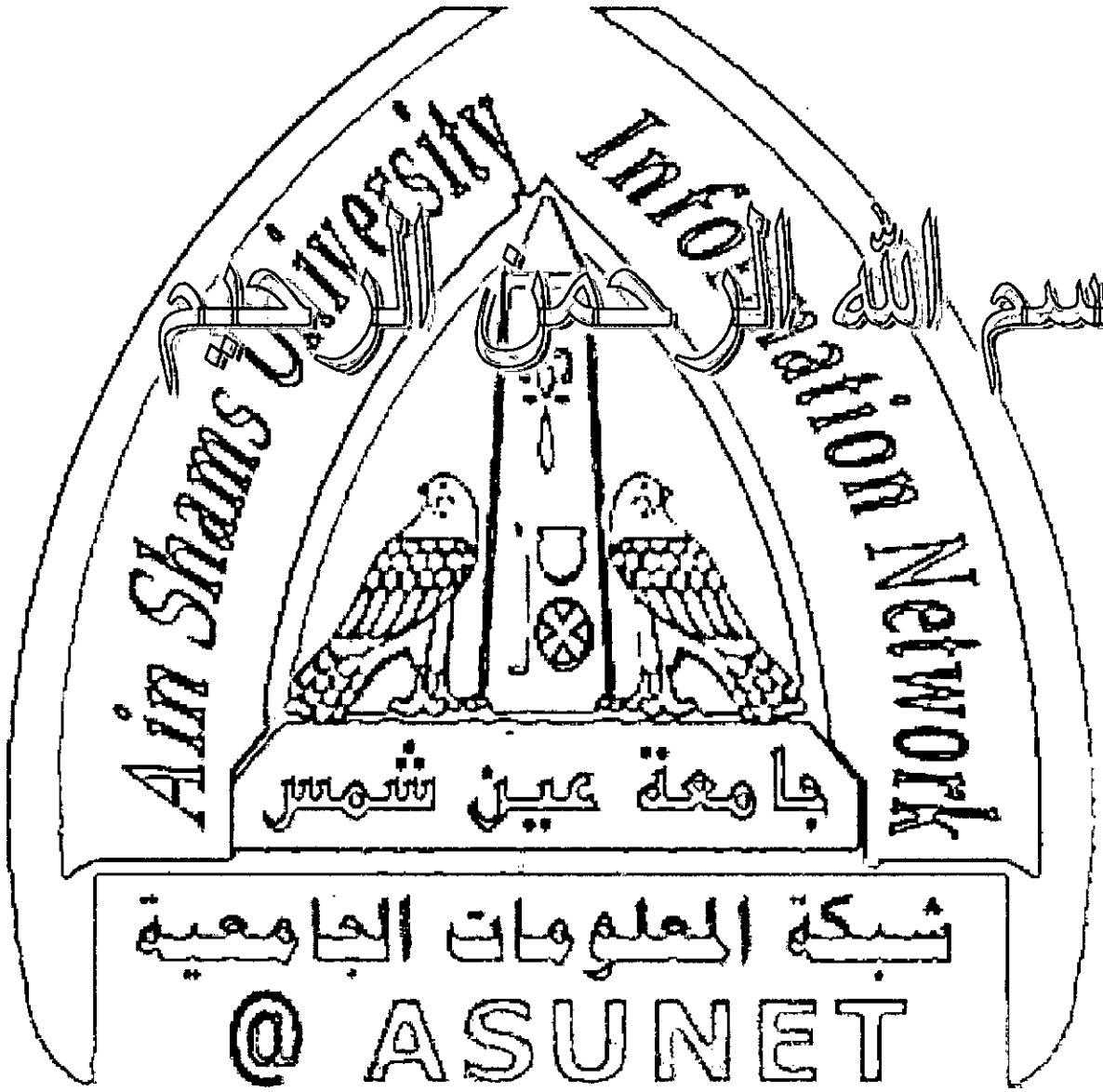
شبكة المعلومات الجامعية



شبكة المعلومات الجامعية

جامعة عين شمس

التوثيق الالكتروني والميكروفيلم

قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
علي هذه الأفلام قد أعدت دون أية تغيرات

يجب أن

تحفظ هذه الأفلام بعيدا عن الغبار
في درجة حرارة من ١٥-٢٥ مئوية ورطوبة نسبية من ٢٠-٤٠%

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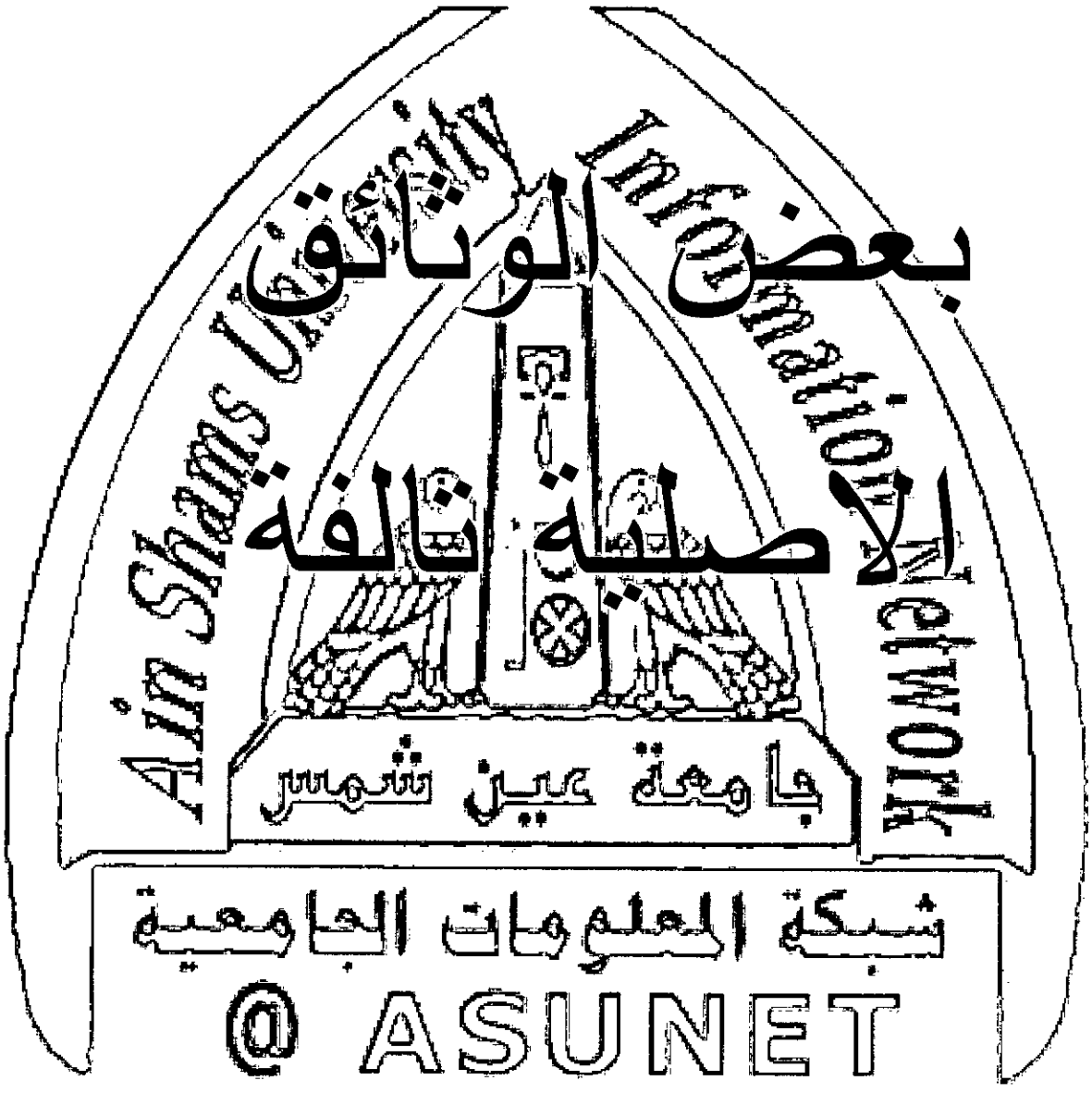
شبكة المعلومات الجامعية

التوثيق الالكتروني والميكروفيلم



بعض الوثائق الأصلية تالفة

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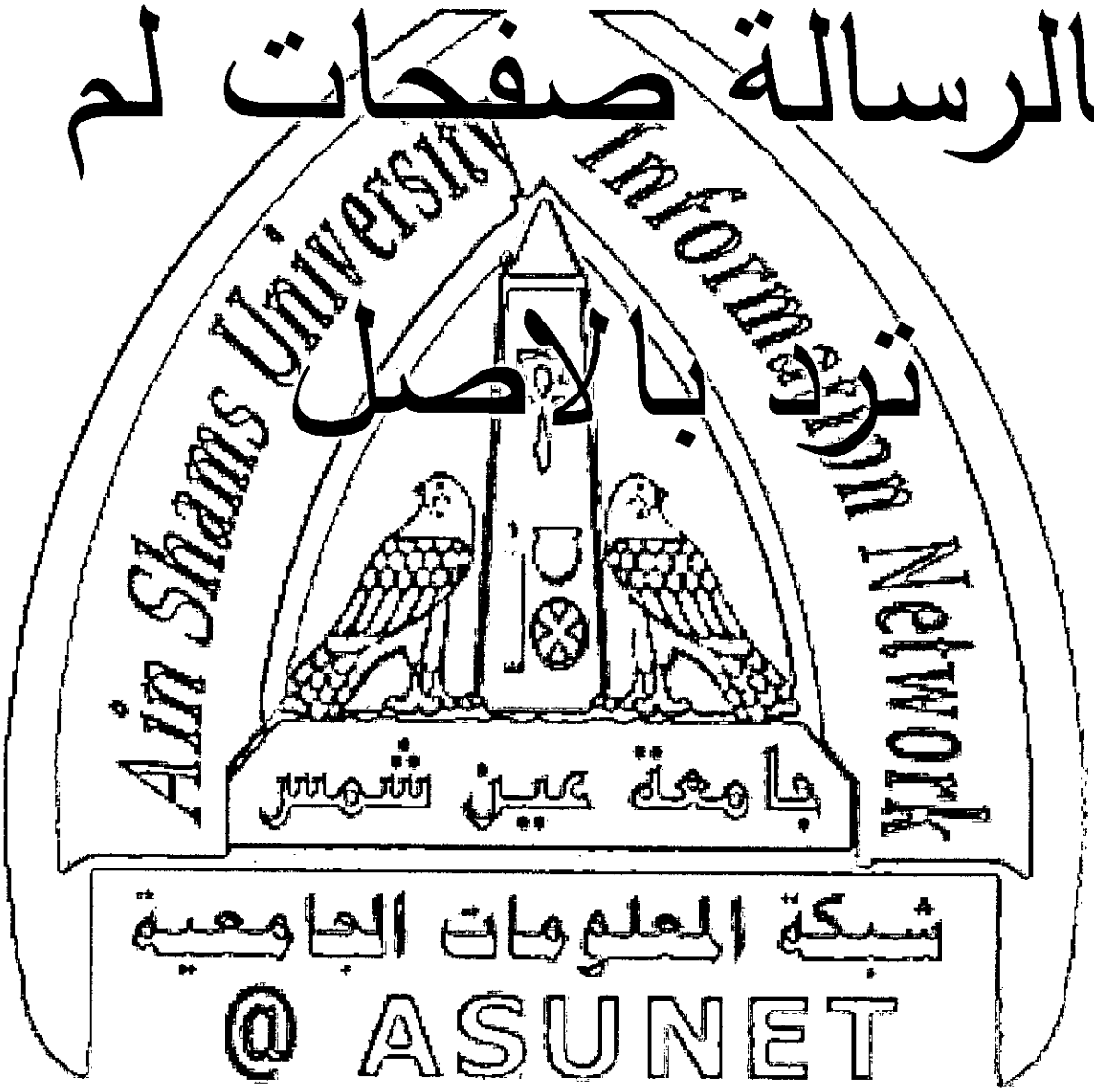

Faculty of Science
Chemistry Department

VOLTAMMETRIC, SPECTROPHOTOMETRIC AND POTENTIOMETRIC STUDIES ON POLY(8 – HYDROXYQUINOLINE)

A Thesis Presented By

Mohamed Mahmoud Ahmed Shahata

B.Sc.-Chemistry Department

Faculty of Science – Assiut University

For

Partial fulfillment of the degree of Master of Science

(Chemistry)

Supervised By

Prof.Dr. Mostafa M. Kamal — Professor of Physical Chemistry

Dr. SeddiqueM.Ahmed — Lecturer of Chemistry

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2004

APPROVAL SHEET

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Examination Committe

External Internal

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30/5/2004

بسم الله الرحمن الرحيم

وَعَلَّمَكَ مَا لَمْ تَكُن تَعْلَمُ وَكَانَ فَضْلُ اللَّهِ عَلَيْكَ عَظِيمًا

صدق الله العظيم

آية (١١٣) سورة النساء

TO MY PARENTS,

TO MY FAMILY

ACKNOWLEDGMENT

ACKNOWLEDGMENT

In the name of ALLAH, grecious, the merciful

We all thanks our God for his gifts and his helping that enables me to make more progress.

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SHORT COMMUNICATION

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Mohamed M. Shahata · Yassien M. Temerk

Differential pulse polarographic determination of poly(8-hydroxyquinoline) in the presence and absence of an insulating poly(vinyl alcohol) matrix

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Abstract The electrochemical activity of poly(8-hydroxyquinoline) (PHQ) in acid and alkaline media has been investigated by use of differential pulse polarography (DPP). The reduction peak height (I_p) of PHQ in universal buffer solutions is not useful as an analytical signal, because it is highly affected by hydrogen evolution in acid media and appears as a small peak located at more negative potential values in alkaline media. A new and highly sensitive reduction peak (E_p=–0.45, pH 9.25) appears, however, after addition of trace amounts of PHQ to Cu(II), or vice versa. This reduction peak is a result of the reduction of Cu(II) chelates in the PHQ–Cu(II) complex and is highly promising for the trace determination of PHQ at nanomolar and submicromolar levels. The response current (I_p/μA) for the reduction peak of Cu(II) chelates in a PHQ–Cu(II) matrix results in sensitivity to the concentration of PHQ at least three orders of magnitude higher than that for the reduction peak of PHQ alone under the same conditions. The limit of detection is as low as 5.264 ppb (μg L^{-1}). The effect of a variety of anions and cations and of an insulating poly(vinyl alcohol) (PVA) matrix has been investigated. Electroactive PHQ–Cu(II) at a level of 0.685% could induce a current of approximately 240 nA in an insulating PVA matrix, suggesting possible application for the preparation of a PHQ–Cu(II)–PVA electroactive composite.

Keywords Differential pulse polarography · Poly(8-hydroxyquinoline) · Copper(II) determination · Poly(vinyl alcohol)

Introduction

Polymer chelates provide a unique structural environment for complexation by multidentate ligands. The complexation of such a ligand is determined by a variety of factors including the nature of the polymer backbone and the nature of the complexing media. Metal-containing polymers are important, because these systems have advantages over non-polymeric metal salts in a variety of chemical reactions [1, 2, 3, 4, 5, 6, 7]. Polymeric metals are, moreover, of great significance in different fields of chemistry, e.g. catalytic reactions, geochemical separations, biochemistry, medicine, environmental chemistry, etc. [8, 9, 10, 11].

Polarographic studies have been performed on 8-hydroxyquinoline (oxine) and 8-hydroxyquinoline-5-sulfonic acid (OSA) [12, 13]. These studies revealed that the reduction process leads to the formation of the di- or tetrahydro compound via single- or double reduction steps. Derivatives of quinoline containing polarographically active or inactive substituents have also been the subject of many investigations [14, 15, 16, 17]. Several extraction-polarographic methods have been applied for determination of metal ions as complexes, with 8-quinolinol (oxine) as the complexing agent [18, 19, 20]. Song et al. [21] have determined PVA by an adsorptive stripping voltammetric (ASV) technique based on its Cu(II) complexes at pH 11.0 in carbonate buffer solution. The adsorptive peak of PVA–Cu(II) had a potential of –0.125 V.

We have previously investigated the complexation of 8-hydroxyquinoline-5-sulfonyl hydrazide with metal ions [22, 23, 24] and recently found that electrical conductivity, electroactivity, and spectroelectroactivity could be induced in poly(*o*-toluidine) and/or polypyrrole emeraldine base form after doping [25, 26, 27, 28, 29].

In this study we investigated the electrochemical reduction of PHQ, Cu(II), and PHQ–Cu(II) systems in aqueous solutions containing 10% DMF, at different pH, by use of differential pulse polarographic (DPP) techniques. The applicability of the reduction peak of Cu(II) chelates in the PHQ–Cu(II) complex for the determination of PHQ has been studied. The calibration constants and the limit of detection were calculated. The procedure was successfully used to determine PHQ in the presence of a variety of anions and cations and of an insulating poly(vinyl alcohol) (PVA) matrix.

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Experimental

Chemicals and solutions

8-Hydroxyquinoline (8-HQ) was obtained from Aldrich (Milwaukee, WI, USA). Poly(vinyl alcohol) (PVA; Mwt=2.2×10^4; degree of hydrolysis, 88%) was purchased from Wako (Osaka, Japan). All other chemicals were of analytical reagent grade quality. A solution of copper(II) was prepared by dissolving a known amount of chemically pure $Cu(NO_3)_2$ (Merck) in twice-distilled deionized water and was standardized complexometrically [30]. Solutions (1 mmol L^{-1}) of the metal ions K(I), Na(I), Ca(II), Ba(II), Sr(II), Mg(II), Cd(II), Pb(II), Mn(II), Co(II), Ni(II), and Zn(II), were prepared from their Analar grade nitrate salts (BDH); solutions of the anions CO_3^{2-}, NO_3^-, SO_4^{2-}, $B_4O_7^{2-}$, PO_4^{3-}, CH_3COO^-, were prepared from their Analar grade sodium salts.

Poly(8-hydroxyquinoline) (PHQ) was synthesized by following a previously described procedure [31]. Oxidation of the 8-hydroxyquinolate anion produces a radical cation which can react further with phenol (8-HQ) to give a predominantly *para*-linked dimeric radical. Subsequent reactions then produce oligomers and, finally, a polymeric material (polyphenylene oxide). The purity of this compound was checked by FTIR and ^1H NMR spectroscopy. The disappearance of the absorption band at 3158 cm^{-1} (ν(O–H)) in the FTIR spectra of PHQ indicates the absence of a free OH group. The presence of peaks at ~1055, 1160, and 1285 cm^{-1} in the FTIR spectrum of PHQ reveals the presence of ether (C–O–C) [32] linkages. The absence of the signal (δ=9.8514 ppm) from the proton of the hydroxyl group of 8-HQ in the ^1H NMR spectra of PHQ (Fig. 1 a, b) confirmed the polymerization of 8-HQ. Molecular modeling calculations (MM+) substantiate this polymerization; they showed the geometrical energy of the PHQ dimer (smallest polymer unit) to be 1.460,397 kcal mol^{-1}, with a gradient of 0.097,576. This means that the geometric configuration of this dimer is highly stable.

A fresh 1 mmol L^{-1} solution of PHQ was prepared by dissolving an accurately weighed amount of the chemically pure product in dimethylformamide (DMF).

Instrumentation

Differential pulse polarograms (DPP) were recorded by means of a polarographic analyzer model PAR 174 equipped with a model 172 A drop timer and electrode assembly. The DP-peaks were recorded at 2 s drop time, 2 mV s^{-1} scan rate. pH was measured with a Fisher Scientific Accument, Digital pH meter model 810. FTIR spectroscopy (KBr pellets) was performed with a Shimadzu (Type 470) spectrometer. ^1H NMR spectra were recorded by use of a JNM-LA 400 MHz FT-NMR spectrometer. Molecular modeling calculations (MM+) were performed by use of Hyper Chem Program Version 5 (Polak-Ribere PM5).

Procedure

Universal buffer solution (pH 3.25–11.25, 1 mL) diluted to 10 mL with deionized water containing 10% DMF was placed in the voltammetric cell. The solution was purged with oxygen-free nitrogen for 20 min and the background DP-polarogram was recorded. A known concentration of the analyte (PHQ and/or Cu(II)) was added to the same cell by means of a micropipette (Voaco, UK) and the mixture was purged for 2 min. In other experiments foreign ions or insulating polymers were injected individually or as a mixture into the cell in the presence of the analyte.

Results and discussion

Electroactivity of PHQ

The DPP behavior of PHQ in universal buffer solution containing 10% DMF, in absence and presence of Cu(II), was investigated as shown in Fig. 2a. The reduction behavior of PHQ is highly dependent on the pH of the solution. In acidic medium (pH 3.25) the reduction peak po-

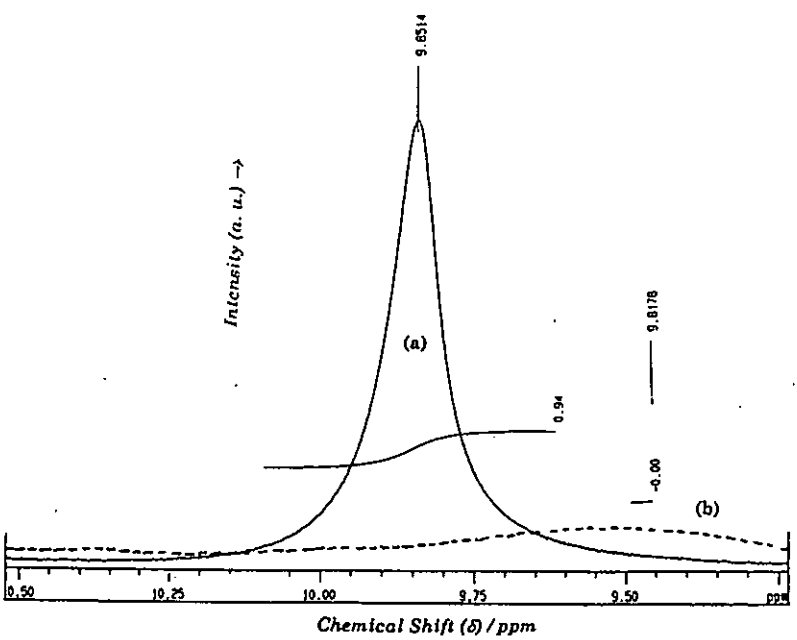


Fig. 1 ^1H NMR spectra of (*a*) 8-hydroxyquinoline (8-HQ) and (*b*) poly(8-hydroxyquinoline (PHQ)

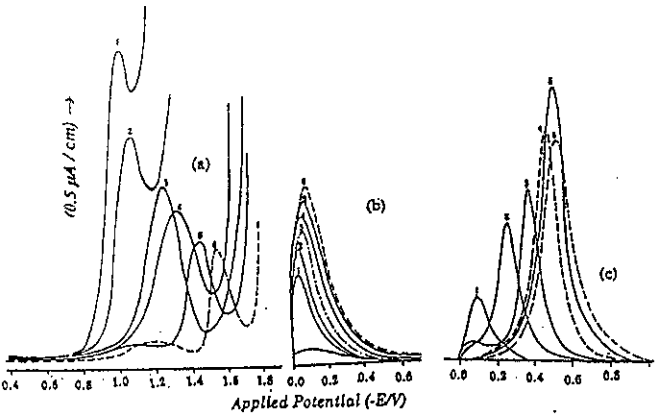
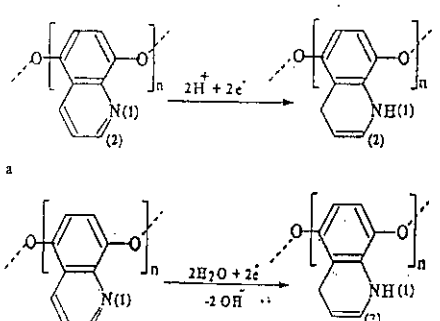


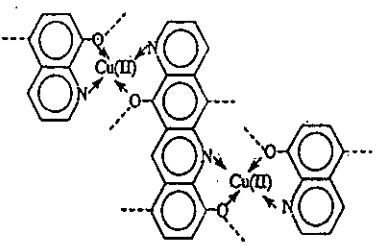
Fig. 2 DP-polarograms (50 μmol L^{-1}) of (a) PHQ, (b) Cu(II), and (c) a+b at different pH in universal buffer solutions containing 10% DMF. The pH are: *1*, 3.25; *2*, 5.25; *3*, 7.25; *4*, 8.00; *5*, 9.25; *6*, 11.25. Scan rate 2 mV s^{-1}, drop time 2 s, and pulse amplitude 100 mV

ential (E_p) and peak height (I_p) (Fig. 2a, 1) were –0.95 V and 8.1 μA respectively, whereas in alkaline medium (pH 11.25) E_p shifted to a more negative potential (E_p= –1.55 V and I_p=1.54 μA) (Fig. 2a, 6). According to the proposed reduction mechanism (Scheme 1a, b) the reduction center is [N(1)=C(2)]. In acidic and alkaline media this reduction center undergoes a totally irreversible electrode reaction according to the mechanism of reduction of quinolinic azomethine (Scheme 1a, b). The reduction peak height of PHQ in acid medium was highly affected by the background discharge (Fig. 2a, 1) whereas in alkaline medium the reduction peak potential of PHQ was shifted to a much more negative potential and decreased with increasing pH (Fig. 2a). These results indicate that the reduction peak height (I_p) of PHQ at the dropping mercury electrode is not useful for the determination of trace amount of PHQ in dilute solutions.



Scheme 1 Mechanism of reduction of PHQ in (a) acid and (b) alkaline media

DP-polarograms of Cu(II) in the absence of PHQ were recorded in universal buffer solutions containing 10% DMF (pH 3.25–11.25). Figure 2b shows the single reduction peak of Cu(II) with a peak potential (E_p) lying in the potential range of –0.04 to –0.12 V. The peak half-width of this reduction is approximately 130 mV, indicating a highly irreversible Cu(II) reduction process. In the presence of PHQ, however, a new peak was observed in the range –0.1 to –0.45 V (pH-dependent) over the pH range studied, as shown in Fig. 2c. This shift in the peak potential of Cu(II) (~350 mV) reflects the strong interaction between Cu(II) and the PHQ matrix via the complexation mechanism shown in Scheme 2. The maximum reduction peak height of Cu(II) chelates was observed at pH 9.25 (Fig. 2c, 5) and this peak was at least three orders of magnitude larger for addition of PHQ to Cu(II) than the reduction peak for PHQ alone under the same conditions (Fig. 2a, 5; c, 5). A medium pH of 9.25 was therefore selected for determination of PHQ.



Scheme 2 Proposed structure of the PHQ–Cu(II) complex