height of up branch is greater than that of down branch, which shows that $i_p$ is the diffusion current. All of the above given matters indicate that in the lower concentration of AR 1, the irreversible peak has adsorption behavior. However, when the concentration of AR 1 is above $1 \times 10^{-4}$ mol l$^{-1}$, the variation of $i_p$ is controlled by diffusion.

Table 2
Recovery test of artificial sample

| Component | Added (mol l$^{-1}$) | Found (mol l$^{-1}$) | Recovery (%) |
|---|---|---|---|
| $1.0 \times 10^{-6}$ mol l$^{-1}$ AR 1 | $2.0 \times 10^{-6}$ | $1.986 \times 10^{-6}$ | 99.30 |
| | $4.0 \times 10^{-6}$ | $4.071 \times 10^{-6}$ | 101.8 |
| | $4.0 \times 10^{-6}$ | $4.003 \times 10^{-6}$ | 100.1 |
| | $6.0 \times 10^{-6}$ | $6.175 \times 10^{-6}$ | 102.9 |
| | $8.0 \times 10^{-6}$ | $7.935 \times 10^{-6}$ | 99.19 |

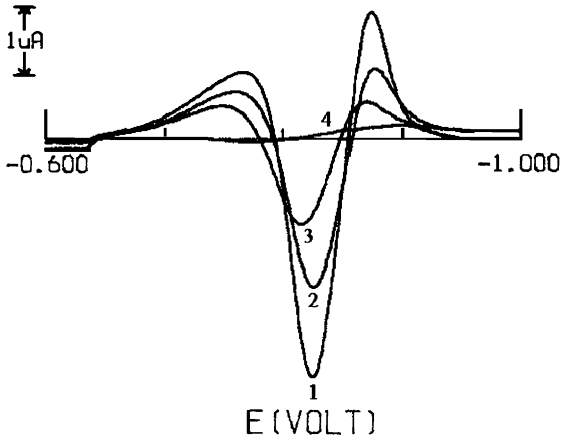


Fig. 3. Linear sweep voltammogram $1.0 \times 10^{-4}$ mol l$^{-1}$ AR 1 in the absence of CDs (1) and presence of $5 \times 10^{-4}$ CDs: (2) α-CD; (3) β-CD; (4) γ-CD.

#### 3.3.3. 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 $1.0 \times 10^{-4}$ mol l$^{-1}$, were prepared and the mole ratio of the AR 1 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 $\Delta i_p''$ ($i_{p_0}'' - i_{p_x}''$) vs. the mole fraction of AR 1 ($x_A$) is shown in Fig. 4. It shows a maximum at $x_A = 0.5$ indicating that the AR 1–CDs inclusion complexes have 1:1 stoichiometry. In this mole ratio, the sharpest decrease of peak current is obtained.

#### 3.3.4. Determination of the inclusion constant

The confirmation of inclusion complexes results in the decrease of the $i_p''$ and the positive shift of the $E_p$ (Fig. 3). The decrease of the peak current is due to the decrease in the apparent diffusion coefficient of AR 1, which has formed the inclusion complexes with CDs.

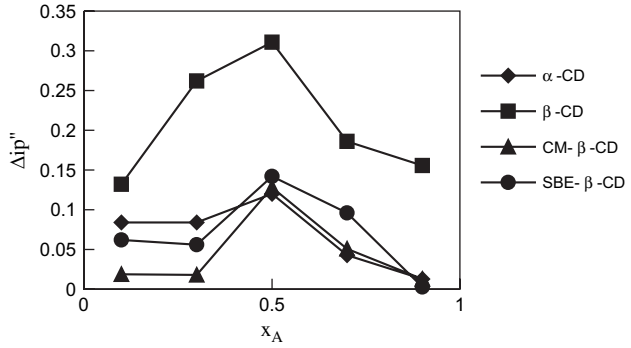


Fig. 4. Continuous variation plot.

The positive shift of the $E_p$ suggests that the reduction of the inclusion complexes at the Hg electrode needs less activation energy.

The inclusion constants are calculated by "electric current method" [20] 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 $i_{p_x}$ is the limited diffusion current of guest molecule in the absence of CDs; $i_p$ is the detected diffusion current of guest molecule in the presence of different concentration of CDs; $i_{p_{x-CD}}$ is the limited diffusion current of AR 1 being concluded by CD; $K_d$ is the dissociation constant. $K$ $(1/K_d)$ is the inclusion constant. Plot of $i_p^2$ vs. $(i_{p_x}^2 - i_p^2)/[CD]$ 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 listed in Table 3.

The experimental results show that the modified α-CD, β-CD (HP-β-CD, DM-β-CD and TM-β-CD) and 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, dimethyl and trimethyl groups leads to the enlargement of the bigger opening of CDs cavity and the contraction of the smaller opening and destroy 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 [21]. However, the inclusion ability of the two anionic cyclodextrins (CM-β-CD, SBE-β-CD) are smaller than that of the parent β-CD. It suggests that there is charge exclusion between them. The inclusive ability of γ-CD with AR 1 is the strongest among the three parent CDs. This is because the cavity of γ-CD has the best size match to AR 1. So that it can most effectively include AR 1. Yet the cavity of α-CD is small, so the inclusive ability is the weakest.

## 4. Conclusion

The electroanalytical method for AR 1 was established. The reduction of AR 1 in sodium chloride solution is an irreversible process. The peak current $(i_p'')$ is proportional to the concentration over the range $5.0 \times 10^{-7}$–$2.0 \times 10^{-3}$ mol l$^{-1}$ ($r = 0.9961$–$0.9986$) and the LOD is $2.0 \times 10^{-7}$ mol l$^{-1}$. The recovery of AR 1 varied from 99.19% to 102.9% and the RSD was 1.8%. The polarographic method is sensitive, rapid, simple and accurate. Polarography has demonstrated the inclusion interaction between AR 1 and CDs. AR 1 can form 1:1 inclusion complex with 10 CDs, respectively. Modified α-CD, γ-CD and β-CD (HP-β-CD, DM-β-CD and TM-β-CD) exhibit stronger inclusive ability. However, the charged-β-CD (CM-β-CD, SBE-β-CD) shows weaker inclusive ability. The inclusive ability of γ-CD with AR 1 is the strongest, yet the inclusive ability of α-CD is the weakest among the parent CDs. This indicates that the major factors affecting inclusive ability are size matching and the charge interaction between CDs and guest. Furthermore, the polarography was proved to be available, easy to perform and less time consuming for the study on the inclusion interaction of supramolecular system.

Table 3
The inclusion constants of AR 1 with 10 CDs

| CD | α-CD | β-CD | γ-CD | HP-β-CD | TM-β-CD |
|---|---|---|---|---|---|
| K | 1833 | $1.25 \times 10^4$ | $5.0 \times 10^4$ | $2.0 \times 10^5$ | $1.4 \times 10^6$ |
| CD | SBE-β-CD | CM-β-CD | HP-γ-CD | HP-α-CD | DM-β-CD |
| K | 1965 | 155 | $1.3 \times 10^5$ | $5.0 \times 10^4$ | $5.6 \times 10^5$ |

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