



Quantitative measurements in electrochemical electron paramagnetic resonance



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ABSTRACT

The quantification of absolute number of paramagnetic centers in continuous wave (CW) Electron Paramagnetic Resonance (EPR) is a demanding measurement, where the interaction between the sample and the EPR spectrometer needs to be understood and controlled precisely. When utilizing electrochemical EPR (EC-EPR), additional challenges are introduced due to the dynamic nature of the electrochemical systems, (e.g. diffusion of radical species on the timescale of EPR experiments). Here we report a full characterization of an EC-EPR setup for quantifying the absolute number of paramagnetic species originating from EC generation. The data reported indicate that with EC-EPR it is possible to quantify intermediates or products from electrode reactions within 3% accuracy over a threefold concentration range, even in organic solvents. The set-up has high sensitivity, with the quantification of 3–4 μM concentrations shown to be routine. Furthermore, sub- μM concentrations can be accessed through signal averaging. These studies provide a platform for the future use of quantitative EPR and new capability for studying and characterizing electrochemical systems.

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1. Introduction

Electron Paramagnetic Resonance (EPR) is a powerful technique in the study of paramagnetic products and intermediates associated with electrode reactions. The most typical studies involve the identification of the radical species by recording the corresponding spectrum and determining the g -value and hyperfine couplings associated with the species of interest [1–4]. In the case of complicated electrode reactions this can help determine, or confirm, reaction mechanisms inaccessible to electrochemical techniques alone [5–8]. Kinetic parameters such as reaction rates of radicals and their lifetimes [9–12] can be measured, and for very short lived species the utility of EPR can be extended through spin trapping [13–16].

Structural studies ranging from organic compounds [17–21] to organometallic [22–25] systems are accessible for the determination of electron delocalization and structure-function relationships between specific oxidation states of different transition metal-ligand complexes. Finally, the determination of EPR line widths

allows the study of homogeneous electron transfer reactions, which can be correlated, for example, to Marcus theory of reaction kinetics [26–29].

Hitherto, electrochemical (EC)-EPR has mainly involved determination of g -factors and their anisotropies, hyperfine couplings, rate constants, lifetimes and line widths of radical species. In some of these studies, quantification involving the double integrated EPR signal intensity has been performed relative to analyte concentration [30], added chemical species [31], time [32], or by determining the ratio of two EPR active species simultaneously present in the studied system [33].

The quantification of the number of radical species in a sample by EPR is a demanding measurement as the nature of the interaction between the sample and the EPR spectrometer has to be understood and controlled precisely for accurate and reproducible results. Usually the biggest sources of error and uncertainty are related to the resonator Q -value, filling factor (η), magnetic field modulation (H_{mod}), microwave power saturation, spectral integration and referencing against a standard sample [34–39]. In EC-EPR these challenges are multiplied by the dynamic nature of the electrochemical experiment, as the radical species generated redistribute within the EPR resonator on the timescale of the

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experiment, as discussed for example by Adams [40] as early as 1964.

As highlighted by Nagy in 1994 [41], to a significant degree, EPR has evolved separately from analytical chemistry and thus, until recently, the analytical potential of the technique has remained largely unrealized. As the EPR signal is a function of several variables, and in EC-EPR the performance is also compromised by the EC cell within the resonator, in order to be deemed quantitative any set-up has to be carefully characterized before reliable results can be obtained.

In this paper, we characterize the EC-EPR set-up, reported recently [42] by us, using benzoquinone (BQ) in acetonitrile as a model system, specifically for the quantification of the number of paramagnetic species originating from electrode reactions. The approach follows considerations for Quantitative EPR (Q-EPR) described by Eaton et al. [43]. Typically the absolute quantification of the number of spins (radicals) in traditional EPR can be performed within an error of $\pm 2\%$ [44] and for inter-laboratory work a percentage standard deviation of 3.1 has been obtained [45]. With previous set-ups, QEC-EPR studies reveal errors of $\pm 15\%$ [46], although typically details of the quantification procedure and associated errors are not discussed [47].

In this paper, we provide a detailed analysis focused on the accuracy and reliability of transient measurements performed in our EC-EPR set-up, in order to emphasize the importance of understanding the interplay between the radical species confined within a time-dependent diffusion field of an EC experiment and the EPR resonator itself. From this we are able to show that EC-EPR measurements can be made with very high precision, making modern EPR highly attractive for applications in electrochemistry.

2. Experimental

2.1. Materials

1,4-benzoquinone (Fluka, certified purity 99.99%), tetrabutylammonium perchlorate (TBAP; Fluka, $\geq 99.0\%$, for electrochemical analysis), 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO; Fluka, $\geq 98\%$), 2,2-diphenyl-1-picrylhydrazyl (DPPH) and anhydrous acetonitrile (99.8%) were purchased from Sigma-Aldrich. The acetonitrile was dried inside a glove box over molecular sieves (Sigma-Aldrich, UOP type 3 Å) 10% m/v for 48 hours [48] and 0.2 M TBAP acted as a supporting electrolyte for all measurements.

Working electrodes (WEs) were 50 μm diameter Pt micro-wires coated with a 7.5 μm layer of polyester (Goodfellow, $\pm 10\%$ tolerance in conductor diameter). Chloridized Ag wire (125 μm in diameter) served as a pseudo reference electrode (RE). A coiled 250 μm diameter Pt wire acted as a counter electrode (CE).

2.2. Methods

The EC-EPR setup, including the electrode preparation, has been described recently [42]. The inner diameter of the sample tube was 0.8 mm. Except for the weighing of chemicals, all solutions were prepared and stored inside a glove box. An aliquot of sample was removed from the glove box just prior to measurements in a gas tight glass syringe that was purged with dry N_2 . This set-up and procedure allowed the study of samples free from water in a low oxygen environment. Nevertheless, despite these precautions there was evidence of some O_2 residues in the solvent, as discussed in section 4.2, although this did not affect our ability to quantitatively assess the analytical capability of EC-EPR.

For quantitative measurements, a fine gauge K thermocouple (RS) was inserted in to the EC-EPR cell, downstream of the WE and outside of the sensitive part of the Loop Gap Resonator (LGR) to

measure the temperature of the sample solution during experiments. Thus, uncertainties related to the temperature dependency of EC and EPR towards quantification could be eliminated.

In continuous wave (CW)-EPR a small high frequency AC component (H_{mod}) is added to the applied external magnetic field (H_0) and the signal is recorded via a lock-in detector at this modulation frequency. Thus, a 1st harmonic (approx. 1st derivative) signal is detected. The number of radicals is proportional to the area under the EPR absorption signal, and so the experimental CW-EPR spectrum must be integrated twice. The result of this procedure is very sensitive to baseline noise and drifts, both of which can result in large errors in recovering the absorption signal. One solution is to fit the EPR spectrum and double integrate the fit to obtain the integrated area, a method that was used here.

In an EPR experiment, the EPR signal is proportional to the square root of microwave (MW) power incident on the sample provided that MW power saturation is avoided. In other words, the MW power level must be sufficiently low, such that spin lattice relaxation can maintain the equilibrium population distribution of the different spin states. Unrecognized MW power saturation can result in large errors in radical concentration estimations, but of course one wants to maximize the signal whilst still retaining accurate quantification.

In the experiments performed herein care was taken to ensure that the MW power was well below that required for saturation by constructing saturation curves for the BQ radical and TEMPOL. For the benzoquinone (BQ) radical, the saturation behavior was measured for the center line, as it has been observed to be the easiest to saturate [49]. When reporting EPR results, signal amplitude (SA) is used to indicate the peak to peak height of the 1st derivative EPR line, and double integrated (DI) signal intensity signifies the area under an EPR absorption spectrum.

3. Theory

3.1. Quantitative EPR

The DI-EPR signal for a constant measurement time depends on the following parameters: [50]

$$DI \propto \chi \times H_{mod} \times \eta \times Q_L \times \sqrt{P} \quad (1)$$

where χ is the magnetic susceptibility of the sample, proportional to the number of paramagnetic centers, Q_L is the loaded Q-value of the resonator and P is the microwave power. The \sqrt{P} relationship relates to the intensity of the microwave magnetic field (H_1) inside the resonator responsible for the magnetic dipole transitions, the source of the signal in EPR spectroscopy. The most important sample related variables are thus Q_L , η and H_1 , which are discussed below.

3.1.1. Q-value

Quantification in EC-EPR is best performed by comparing the DI-EPR signal of the unknown sample against a reference standard such as TEMPOL, the concentration of which is known. In liquid phase EPR, matrix effects also need to be considered, as shown by Blackley et al. [35]. This is especially true in EC-EPR, as the addition of supporting electrolyte can change the dielectric properties of the sample from that expected for pure solvent [51,52]. TEMPOL can serve as an ideal reference, as it can be dissolved in acetonitrile containing 0.2 M TBAP, thus matching the Q-value between the unknown and the reference exactly.

For samples with high dielectric constant, it has been shown that the EPR signal intensity is affected by the real (ϵ') and imaginary (ϵ'') parts of the sample's dielectric constant [39]. The ϵ'' leads to power losses due to the absorption of the electric field

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