



Voltammetric determination of water with inner potential reference and variable linear range based on structure- and redox-controllable hydrogen-bonding interaction between water and quinones

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ABSTRACT

This communication describes a new voltammetric method for the determination of water in nonaqueous solvent by taking advantage of the structure- and redox-controllable hydrogen-bonding interaction between quinone species and water. Three kinds of quinones, i.e., tetrachloro-*p*-benzoquinone (TCBQ), benzoquinone (BQ), and tetramethyl-*p*-benzoquinone (TMBQ), are employed in this study in terms of their different structures and thereby different basicities and hydrogen-bonding interaction activities with water. The hydrogen-bonding interaction activities of the quinone species with water actually depend on the structures and the species of quinones, where the interaction activity between quinone dianion and water remains remarkably greater than that between quinone monoanion and water. The former interaction activity eventually leads to the positive shift of the half-wave potential of quinone monoanion/dianion couple, which can be essentially used for the voltammetric determination of water. The structure- and redox-controllable hydrogen-bonding interaction activities of quinones and water substantially make it possible to determine trace amount of water in the nonaqueous solution with inner reference potential and variable dynamic linear range.

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1. Introduction

Determination of water is of great industrial and environmental importance and has been one of the commonest routine procedures in many research and industrial processes since water is often used in the preparation of many materials and remains as one of the most common contaminants in the organic solvents and in the industrial products [1]. So far, many methods, such as gravimetric, spectroscopic, and amperometric methods have been employed for water determination, of which Karl Fischer method has been used most frequently [2–4]. In spite of their applications in the determination of water content in moisture, most of those methods are still experimentally complicated and may not be suitable for the determination of water content in organic solutions [1,5]. Although voltammetric methods based on the redox properties of the analytes have been proved to be both theoretically and experimentally simple and, as such, have been widely used for electroanalytical purposes, the poor redox property of water itself under the conditions generally employed for electrochemical measurements substantially makes the voltammetric determination of water a challenge in electrochemical studies.

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This communication describes a new voltammetric method for the determination of water in nonaqueous solution. The strategy is essentially based on the structure- and redox-controllable hydrogen-bonding interaction between water and quinones, as shown in reactions (1)–(4). In aprotic media, quinone undergoes two successive one-electron electrochemical redox processes to form radical monoanion ($Q^{\cdot-}$) (reaction (1)) and dianion (Q^{2-}) (reaction (3)), which have different hydrogen-bonding interaction activity with water (reactions (2) and (4)). The hydrogen-bonding interaction stabilizes the radical monoanion and dianion and eventually leads to the positive shift of the half-wave potentials of the quinone species [6,7], which can be employed for the determination of water content in the organic solvent. Although the hydrogen-bonding interaction has been known to be ubiquitously involved in many biological processes and has been previously investigated with quinones as the model receptors [8–11], such an interaction has not been used for the voltammetric determination of water in organic solutions so far. This study essentially offers a simple and straightforward voltammetric method for water determination.



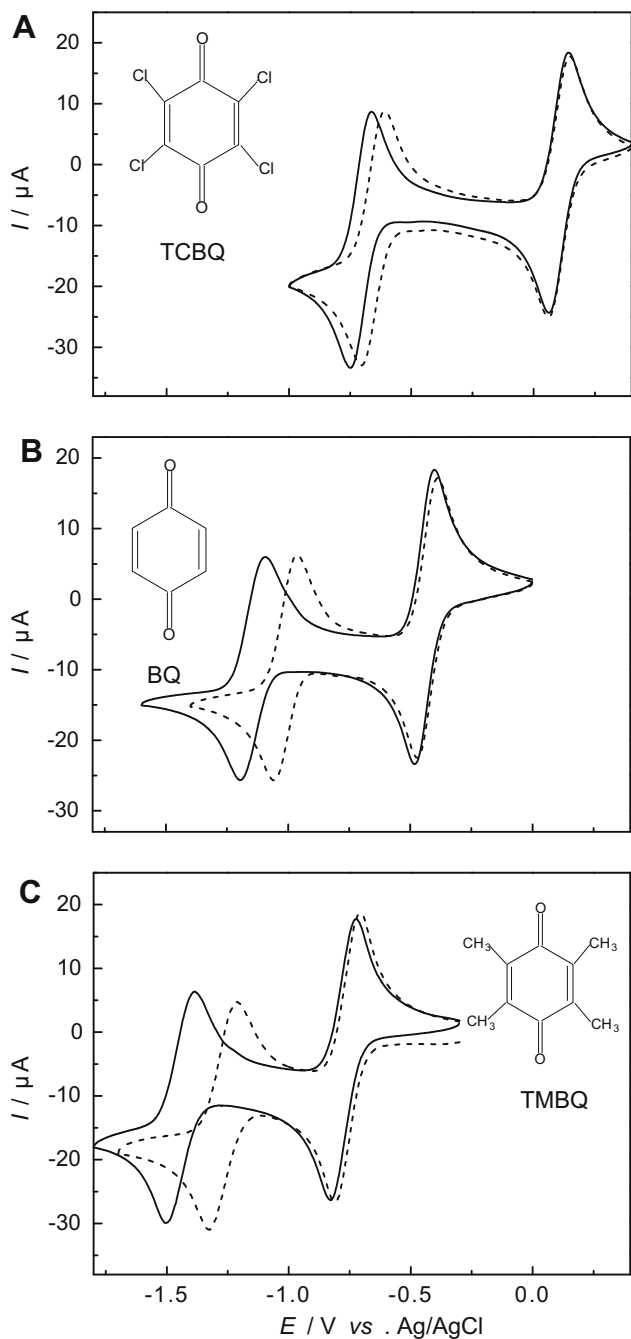


Fig. 1. CVs obtained at GC electrodes in acetonitrile containing TCBQ (A), BQ (B), or TMBQ (C) in the absence (solid curves) and presence (dashed curves) of water ($V_{\text{H}_2\text{O}}/V_{\text{ACN}} = 0.001$). The concentrations of TCBQ, BQ, and TMBQ were 1.0 mM. A 0.1 M Bu_4NClO_4 was used as the electrolyte. Potential scan rate was 50 mV s^{-1} .

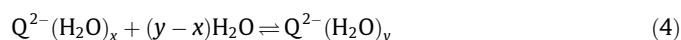


Table 1

Parameters involved in the redox processes of quinones and in the voltammetric determination of water.

	x	$K_{\text{eq}}^{(1)}$	y	$K_{\text{eq}}^{(2)}$	Linear regression	R	Linear range
TCBQ	0.60	2	4.1	3.3×10^4	$\Delta E_{1/2} = -0.090 \ln(V_{\text{H}_2\text{O}}/V) + 0.30$	0.9972	0.6–60%
BQ	1.4	29	5.7	1.4×10^9	$\Delta E_{1/2} = -0.080 \ln(V_{\text{H}_2\text{O}}/V) + 0.03$	0.9989	0.04–6%
TMBQ	1.5	32	5.8	2.1×10^9	$\Delta E_{1/2} = -0.074 \ln(V_{\text{H}_2\text{O}}/V) - 0.01$	0.9902	0.03–3%

2. Experimental

2.1. Chemicals

Tetrachloro-p-benzoquinone (TCBQ), benzoquinone (BQ), tetramethyl-p-benzoquinone (TMBQ) and tetrabutylammonium perchlorate (Bu_4NClO_4) were purchased from Aldrich. Acetonitrile (ACN) was obtained from Tianjin Siyou Chem. Co., Ltd. (Tianjin, China) and was distilled from CaH_2 prior to use. Doubly distilled water was used throughout the experiments.

2.2. Apparatus and electrochemical measurements

Glassy carbon (GC, 3 mm diameter) electrodes were used in this study. The electrodes were polished with 0.3 and $0.05 \mu\text{m}$ alumina slurry on a polishing cloth, cleaned under bath sonication for 5 min in acetone and distilled water, and thoroughly rinsed with doubly distilled water. Cyclic voltammetry was performed on an electrochemical analyzer (CHI 660A, CH Instruments) in ACN solution containing 0.10 M Bu_4NClO_4 with a three-electrode configuration with GC electrodes as working electrode and a Pt wire as counter electrode. All potentials were biased versus Ag/AgCl electrode with a glassy salt bridge with two compartments. One compartment connected to the ACN solution was filled with ACN containing 0.1 M Bu_4NClO_4 and the other one connected to the KCl-saturated aqueous solution was filled with saturated KCl solution. Prior to electrochemical measurements, the electrolyte was bubbled with N_2 gas for more than 30 min and the measurements were conducted under N_2 atmosphere. All electrochemical measurements were performed at ambient temperature.

3. Results and discussion

Fig. 1 compares cyclic voltammograms (CVs) of three kinds of quinones in ACN solution in the absence and presence of water. In dry, neutral and proton-deficient media, such as ACN, all quinones exhibit two pairs of well-defined redox waves (solid curves), which were attributed to two successive one-electron redox processes to give quinone monoanions (Q^-) and dianions (Q^{2-}) [6,7]. The small peak-to-peak separation and the linear relationship between the peak currents and the square root of potential scan rate in a range from 50 to 400 mVs^{-1} (data not shown) essentially suggest that the redox processes are diffusion-controlled fast electron transfer processes. In addition, the half-wave potentials ($E_{1/2}$) of both redox waves essentially vary with quinone structures, of which TCBQ with four electron-withdrawing chloro groups has the most positive $E_{1/2}$ and, in contrast, TMBQ bearing four electron-donating methyl groups has the most negative one, among all quinones used here. The structurally dependent half-wave potentials of quinones actually reflect the variable basicity and the capability of quinones as the receptors in the hydrogen-bonding interaction with water and such dependency substantially makes it possible to tune the analytical properties for the voltammetric determination of water, as described below.

The addition of water in solution results in a clear positive shift of the half-wave potential for Q^-/Q^{2-} ($E_{1/2}^{(2)}$) (dashed curves, Fig. 1), which could be elucidated in terms of the hydrogen-bonding

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