Intra- and Inter-molecular Sulfhydryl Hydrogen Bonding: Facilitating Proton Transfer Events for Determination of pH in Sea Water

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Abstract

This work presents the electrochemical response of a 2-(methylthio)phenol glassy carbon based electrode for a promising voltammetric pH sensor in both buffered and low-buffered solutions. Electropolymerization of the redox species was performed with the resulting polymer presenting a Nernstian response in buffered media, with a sensitivity of 51 mV/pH unit. The effectiveness of the sulfhydryl bond to facilitate proton transfer from the bulk solution to the phenol molecules has been confirmed, providing an accurate pH measurement of 8.28 in sea water media, compared to that measured with a calibrated glass pH probe of 8.30.

Keywords: Electropolymerization, pH, sulfhydryl hydrogen bond, square wave voltammetry.

Accurate pH measurements are important for many applications such as agronomy, medicine, biology, chemistry, agriculture, environmental science, oceanography, water treatment and water purification, amongst others [1]. For nearly a century, pH has most commonly been measured using a glass electrode, mainly owing to their high selectivity over a wide pH range [2,3]. The glass electrode is a combined system of both glass and reference electrodes in one body [4]. Despite their longevity, glass electrodes show some disadvantages regarding the limited use in many industries because of their fragility, requirement of frequent calibration prior to and during use, and the need to be stored wet [5,6]. As such, there has been a need for a new method of determining pH that overcomes these operational problems.

An alternative to electrochemical systems are colorimetric measurements. An example of which was reported by Rérolle *et al*. who developed a precise and accurate micro-fluidic system. [7] However, their deployment for real-time measurement is challenging due to the need to collect samples and mix with the pH indicator dye, meaning they can only provide low temporal resolution measurements.

Voltammetric determination of pH has long been studied. The ability for molecules to undergo combined electron/proton transfer reactions, meaning their redox couple is dependent on the pH of the solution, makes them a useful tool for determining pH [8,9]. Rubinstein [10] first disclosed the ability to combine such molecules with reference molecules whose redox potential is independent of pH. This was subsequently improved upon by Compton et al., and others, who produced robust stable carbon matrices [11-14].

Recently there has been significant work in the development of pH sensors for use in the water industry, where the concentration of dissolved buffer and/or ionic salt is low. Interest in this area stemmed from further work by Compton *et al.* [15], who showed the ineffectiveness of using the classical quinone/hydroquinone voltammetry to monitor pH in low buffered system. It was demonstrated that the proton coupled electrochemical process perturbed the pH of the solution locally to the electrode when consuming or releasing protons at the surface in low buffer and/or ionic salt solutions.

This issue can be overcome by manipulating the structure of the compounds on the electrode surface, in order to facilitate proton transfer in the electrochemical process. The use of a variety of quinone and phenol based systems, which provide a means of internal hydrogen bonding of the proton being transferred between water molecules and the redox active moiety, have been

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demonstrated to allow the determination of pH in water and ocean solutions [16-18].

Hydrogen bonding occurs between a proton donor group D-H, where D corresponds to any electronegative element, and an acceptor group that is either a lone pair of electrons or a π bond [19]. Sulfur is generally considered as a weak hydrogen bonding acceptor because of its low electronegativity. However, due to the slight electronegativity difference between H and S (0.38, Pauling scale [20]), sulfur-hydrogen bonding can occur [21-24]. These sulfur containing hydrogen-bonds play an important role in some biological processes, mainly in structure and function of proteins [25-27]. Despite being a weak hydrogen bond, compared to the oxygen system, this paper demonstrates for the first time that the hydrogen bonding capabilities of 2-(methylthio)phenol (MTP) compound facilitates the proton mechanism to allow the determination of pH in low buffered media.

2-(Methylthio)phenol is found in coffee and coffee products, and it is generally used as a flavoring agent. However, its ability to form internal hydrogen bonding through the formation of a five-membered hydrogen bond ring structure [28-30] makes this compound suitable as a redox based proton-exchange agent to facilitate proton transfer to and from the bulk solution.

Previous results using substituted polymerized phenol systems to determine the pH of a solution, have shown that initial electropolymerisation has to occur to produce the pH active, redox active moiety, on the electrode surface [16]. This is also the case with the MTP system: the response of MTP was first interrogated using repetitive square wave voltammetry over various potential ranges, to understand when electropolymerisation occurred through the oxidation of the phenol group. Figure 1 details scans 1, 2, 10 and 20 of the modified electrode when placed in a pH 4 solution. Analysis of this result shows the onset of oxidation at +0.10 V, which shows a rising oxidative wave until +0.40 V and the presence of a peak at +0.31 V. Upon repetitive scanning, the oxidative current observed at +0.10 V lowers, enabling the peak at +0.31 to be discerned, whilst the background current rising to +0.40 V on the first scan decreases. To understand this further, the experiment was repeated, however the potential range was increased to +0.60 V (not shown). In this case on the first scan, a large oxidative peak was observed at *ca.* +0.54 V. along with the shoulder at 0.31V. However, upon repetitive scanning both oxidative waves decreased and no defined waves were observed after twenty scans, consistent with the redox active species over polymerizing.

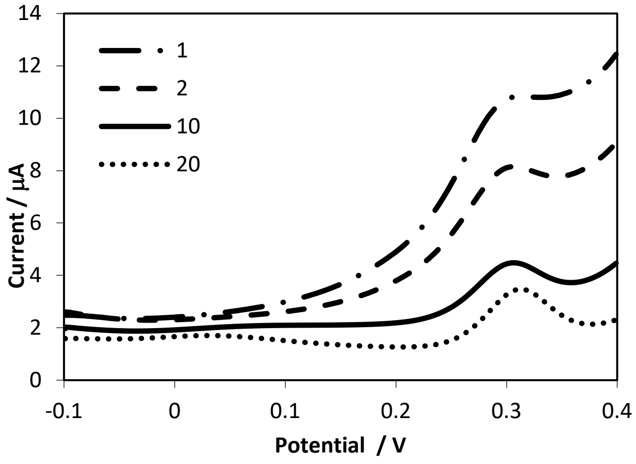
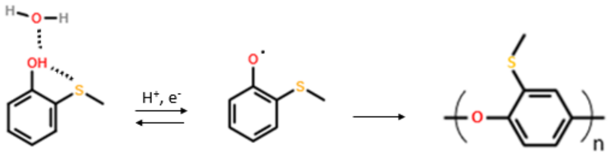


Fig. 1: Repetitive voltammetric responses of an MTP modified electrode when placed in pH 4 buffer solution.

The main redox wave with an onset at +0.1 V and a peak at *ca.* +0.54 V is due to the oxidation of the phenol to form the radical which subsequently undergoes electropolymerization. The radical formation and polymerization pathway is shown in scheme 1. At higher potentials, over-polymerization of the phenol occurs, leading to the formation of a passivating layer, consistent with oxidation of phenol based molecules [31]. The redox wave at +0.31 V can be attributed to the generation of a new electroactive species formed when the phenol moiety is oxidized, which is consistent with the oxidation of salicylaldehydes [16]. Controlling the oxidation potential of the phenol moiety allows this newly generated adduct to form further and ultimately stabilize. The response of scans 10 and 20 in Figure 1, show the formation of this non-passivating electroactive polymeric species on the sensor electrode, the enhancement and resolution of this new oxidation wave and the subsequent loss of the background current attributed to the parent phenol oxidation. The data from Figure 1 shows the MTP system can be electropolymerized similar to that reported for oxygen modified phenol systems, with the formation of electroactive adduct [16].



Scheme 1: Propagation radical forming pathway and electropolymerization for 2-(methylthio)phenol.

Next, the polymerized layer was tested in a range of pH solutions to understand if the sulfur-hydrogen bonding facilitated proton transfer thus enabling the determination of pH in low buffered media. Figure 2A details the voltammetric response of the modified electrode when placed in pH 4, 7, 7.8 and 9 solutions. It can be clearly seen that as pH increases the peak potential of the redox wave attributed to the newly formed polymer shifts to lower potentials. This is because the species is easier to oxidize, providing pH sensitivity. Figure 2B shows a plot of peak potential as a function of pH, which was found to be linear with a sensitivity of 51 mV/pH unit, consistent with previous data of 55 mV per pH unit at 20°C for electropolymerized phenol species [16].

The response of the modified electrode was also tested in sea water. The voltammetric profile is overlaid in Figure 2A, which shows the oxidation wave of the polymer moiety in sea water between pH 7.8 and pH 9 solutions, consistent with the pH being 8.30 (measured using a calibrated standard glass electrode). A well-defined oxidation wave is observed showing the sea water had minimal impact on the voltametric profile and thus the sea water had no interference on the signal. Using the data obtained from the calibration plot shown in Figure 2B, the pH of seawater was found to be 8.28, which was consistent with the pH 8.30 measured. Furthermore, the stability of the system was assessed, this was achieved by monitoring the response to continuous measurements over a period of time. The signal was found to show a discernable signal after 1500 scans. In a final device, this stability can be improved by incorporation of the MTP into a solid carbon matrix.

The ability to accurately measure pH in an unbuffered solution confirms the sulfur-hydrogen bonding capabilities of 2-(methylthio)phenol (MTP) compound to facilitate the proton mechanism and allowing an accurate determination of pH in sea water. Thus, even if S---H bond is weaker than O---H due to the lower electronegativity of sulfur, the hydrogen bond is strong enough to allow the proton transfer between the bulk solution and electrode surface, meaning that the redox reaction does not perturb the environment local to the electrode surface.

In conclusion, this work demonstrated the ability of the electropolymerizing 2-(methylthio)phenol to form an electro-active polymer with a redox potential of ca. +0.31 V in pH 4 buffer solution. The resulting polymer was found to provide a Nernstian response in buffered media, with a sensitivity of 51 mV/pH unit, and it has confirmed the effectiveness of the sulfhydryl bond to facilitate proton transfer from the bulk solution to the phenol molecules, in order to successfully sense the pH in sea water, leading to a promising sensor for pH sensing in buffered and unbuffered media.

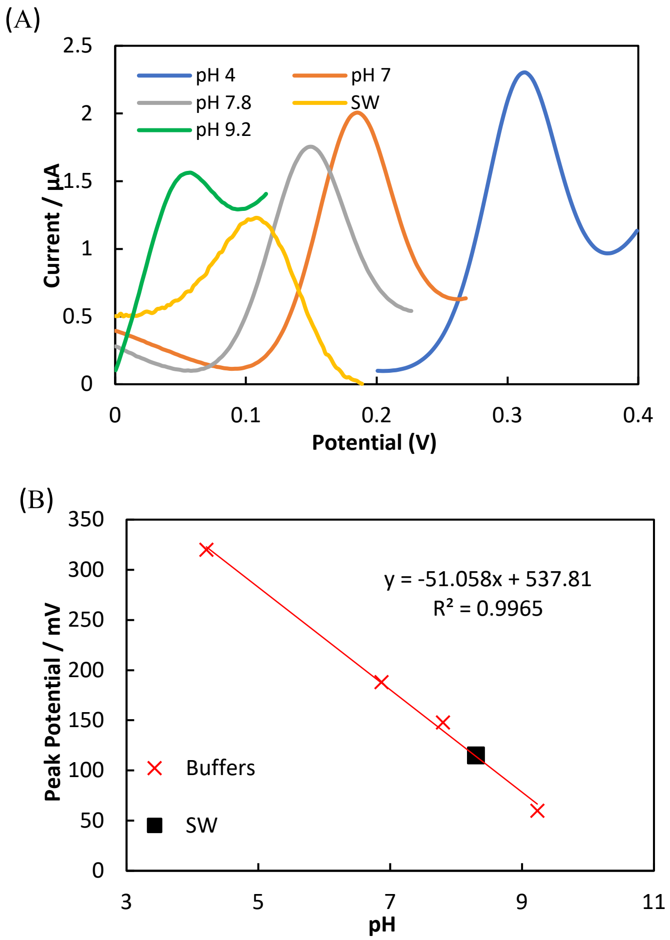


Fig. 2: (A) Square Wave Voltammograms and (B) calibration plot of 2-(methylthio)phenol carbon based electrode in IUPAC standard buffers and sea water solution.

Experimental

All chemicals were purchased from Sigma–Aldrich and used without further purification (unless specified). Standard IUPAC buffer solutions (pH 4, 7, 9) were prepared as follows: pH 4.21, 0.05 M potassium hydrogen phthalate; pH 6.86, 0.025 M potassium dihydrogen phosphate and sodium phosphate dibasic; pH 9.23, 0.05 M sodium tetraborate, all in deionized water

(Hexeal, UK). All buffers contained 0.1 M KCl as the supporting electrolyte.

Sea water, H2Ocean Natural Reef Salt, was purchased from Maidenhead Aquatics (UK) in which 1 Kg of this salt was dissolved in 25 L of water.

The modified electrode was prepared by first dissolving 2-(methylthio)phenol (purchased from Tokyo Chemical Industry, TCI, UK) in dichloromethane (1:10 proportion) and then casting 20 μL of the resulting solution on the surface of the glassy carbon electrode.

Electrochemical measurements were conducted using an Ana Pot potentiostat (Zimmer & Peacock, UK) with a standard three-electrode configuration. A modified glassy carbon electrode was used as a working electrode, a carbon counter and an Ag/AgCl (BASi, USA) acted as the reference electrode. All square wave voltammetry (SWV) was conducted using the following parameters: frequency = 100 Hz, step potential = 1 mV, amplitude = 20 mV, no pre-treatment.

Absolute pH measurements were performed using a standard glass electrode (Sensorex, California, USA). Prior to the measurement of the solutions, the pH meter was calibrated using Reagecon buffers of pH 4.01 ± 0.01, pH 7.00 ± 0.01 and pH 10.01 ± 0.01 (Reagecon Diagnostics Ltd., Ireland). Measurement of the pH was carried out on each freshly made solution prior to experiments. All the experiments were carried out in baths thermostatted at 18 ± 1 °C.

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Data Availability Statement

Due to the commercial nature of the work the data is not available.

Conflicts of Interest

The authors declare no conflict of interest.

Figure Legends

Scheme 1: Propagation radical forming pathway and electropolymerization for 2-(methylthio)phenol.

Fig. 1: Repetitive voltammetric responses of an MTP modified electrode when placed in pH 4 buffer solution.

Fig. 2: (A) Square Wave Voltammograms and (B) calibration plot of 2-(methylthio)phenol carbon based electrode in IUPAC standard buffers and sea water solution.

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