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Determination of Orange II and the supramolecular system of Orange II with cyclodextrins by polarography

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Abstract

In this paper, a method for the determination of Orange II has been established and the supramolecular system of Orange II with cyclodextrins has been studied by polarography. A sensitive and stable linear-sweep voltammetric peak was obtained at −364 mV (vs SCE) in HAc–NaAc (pH 3.62) buffer solution. The peak current (i_p'') is proportional to the concentration over the range 1×10^{-8}–1×10^{-3} mol l^{-1} ($r = 0.9887$–0.9986) and the limit of detection is 2.0×10^{-9} mol l^{-1}. The mean recovery of Orange II was 99.1% and the relative standard deviation was 1.6%. Orange II can form 1:1 inclusion complex with 6 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 Orange II and cyclodextrins.

Keywords: Polarography; Orange II; Cyclodextrin; Supramolecular system; Inclusion constants

1. Introduction

Orange II is one of the azo dyes, which is widely used in a variety of products, such as textile, paper, foodstuffs, hairdye and leather. However, it poses a potential risk to human health and is even carcinogenic [1–4]. Therefore, it is necessary to optimize the analytical procedures for the determination of Orange II at low levels. Several methods have been reported, including HPLC and MS [5–8], photocatalysis [9], capillary electrophoresis [10–12] and thin layer chromatography [13]. 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.

We also investigate the supramolecular system of Orange II with cyclodextrins 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 [14–16]. Various methods have been used for the study of the formation of inclusion complexes of Orange II, such as spectroscopy [17–19] and volumetry [20]. No report has been published on polarographic

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and voltammetric method for the supramolecular system of Orange II.

In this paper, the interaction of 6 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) with Orange II has been studied by polarography. Their inclusion constants are calculated by "electric current method" and the inclusion capacity of different CDs was compared.

2. Experiment

2.1. Reagents and apparatus

Orange II was purchased from Beijing Xuanwu Chemical Factory. β-CD (YuNan Gourmet Factory) was purified by recrystallization in double distilled water. α-CD and 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. 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-2 single-sweep oscillopolarograph with three electrode system (Chengdu Instrument Factory, China) was used for the quantitative analysis of Orange II.

2.2. Method

Appropriate amounts of Orange II working solutions were added to a 10 ml volumetric flask, 1 ml 0.1 mol l^{-1} HAc–NaAc (pH 3.62) buffer solution was added, and the solutions were diluted to final volume with distilled water.

To measure the inclusion constants, 1 ml Orange II of the stock solution (1.0×10^{-3} mol l^{-1}) was transferred into a 10 ml volumetric flask and an appropriate amount of 0.01 mol l^{-1} α-CD (β-CD, γ-CD, DM-β-CD, TM-β-CD, HP-β-CD) and 1 ml 0.1 mol l^{-1} HAc–NaAc (pH 3.62) buffer solution were added and the solution was diluted to final volume with distilled water. This was shaken thoroughly and allowed to equilibrate at room temperature for 30 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 experiment results show that a reduction peak is obtained for Orange II in all the cases. However, this peak is more clear and sensitive in acetic acid–sodium acetate buffer (pH 3.62). In the presence of CDs, the peak current (i_p) of Orange II decreases and the peak potential (E_p) shifts to a more negative potential (Fig. 1). The effect of CDs on both the i_p and the E_p is more remarkably changed in this buffer than in the others. So 0.1 mol l^{-1} acetic acid–sodium acetate buffer

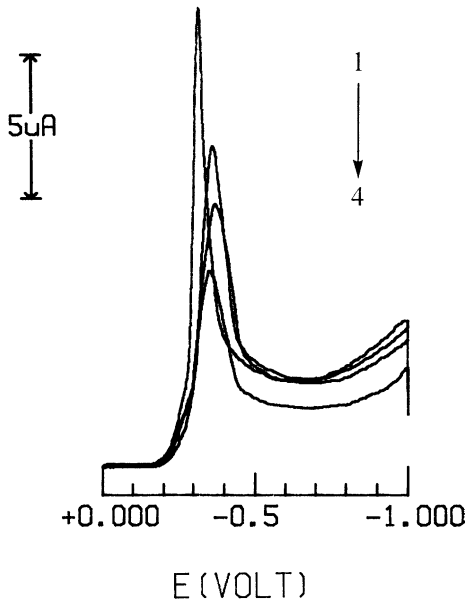


Fig. 1. Linear-sweep voltammogram of 1.0×10^{-4} mol l^{-1} Orange II in the absence of CDs (1) and presence of 5×10^{-4} CDs: (2) α-CD, (3) β-CD, (4) γ-CD.

(pH 3.62) was selected as the supporting electrolyte. In the above-mentioned buffer, a sensitive and stable linear-sweep voltammetric peak was obtained at −0.364 V (vs SCE).

3.2. Reduction peak current

To elucidate the electrode reaction of Orange II, a cyclic voltammogram at an SMDE was examined: the cathodic peak potential $E_{p_c} = -0.364$ V and no anodic peak. It indicates that the electrode reaction is irreversible. The repetitive cyclic voltammogram (Fig. 2) shows that the cathodic peak current decreases in the second cyclic and reaches a constant value which means that the variation of i_p is controlled by diffusion in the experimental condition.

The effect of scan rate (v) on the peak current was investigated. When the concentration of Orange II is above 1×10^{-4} mol l^{-1}, the peak current is proportional to $v^{1/2}$. The linear regression equation may be represented as $i_p = 0.0484c + 5.7092$ ($r = 0.9449$, $i_p \sim v$) and $i_p = 0.7903c + 3.0262$ ($r = 0.9921$, $i_p \sim v^{1/2}$). The first derivative curve shows that the height of up branch is greater than that of down branch, which indicates that i_p is the diffusion current. All of these data indicate that in lower concentrations of Orange II, the irreversible peak has adsorption behavior. However, when the concentration of Orange II is above 1×10^{-4} mol l^{-1}, the variation of i_p is controlled by diffusion.

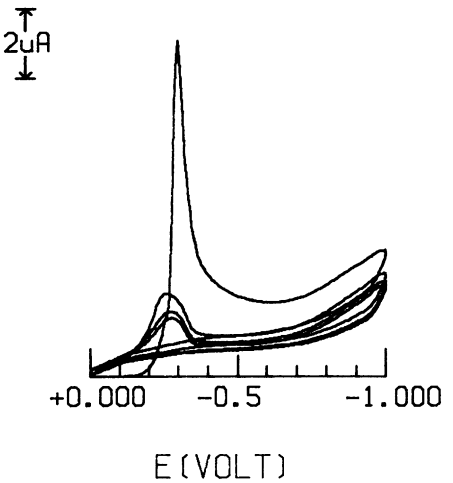


Fig. 2. Repetitive cyclic voltammogram of 1.0×10^{-4} mol l^{-1} Orange II in the acetic acid–sodium acetate buffer (pH 3.62).

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

Equation	Range of concentration (mol l^{-1})	r
$i_p = 8.56 + 0.69c$	1×10^{-8}–1×10^{-7}	0.9887
$i_p = 16.0 + 1.60c$	1×10^{-7}–1×10^{-6}	0.9923
$i_p = 21.7 + 1.65c$	1×10^{-6}–1×10^{-5}	0.9986
$i_p = 3.28 + 4.08c$	1×10^{-5}–1×10^{-4}	0.9963
$i_p = 34.9 + 10.3c$	1×10^{-4}–1×10^{-3}	0.9961

3.3. Analytical method of Orange II

In the presence of 0.1 mol l^{-1} HAc–NaAc (pH 3.62) buffer solution different concentrations of Orange II were added and the experiment was carried out by the method described in Section 2.2. The dependence of the second derivative peak height (i_p'') on the concentration of Orange II was investigated by single-sweep oscillopolarograph. There is a good linear relationship between the analytical characteristics (i_p'') and concentration of Orange II in the range of 1×10^{-8}–1×10^{-3} mol l^{-1}. The results are shown in Table 1.

The limit of detection is 2.0×10^{-9} mol l^{-1}. The precision of the determination of Orange II by single-sweep oscillopolarograph is excellent, and at a concentration of 5×10^{-5} mol l^{-1} the relative standard deviation (RSD) was 1.6% ($n = 9$).

The content of artificial sample of Orange II was 5×10^{-5} mol l^{-1}, in which standard solutions of different concentrations of Orange II 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 Orange

Table 2
Recovery test of artificial sample

Component	Added (mol l^{-1})	Found (mol l^{-1})	Recovery (%)
5×10^{-5} mol l^{-1} Orange II	3×10^{-5}	2.9×10^{-5}	96.7
	3×10^{-5}	3.1×10^{-5}	103.3
	4×10^{-5}	3.8×10^{-5}	95.0
	4×10^{-5}	3.9×10^{-5}	97.5
	5×10^{-5}	4.9×10^{-5}	98.0
	5×10^{-5}	5.2×10^{-5}	104.0

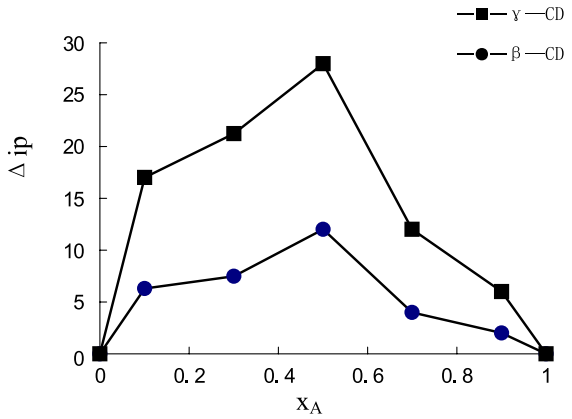


Fig. 3. Continuous variation plot.

II varied from 95.0% to 104.0% and the mean recovery is 99.1%.

3.4. Supramolecular system of Orange II with cyclodextrins

3.4.1. Determination of stoichiometry

The determination of stoichiometry of the inclusion complex was performed using equimolar variation method. A series of solutions, in which the total concentration is 8×10^{-4} mol l^{-1}, were prepared and the mole ration of the Orange II changed from 0 to 1. The peak currents in absence (i_{p_0}) and presence of CDs (i_{p_x}) were determined. A plot of $\Delta i_p (i_{p_0} - i_{p_x})$ versus the mole fraction of Orange II (x_A) is provided in Fig. 3. It shows a maximum at $x_A = 0.5$, indicating that the Orange II–CDs inclusion complexes have 1:1 stoichiometry. In this mole ration, the sharpest decrease of peak current is obtained.

3.4.2. Determination of the inclusion constant

The inclusion complexes of Orange II with all the 6 CDs give rise to a decrease of the i_p and to a negative shift to the E_p (Fig. 1). It was implied that all the 6 cyclodextrins can form inclusion complexes with Orange II in acetic acid–sodium acetate (pH 3.62) buffer solution. The decrease of the peak current is due to the decrease of the apparent diffusion coefficient of Orange II, which has formed the inclusion complexes with CDs. The negative shift of the E_p suggests that the reduction of the inclusion complexes at the Hg electrode needs more activation energy.

The host:guest ratio detected is 1:1. This is the same as reported with spectrophotometry by T. Iijima [19].

The inclusion constants are calculated by "electric current method" [21] in this paper. The formula is:

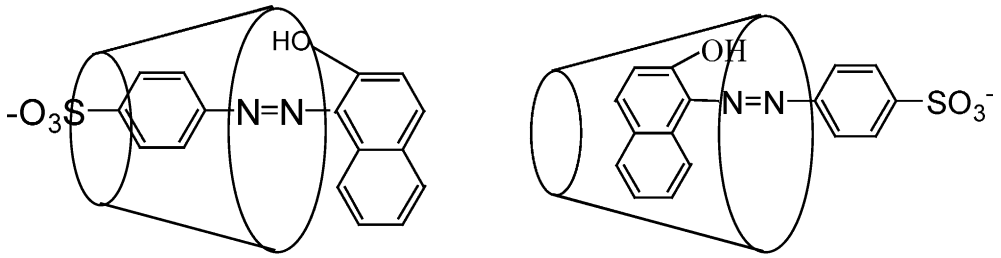
$$i_p^2 = \frac{K_d}{[CD]}(i_{p_x}^2 - i_p^2) + i_{p_{x-CD}}^2$$

where i_{p_x} is the limited diffusion current of Orange II in the absence of CDs; i_p is the detected diffusion current of guest molecule in the presence of different concentrations of CDs; $i_{p_{x-CD}}$ is the limited diffusion current of Orange II being included by CD; K_d is the dissociation constant and K ($1/K_d$) is the inclusion constant. Plot of i_p^2 versus $(i_{p_x}^2 - i_p^2)/[CD]$ 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 β-CD (HP-β-CD, DM-β-CD, and TM-β-CD) exhibited stronger binding ability than the parent β-CD implying that the cavity of the modified β-CD provided a better protective microenvironment. Strong inclusive ability can be understood from the fact that the substitution by hydroxypropyl, dimethyl, and trimethyl groups leads to the enlargement of the bigger opening of β-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 β-CD cavity and to have bigger inclusion constants [22]. So strong inclusion

Table 3
The inclusion constants of Orange II with 6 CDs

CD	α-CD	β-CD	γ-CD	HP-β-CD	DM-β-CD	TM-β-CD
K	473	5.0×10^3	5.0×10^4	3.3×10^4	1.4×10^4	1.0×10^4



β -CD γ -CD

Fig. 4. Structures of inclusion complexes of β-CD and γ-CD with Orange II.

complex by modified β-CD is supposed to be applied more extensively. The inclusive ability of γ-CD with Orange II is the strongest of the 6 CDs. This is because the cavity of γ-CD has the best size match to the naphthalene ring of Orange II, so that it can most effectively include Orange II. However, the cavity of α-CD is too small, so the inclusive ability is very weak. The possible structures of inclusion complexes of β-CD and γ-CD with Orange II are shown in Fig. 4.

4. Conclusion

Analytical method for Orange II was established by polarography. The reduction of Orange II in HAc–NaAc (pH 3.62) buffer solution is an irreversible process. The peak current (i_p'') is proportional to the concentration over the range 1×10^{-8}–1×10^{-3} mol l^{-1} ($r=0.9887$–0.9986) and the limit of detection is 2.0×10^{-9} mol l^{-1}. The mean recovery of Orange II was 99.1% and the RSD was 1.6%. The polarographic method is sensitive, rapid, simple, and accurate. Polarography has demonstrated the inclusion interaction between Orange II and CDs. Orange II can form 1:1 inclusion complex with 6 CDs. Modified β-CD such as HP-β-CD, DM-β-CD and TM-β-CD exhibits stronger inclusive ability. The inclusive ability of γ-CD with Orange II is the strongest, therefore the inclusive ability of α-CD is very weak. This indicates that the major factors affecting inclusive ability are size matching between CD and guest and the hydrophobicity of the guest molecule. 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.

Acknowledgements

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