

# The Electrochemistry of the Inclusion Complex of Anthraquinone with $\beta$ -Cyclodextrin Studied by Means of OSWV

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**Abstract.** The reduction of anthraquinone (AQ) in the presence of  $\beta$ -Cyclodextrin ( $\beta$ -CD) has been investigated by Osteryoung square wave voltammetry (OSWV) in phosphate buffer (pH = 7.0).  $\beta$ -CD forms a 1:1 inclusion complex with AQ. The experimental results show that  $\beta$ -CD causes a decrease in the peak current ( $I_p$ ) and a negative shift in the peak potential ( $E_p$ ) for AQ reduction. The relationship between  $I_p$  (and  $E_p$ ) and the concentration of  $\beta$ -CD has been studied. The dissociation constant of the inclusion complex,  $K_d = 3.5 \times 10^{-3}$  mol/L, was obtained from the plot of  $I_p^2$  vs.  $(I_{p(AQ)}^2 - I_p^2)$  [CD]. The diffusion coefficients of free AQ and in the presence of  $\beta$ -CD have been determined by means of chronocoulometry (CC). The adsorption properties of  $\beta$ -CD on glassy carbon and gold electrodes was investigated. UV-vis spectra gave further evidence for complexation and the dissociation constant determined spectroscopically,  $K_d' = 4.5 \times 10^{-3}$  mol/L, was in agreement with that obtained electrochemically.

**Key words.** Osteryoung square wave voltammetry, anthraquinone,  $\beta$ -cyclodextrin.

## 1. Introduction

The cyclodextrins are among the most important and widely studied examples of host molecules that can form inclusion complexes with a variety of organic and inorganic compounds [1–6]. The included guest, being in a new chemical environment, is capable of undergoing novel and interesting reactions. For example, these systems are used as enzyme models to better understand site-recognition reactions [7], as synthetic tools, and in industrial applications such as molecular encapsulation. Considerable data have been obtained on the formation and structure of inclusion complexes in the crystalline state as well as on their kinetics, physical and chemical properties in solution [8]. However, relatively little information is available on the electrochemical behavior of CD systems.

Inclusion phenomena of CD systems are usually characterized by the dissociation constants or the formation constants of the inclusion complexes. Among various methods used for the determination of these constants, electrochemical methods are very effective when the guest molecule is electroactive. Matsue *et*

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*al.* [9] discussed the application of cyclic voltammetry (CV) to the evaluation of stability and dissociation constants of CD complexes.

Pulse voltammetry is a sensitive electrochemical method, especially for kinetic studies. In general, these experiments impose a stepwise change in potential, and the resulting current is sampled at the end of each potential pulse. Since the current is measured at constant potential, the current arising from the change in potential can be made negligible in comparison with the Faradaic current [10]. This permits the collection of excellent data at low concentrations of electroactive guests and it is a significant attribute considering the solubility of the electroactive guests. In our work, the inclusion phenomenon was investigated by Osteryoung square wave voltammetry.

Quinones play important roles in both electron and proton transportation in the inner layer of biological membranes. The chemistry of quinones has attracted much attention for a long time and quinone/hydroquinone (Q/QH<sub>2</sub>) couples have been widely used in electrochemical studies because they are readily available, easily handled under ordinary experimental conditions, and often exhibit 'well-behaved' electrochemistry. In this paper, a suitable model system, anthraquinone and  $\beta$ -CD, was investigated by means of OSWV. Some parameters, such as the dissociation constant and diffusion coefficients, were determined.

## 2. Experimental

### 2.1. CHEMICALS

Anthraquinone (Beijing Chemical Works, Beijing, China) was purified by sublimation before use.  $\beta$ -Cyclodextrin (Sigma) was used without further purification. The solvent was deionized water containing 0.25 mol/L NaH<sub>2</sub>PO<sub>4</sub>-NaOH (pH 7.0) as supporting electrolyte.

### 2.2. PREPARATION OF INCLUSION COMPLEX

A methanol solution of AQ was evaporated to dryness, then  $1.2 \times 10^{-3}$  mol/L to  $12 \times 10^{-3}$  mol/L  $\beta$ -CD aqueous solutions were added. The mixture was sonicated for 2 h and kept in darkness over night. The aqueous solution of the inclusion complex of AQ with  $\beta$ -CD was obtained.

### 2.3. APPARATUS

Electrochemical measurements were performed using a Bioanalysis system BAS 100B electrochemical analyzer with a HP747 plotter. A personal computer was used for data storage and processing. All experiments were carried out in a three-electrode cell system. The working electrode was a 0.25 cm diameter gold disk mounted in a Teflon sheath, polished to a mirror with 0.05  $\mu$ m alumina and rinsed with water in an ultrasonic cleaning bath. All potentials reported are vs. a Ag/AgCl

in 3 mol/L NaCl reference electrode and all experiments were performed at room temperature.

UV-Visible spectra were recorded on a Shimadzu UV-260 spectrophotometer.

### 3. Results and Discussion

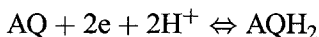
#### 3.1. EFFECT OF ELECTROLYTE

The kind of electrolyte has a significant influence on the stability constants of inclusion complexes [11,12]. Complexion of alkali metal cations is not as obvious as that of other inorganic anions [13, 14]. It was found that the most strongly complexed anions were  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{SCN}^-$  and  $\text{I}^-$ , while  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  did not seem to be complexed by CD. The concentration of electrolyte also affects the stability constants [2]. Experimental results showed that in the phosphate buffer, the values of the stability constants of inclusion complexes in 0.5 mol/L were about 20–25% greater than that in 0.1 mol/L solution.

In this report, all of the experiments were performed in 0.25 mol/L  $\text{NaH}_2\text{PO}_4$ –NaOH buffer (pH 7.0).

#### 3.2. OSWV BEHAVIOR OF AQ/ $\beta$ -CD COMPLEX

Free AQ exhibits an OSWV signal with a peak at  $-200$  mV vs. a Ag/AgCl reference electrode. The electron transfer mechanism under our experimental condition (aqueous solution, pH 7.0) can be outlined as [15]



The solutions of complexes of AQ with  $\beta$ -CD have similar electrochemical characteristics to those of free AQ, but the reduction peak potentials are shifted in a negative direction (Figure 1). This means that AQ is more difficult to reduce in the presence of  $\beta$ -CD because it is more strongly bound in the hydrophobic cavity than its reduced form ( $\text{AQH}_2$ ). A decrease of peak current is also observed upon addition of  $\beta$ -CD due to the smaller diffusion coefficient of the bulk cyclodextrin complex compared to that of free guest. The decrease of peak current as a function of the concentration of  $\beta$ -cyclodextrin is shown in Figure 2.

#### 3.3. DETERMINATION OF DISSOCIATION CONSTANT

It is known that  $\beta$ -CD forms a 1 : 1 inclusion complex with AQ [16]. We investigated the cyclic voltammetric behavior of this system and the experimental results show that with increasing scan rate ( $v$ ), the ratio of the cathodic peak current to  $v^{1/2}$  becomes smaller, see Table I, which is expected for a CE mechanism. The chronocoulometry results (see below) gave further evidence for this mechanism. This indicates that the inclusion complex is reduced via a CE scheme in which the complex first dissociates to AQ and  $\beta$ -CD followed by reduction of the free AQ.

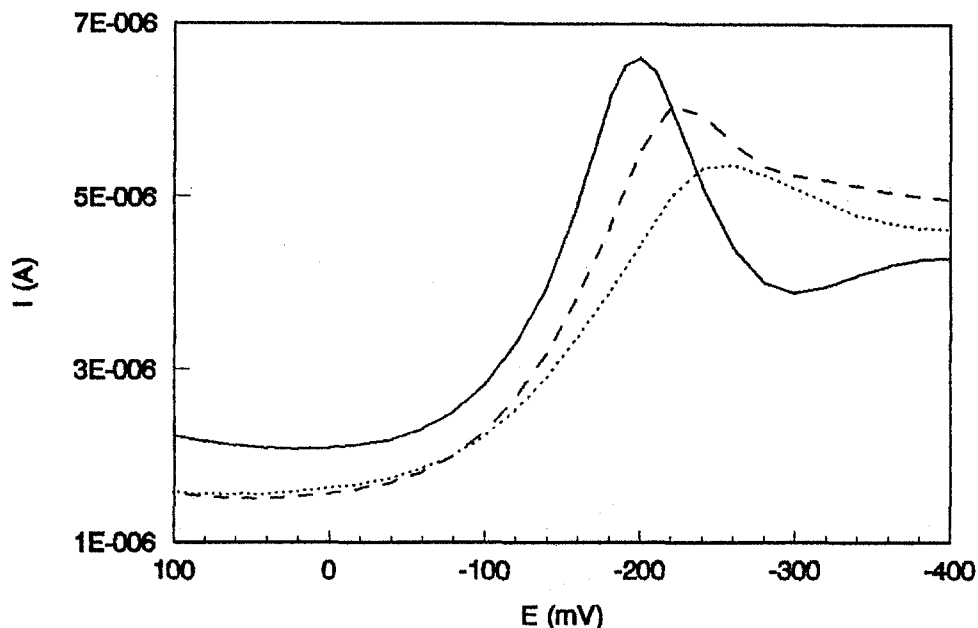
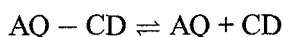


Fig. 1. OSWVs of  $1.2 \times 10^{-4}$  mol/L AQ in the absence (—) and presence of  $2.4 \times 10^{-3}$  mol/L (---) and  $12.0 \times 10^{-3}$  mol/L (...)  $\beta$ -CD. Step height = 4 mV, square-wave amplitude = 25 mV, frequency = 15 Hz.

Table I. The ratio of the cathodic peak current ( $I_p$ ) to the square root of the scan rate at different scan rates ( $v$ ).

$v$ (mV/S)	10	50	100	500	800	1000
$I_p/v^{1/2}$ ( $\mu\text{A}/(\text{mV/S})^{1/2}$ )	0.76	0.70	0.67	0.65	0.61	0.59

For the equilibrium



the dissociation constant ( $K_d$ ) is

$$K_d = \frac{[\text{AQ}][\text{CD}]}{[\text{AQ} - \text{CD}]}, \quad (1)$$

where [CD], [AQ] and [AQ - CD] are the concentrations of  $\beta$ -CD, free AQ and inclusion complex, respectively.

In our experiments, the pulse width of OSWV was wide enough and the formation and dissociation of inclusion complex are fast enough to maintain equilibrium

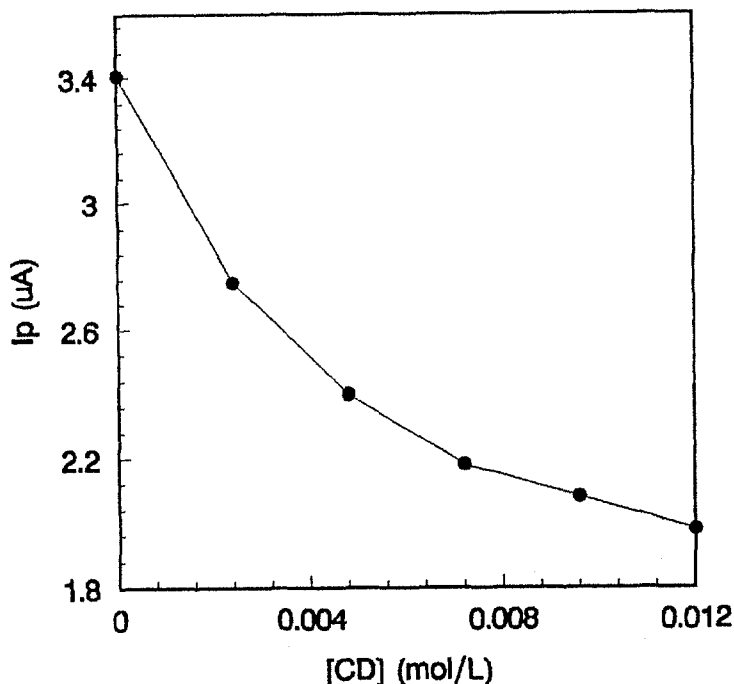


Fig. 2. Peak current for  $1.2 \times 10^{-4}$  mol/L AQ as a function of the total concentration of  $\beta$ -CD.

on the time scale of the experiment. Thus the observed diffusion coefficient ( $D_{\text{obs}}$ ) can be calculated according to [17,18] as:

$$D_{\text{obs}} = \frac{D_{\text{AQ}}[\text{AQ}] + D_{\text{AQ-CD}}[\text{AQ-CD}]}{[\text{AQ}] + [\text{AQ-CD}]} \quad (2)$$

where  $D_{\text{AQ}}$ ,  $D_{\text{AQ-CD}}$  are the diffusion coefficients of free guest and inclusion complex.

For OSWV, we know [10] that

$$I = \psi n F A C_o^* (D_0 / \pi t_p)^{1/2} \quad (3)$$

where  $A$  is the electrode area,  $C_o^*$  is the concentration of the guest, and  $D_0$  denotes the diffusion coefficient of the diffusing species,  $\psi$  is the dimensionless current function which depends on the chemistry of the redox process and the applied potential waveform.

From Equations (1), (2) and (3), the relationship between current and dissociation constant is obtained

$$I_p^2 = \frac{K_d}{[\text{CD}]} (I_{p(\text{AQ})}^2 - I_p^2) + I_{p(\text{AQ-CD})}^2 \quad (4)$$

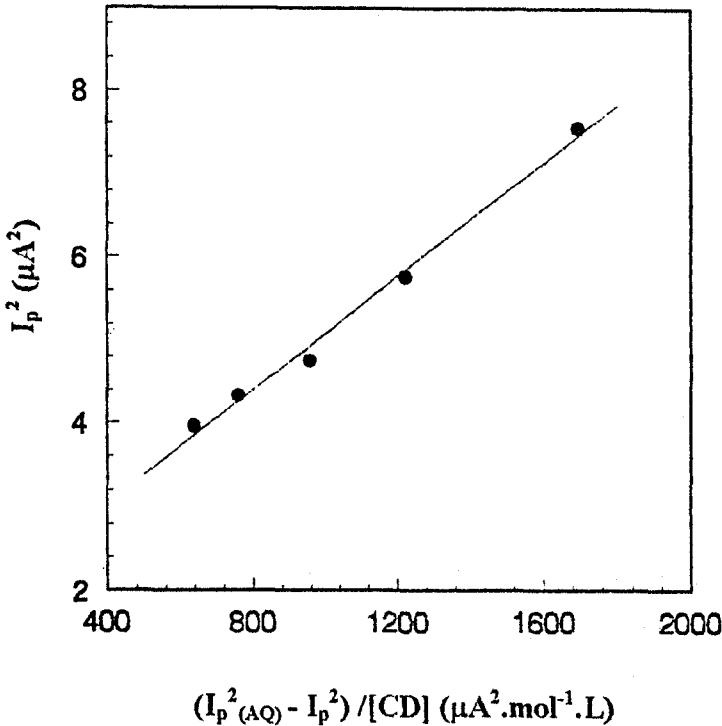


Fig. 3. The plot of  $I_p^2$  vs.  $(I_p^2(\text{AQ}) - I_p^2)/[\text{CD}]$ . The concentration of AQ is  $1.2 \times 10^{-4}$  mol/L. Solid line is the regression line with slope ( $K_d$ ) =  $3.5 \times 10^{-3}$  mol/L.

where  $I_p$  is the observed current,  $I_{p(\text{AQ}-\text{CD})}$  and  $I_{p(\text{AQ})}$  are the peak currents of inclusion complex and free AQ, respectively.  $I_p$  and  $I_{p(\text{AQ})}$  can be determined from the experiments. The value of  $K_d$  can be obtained from the slope of the linear plot of  $I_p^2$  vs.  $(I_p^2(\text{AQ}) - I_p^2)/[\text{CD}]$ .

In our work, the dissociation constant ( $K_d = 3.5 \times 10^{-3}$  mol/L) for the inclusion complex of AQ with  $\beta$ -CD was calculated according to Equation (4) by regression analysis, see Figure 3.

#### 3.4. EVALUATION OF DIFFUSION COEFFICIENTS

The diffusion coefficients of AQ in the absence and in the presence of  $\beta$ -CD have been determined by means of Chronocoulometry (CC). The total charge ( $Q$ ) can be described by [19]

$$Q = \frac{2nFAD^{1/2}Ct^{1/2}}{\pi^{1/2}} + Q_{\text{dl}} + Q_{\text{ads}} \quad (5)$$

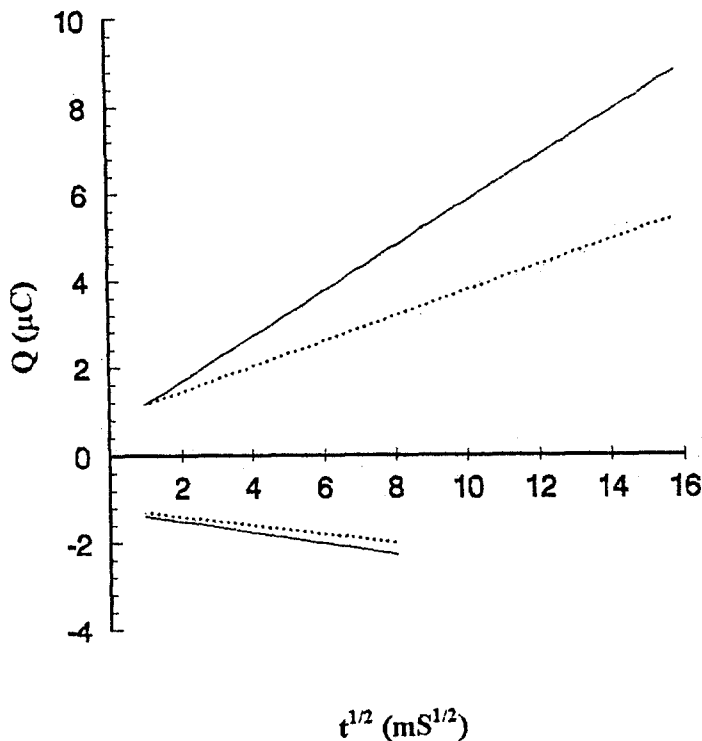


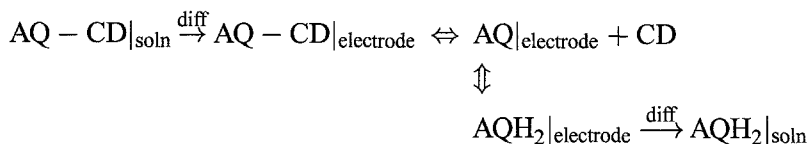
Fig. 4. Anson plots of chronocoulometry of  $1.2 \times 10^{-4}$  mol/L AQ in the absence (—) and presence (----) of  $9.6 \times 10^{-3}$  mol/L  $\beta$ -CD. Pulse width = 250 mS.

where  $Q_{dl}$  is the capacitive charge (double layer) and  $Q_{ads}$  is the charge caused by adsorption. From Equation (5), it can be seen that a plot of  $Q$  vs.  $t^{1/2}$  should be linear, and  $D$  can be determined from the slope of this line.

In this paper, a suitable system,  $\text{Fe}(\text{CN})_6^{3-/4-}$ , whose diffusion coefficient is known to be  $7.6 \times 10^{-6}$  cm<sup>2</sup>/S [20], was employed to evaluate the electrode area ( $A$ ) by CC. The diffusion coefficients of AQ in the absence ( $D_f = 1.5 \times 10^{-6}$  cm<sup>2</sup>/S) and in the presence of  $9.6 \times 10^{-3}$  mol/L  $\beta$ -CD ( $D_c = 0.8 \times 10^{-6}$  cm<sup>2</sup>/S) were determined from the slopes of the corresponding upper lines in an Anson plot (Figure 4). It is also known that  $\beta$ -CD could cause an increase in the solution viscosity with a corresponding decrease in the diffusion coefficients. However, over the range of  $0$ – $10 \times 10^{-3}$  mol/L, no change in solution viscosity could be detected [1]. So the decrease of the diffusion coefficient can be attributed to the complexation between AQ and  $\beta$ -CD.

From the Anson plot, we see that the upper lines, which refer to the forward reaction, show different slopes with regard to the different diffusion coefficients of free AQ and the AQ- $\beta$ -CD complex, while the lower ones have almost the same slopes, which indicates that the reduction product was freed from the cavity of  $\beta$ -

CD and diffused away from the electrode surface. The difference of the intercepts of the corresponding lines could be explained by the influence of  $\beta$ -CD on the capacitive charge. The overall process might be as follows (Scheme I):



Scheme I

### 3.5. ADSORPTION OF $\beta$ -CD ON ELECTRODES

It is known that  $\beta$ -CD adsorbs on glassy carbon electrodes [1]. However, this phenomenon has been ignored in most previous electrochemical studies of cyclodextrins at glassy carbon electrodes. According to the study of Osteryoung [10], this leads to two complications. First,  $\beta$ -CD is desorbed at a potential negative to the potential of zero charge, which results in a large tensametric peak. This distorts the shape of the voltammetry and makes it impossible to obtain accurate values of characteristics, such as  $E_p$  and  $I_p$ . Second, the model developed for the pseudo-first-order CE mechanism requires that the concentration of the host be independent of time and position. Clearly, this condition is violated if the host is adsorbed and then desorbed at the electrode.

The influence of quiet time on the peak current in OSWV on a glassy carbon electrode and on a gold electrode was investigated. The plot of current density, the ratio of the cathodic peak current to the electrode area, vs. quiet time is shown in Figure 5. It is obvious that the adsorption of  $\beta$ -CD is poor on a gold electrode, while that on a glassy carbon electrode is strong, which may affect the measurement of the peak current on our experimental time scale. That is to say that a gold electrode is more effective than a glassy carbon electrode in the study of inclusion phenomena of cyclodextrins.

### 3.6. ABSORPTION MEASUREMENTS

Further evidence for complexation of anthraquinone by  $\beta$ -cyclodextrin was found in the UV-visible spectra. An increase in absorbance was observed upon addition of  $\beta$ -CD to a solution of AQ. Figure 6 shows the effect of  $\beta$ -CD on the UV-vis absorption spectrum. With the increase of the concentration of  $\beta$ -CD, the absorbance of AQ in the 200–350 nm region increased. The dissociation constant ( $K'_d$ ) of this complex was determined according to the Benesi–Hildebrand equation [21]. Under the condition of 1 : 1 inclusion complex formation equilibrium with an excess of the



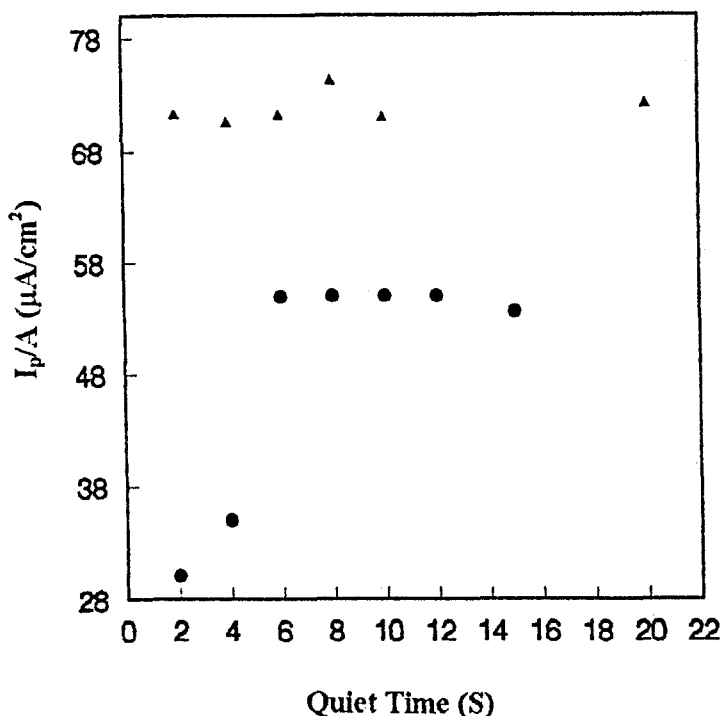


Fig. 5. Plot of the cathodic peak current density vs. the quiet time on a glassy carbon electrode (●) and on a gold electrode (▲) in a solution containing  $1.2 \times 10^{-4}$  mol/L AQ and  $6.0 \times 10^{-3}$  mol/L  $\beta$ -CD.

concentration of  $\beta$ -CD compared with the total concentration of AQ, the equation can be represented as follows:

$$A_0 = \varepsilon_0 l [AQ]_0 \quad (6)$$

$$[AQ]_e + [AQ - CD]_e = [AQ]_0 \quad (7)$$

$$A = \varepsilon_{AQ} l [AQ]_0 + (\varepsilon_{AQ-CD} - \varepsilon_{AQ}) l [AQ - CD]_e \quad (8)$$

where  $A_0$  and  $A$  are the absorbance of free AQ and complexed AQ (i.e. AQ- $\beta$ -CD).  $[AQ]_0$  denotes the initial concentration of AQ.  $[AQ]_e$  and  $[AQ - CD]_e$  are the equilibrium concentrations of AQ and AQ- $\beta$ -CD.  $\varepsilon_{AQ}$  and  $\varepsilon_{AQ-CD}$  are the adsorption coefficients of AQ and AQ- $\beta$ -CD.  $l$  is the length of the light path, which is 1 cm in our experiments.

By combining Equations (1), (6), (7) and (8), we obtain

$$\frac{A_0}{A - A_0} = \frac{\varepsilon_{AQ}}{\varepsilon_{AQ-CD} - \varepsilon_{AQ}} + \frac{\varepsilon_{AQ}}{\varepsilon_{AQ-CD} - \varepsilon_{AQ}} \times \frac{K'_d}{[CD]} \quad (9)$$

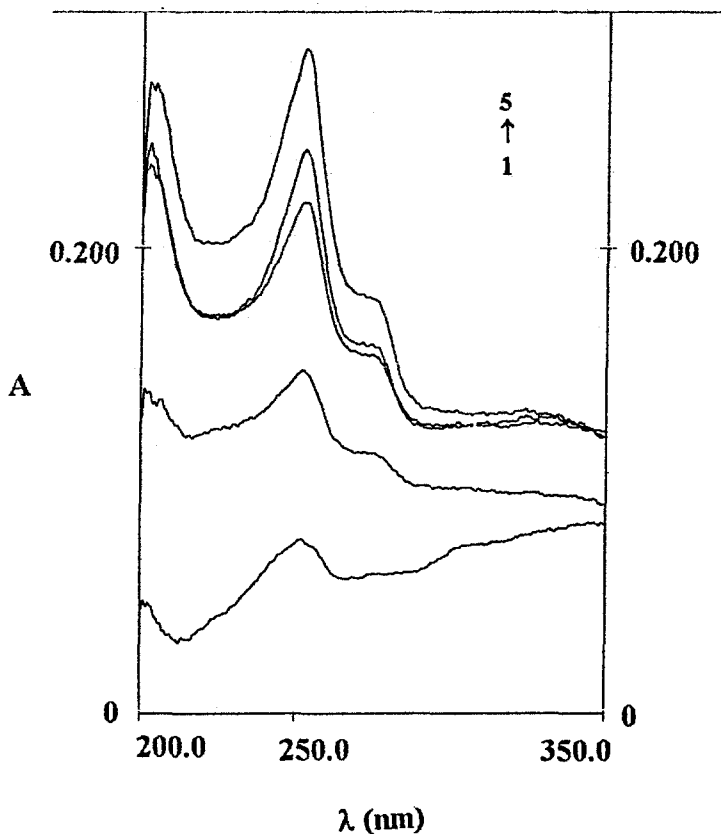


Fig. 6. UV-vis spectra of  $1.2 \times 10^{-4}$  mol/L AQ in the absence (1) and presence of  $1.2 \times 10^{-3}$  mol/L (2),  $3.6 \times 10^{-3}$  mol/L (3),  $4.8 \times 10^{-3}$  mol/L (4) and  $6.0 \times 10^{-3}$  mol/L (5)  $\beta$ -CD.

According to Equation (9), from the  $A_0/(A - A_0)$  vs.  $1/[\text{CD}]$  plot, the ratio of the slope to the intercept gives the value of the dissociation constant. Our experimental data are shown in Figure 7, and the dissociation constant of AQ- $\beta$ -CD complex was evaluated to be  $4.5 \times 10^{-3}$  mol/L. This value agrees with that determined electrochemically with regard to the deviation of different methods.

#### 4. Conclusion

This paper demonstrates that OSWV is a successful method for the investigation of inclusion reactions. A suitable electrolyte was selected according to the literature. OSWVs of free AQ and the inclusion complex were studied. The quantitative parameters, such as dissociation constant ( $K_d = 3.5 \times 10^{-3}$  mol/L) and diffusion coefficients ( $D_f = 1.5 \times 10^{-6}$  cm<sup>2</sup>/S and  $D_c = 0.8 \times 10^{-6}$  cm<sup>2</sup>/S) for the AQ/ $\beta$ -CD inclusion complex, were obtained from the electrochemical experiments. UV-vis spectroscopy was used not only to study this inclusion phenomenon, but also to

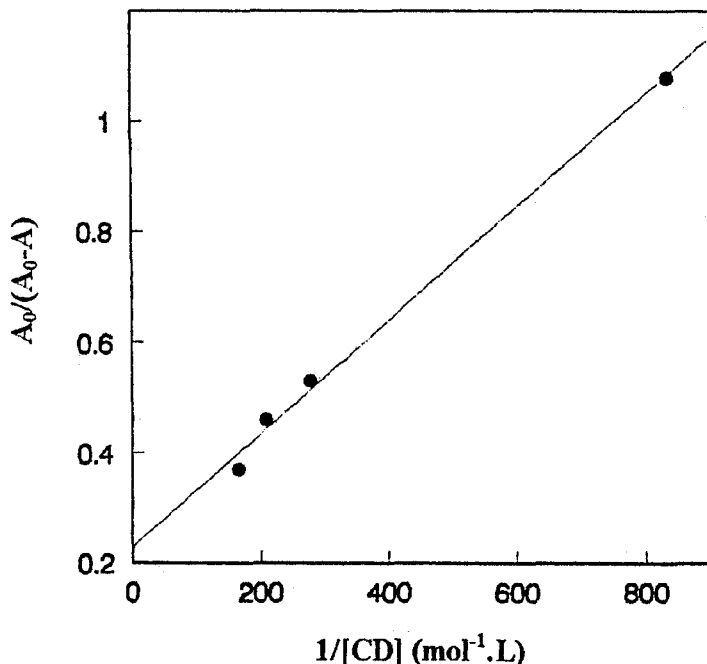


Fig. 7. The plot of  $A_0/(A - A_0)$  vs  $1/[CD]$ . The solid line is the regression line with slope ( $K'_d$ ) =  $4.5 \times 10^{-3}$  mol/L.

evaluate the dissociation constant ( $K'_d = 4.5 \times 10^{-3}$  mol/L) which is in agreement with that determined by OSWV. Considering the strong adsorption of  $\beta$ -CD on a glassy carbon electrode, a gold electrode should be used to obtain accurate data.

### Acknowledgment

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