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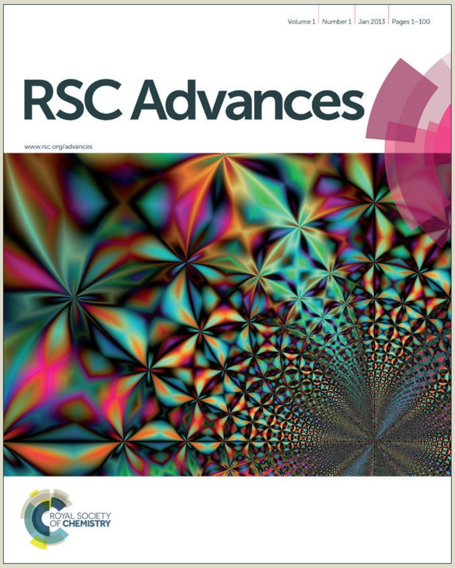

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ARTICLE

A Novel Sensor Based on Electropolymerized Substituted-phenols for pH Detection in Unbuffered Systems

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This work summarizes the electrochemical response of a range of substituted phenols, including salicylaldehyde and salicylic acid, for use as a voltammetric pH sensor for the determination of pH in both buffered and unbuffered media. Suitable candidates are identified and mechanistic insights into oxidation mechanism of the electro-polymerization by comparing with other subsituted phenols are given. Square wave voltammetry measurements suggest the peak achieved through the electrochemical polymerization directly after the 1-electron 1-proton oxidation for both salicylaldehyde and salycilic acid shows a Nernstian response with good definition through a pH range from 2 to 10. In addition, hydrogen bonding enables the compound to sense the pH of unbuffered solutions with an error of less than 1%.

Introduction

There is a strong demand for more robust pH sensors due to the ubiquitousness of hydrogen ions participating in most chemical reactions. The capability of accurately sensing pH in low ionic strength solutions and unbuffered (natural buffer) solutions is extremely important in environmental monitoring especially in water quality, treatment works, marine research including sea water monitoring, home/commercial aquarium, as well as blood pH measurements. However, this is a tough measurement to accomplish due to the propensity of the pH sensor to locally perturb the solution pH close to the device[1, 2], in addition to the device suffering from instability and/or drift and consequently requiring constant recalibration[3, 4]. There are various methods/probes currently used for pH sensing, including simple chemical indicators, e.g. litmus paper, conventional glass pH electrodes, and sophisticated pH systems employing spectrometers such as nuclear magnetic resonance (NMR) spectroscopy[5, 6]. Currently, the most common pH sensing devices are based on potentiometric measurement[3, 7]. The most popular potentiometric method utilizes glass electrodes because of their facile handling and high selectivity towards pH sensing[8, 9]. In addition, voltammetric methods have also been widely studied, such as the two-terminal sensor systems, which measure the potential difference between a pH-sensitive and redox-active species and a pH-insensitive but redox-active species. The pH in this system can therefore be calculated according to the Nernst equation[10-14], which can be expressed as:

$$E_p = E^0_{formal} - 2.303\left(\frac{mRT}{nF}\right)\mathrm{pH}$$

where E_p is the peak potential, E^0_{formal} is the formal potential, R is the gas constant, T is the temperature, F is the Faraday constant, and m, n are the number of proton and electrons involved in the redox process, respectively. Hence the theoretical slope for a two electron, two proton transfer is 59.2 mV per pH unit at 25 °C. Other frequently used transducers in potentiometric devices include ion-selective membranes or film electrodes[15, 16], and ion-selective field transistors[9, 17]. A variety of optical[18] and conductometric[19] methods were also developed.

Lawrence *et al.*[20-22] demonstrated a novel type of voltammetric pH sensor based on pH-sensitive dihydroxyanthraquinone derivatives. It was shown that the incapability of measuring pH of unbuffered media observed with the quinone system used in the traditional two-terminal system can be eliminated by manipulating the structure of the compound/compounds on the electrode surface. The inter and intra molecular hydrogen bonding brought about by the dihydroxyanthraquinone species can facilitate proton transfer between the water molecules and the redox active quinone moiety without affecting the pH of the solution at the electrode surface. Hence, the pH of unbuffered media can be detected accurately. Nevertheless, this kind of pH sensor is still suffering from the chemical instability caused by the nucleophilic attack by hydroxide ions at high pH, which results in unexpected reactions leading to the deviation from a typical Nernstian response when the pH is relatively high.

The electrochemical oxidation of phenol typically occurs via a 1-electron 1-proton oxidation and results in a passivating layer forming on the electrode surface thus rendering the electrode no longer active[23, 24]. In the case of substituted phenols, it has

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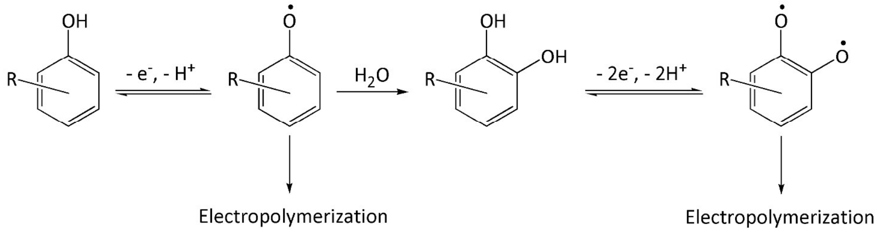


Scheme 1. The ECE reaction and electropolymerization pathways for substituted phenols.

been postulated that the mechanism follows an electrochemical-chemical-electrochemical (ECE) reaction process in which the phenol is initially oxidized by a 1-electron 1-proton transfer, generating a radical species. This radical species can react with water molecules and then be further oxidized and followed by electropolymerization (scheme 1)[25]. Meanwhile, the radical species generated through the 1-electron 1-proton step and its tautomers can alternatively produce a self-electropolymerization, such that a novel type of pH-sensitive redox compound with potential hydrogen bonding and better stability can be expected.

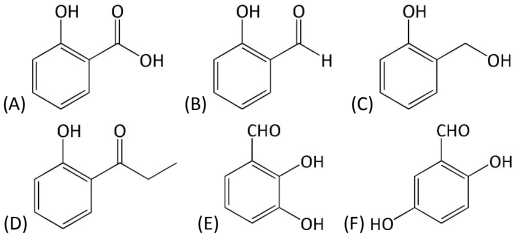
Electrodes consisting of carbon-related materials are widely applied in electrochemistry and extensively studied due to their desirable chemical and physical properties as well as the suitability for modification[26-28]. Commercially they are generally low cost and readily available. The most typical carbon materials applied in electrochemistry include graphite, glassy carbon, carbon fiber, carbon black, boron-doped diamond, carbon nanotubes and graphene. Carbon materials with surface modification through physical absorption have been developed for reliable pH determination[21, 26, 27, 29-31]. Glassy carbon electrodes modified with the substituted phenols were employed in the following work.

Experimental

Apparatus

Electrochemical measurements were conducted using a PGSTAT30 Autolab potentiostat (Ecochemie, Netherland) with a standard three-electrode configuration. The glassy carbon electrode, a platinum (Pt) mesh counter and a saturated calomel electrode (SCE) (Radiometer, UK) acted as the working, counter and reference electrodes respectively. All voltammetry experiments were conducted using the following parameters, unless otherwise stated; frequency = 25 Hz, step potential = 2 mV, amplitude = 0.02 V.

Absolute pH measurements were performed using a standard glass electrode (Radiometer, UK). Prior to the measurement of the solutions, the pH meter was calibrated using Duracal buffers of pH 4.01 ± 0.01, pH 7.00 ± 0.01 and pH 10.01 ± 0.01 (Hamilton, China). Measurement of the pH was carried out on each freshly made solution prior to experiments. Electrochemical interrogation was sought by immobilizing the molecules on the surface of the glassy carbon electrode by solvent evaporation. The substituted phenol compound was dispersed in dichloromethane (DCM) from which a 10 µL aliquot was dispersed onto the glassy carbon electrode and allowed to dry. All the experiments were carried out at 25 ± 1 ^{o}C.



Scheme 2. Structure of (A)Salicylic acid, (B) salicylaldehyde, (C) 2-hydroxybenzylalcohol, (D) 2-hydroxypropiophenone, (E) 2,3-dihydroxybenzaldehyde and (F) 2,5-dihydroxybenzaldehyde.

Reagents

All chemicals were purchased from Sigma-Aldrich and used without further purification. Solutions were prepared with deionized water and had resistivity no less than 18.2 MΩ·cm at 25 ^{o}C (Millipore, UK). Standard IUPAC buffer solutions (pH 4, 7, 9) were prepared as follows: pH 4.17, 0.05 M potassium hydrogen phthalate; pH 6.86, 0.025 M potassium dihydrogen phosphate and sodium phosphate dibasic; pH 9.17, 0.05 M sodium tetraborate. Britton-Robinson (BR) buffer was prepared with 0.04 M boric, phosphoric and acetic acids and its pH varied from 2-12 with successive KOH additions. All solutions contained 0.1 M KCL as the supporting electrolyte.

Results and Discussion

Electrochemical characterization of the substituted phenol compounds

Salicylic acid and salicylaldehyde (shown in scheme 2A&B) were first coated onto the electrode to be tested by square wave voltammetry (SWV) to assess the electrochemical response.

Figure 1A&B details the repetitive SWV responses of (A) salicylic acid and (B) salicylaldehyde. It can be seen that the initial scan for each shows a large oxidative wave at +0.99 V and +0.95 V respectively. The second and subsequent scan shows a large decrease in this oxidative peak current and emergence of a new redox wave at +0.66 V and +0.59 V respectively. The generic nature and pH dependence of this voltammetric profile is shown in figure 1C, in this case the SWV response of the salicylaldehyde is shown when the electrode was placed in pH 2 BR buffer solution. As with the response at pH 4, the initial scan shows a large oxidative wave at +1.01 V, with a new wave emerging at +0.71 V upon repetitive scanning.

To understand the origin of the voltammetric profiles obtained upon repetitive scanning, experiments were conducted using other molecules with a similar structure to those shown in scheme 5, namely 2-hydroxybenzylalcohol and 2-hydroxypropiophenone (scheme 2C&D). Figure 2 details repetitive square wave voltammograms for 2-hydroxybenzylalcohol and 2-hydroxypropiophenone in pH 4 buffer solution. In each case a large oxidation wave is observed at +0.82 V and +1.12 V respectively, analogous to the previous two phenols shown in figure 1A&B. On the second scan a large decrease is observed on this wave and new waves emerge at +0.35 V and +0.80 V respectively.

Electrochemical pH sensing by the substituted phenol compounds

The properties of this influence on the newly formed electroactive species was assessed for both salicylaldehyde and salicylic acid. Figure 3A details the SWV response when the newly formed electroactive species after the oxidation of salicylaldehyde was placed in Britton-Robinson buffer (pH 2.0) and the pH of the solution increased by addition of concentrated NaOH solution. As predicted, the oxidative peak shifts to lower potentials as the pH is increased from 2 to 10. The corresponding plot of oxidative peak potentials as a function of pH is shown in figure 3B (squares). This was found to be linear over the entire pH range studied with a slope of 60.4 mV per pH unit, consistent with an n-electron n-proton redox process.

A similar experiment was conducted using the salicylic acid layer, the resulting square wave voltammetric responses are detailed in figure 3C when the modified electrode was placed

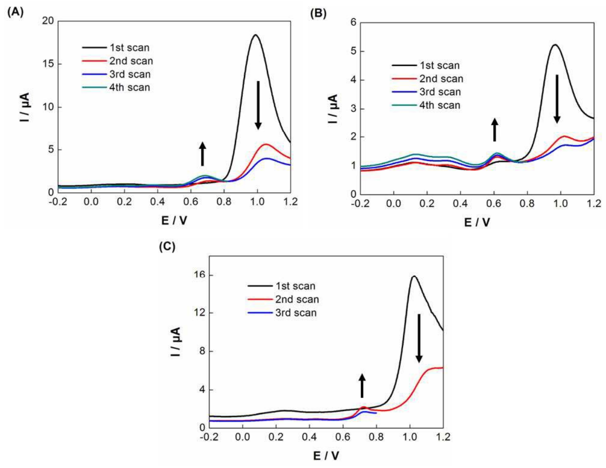


Figure 1. Repetitive square wave voltammetric responses of of (A) salicylic acid and (B) salicylaldhyde, when placed in pH 4 buffer solution, and (C) salicylaldehyde, when placed in pH 2 BR buffer solution

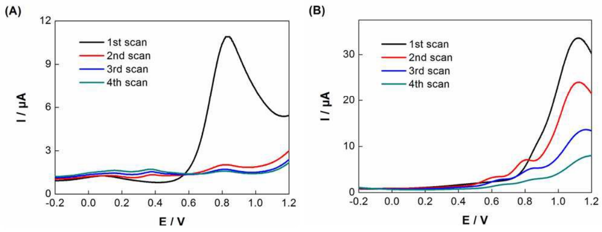


Figure 2. Repetitive square wave voltammetric responses of (A) 2-hydroxybenzylalcohol and (B) 2-hydroxypropiophenone, when placed in pH 4 buffer solution.

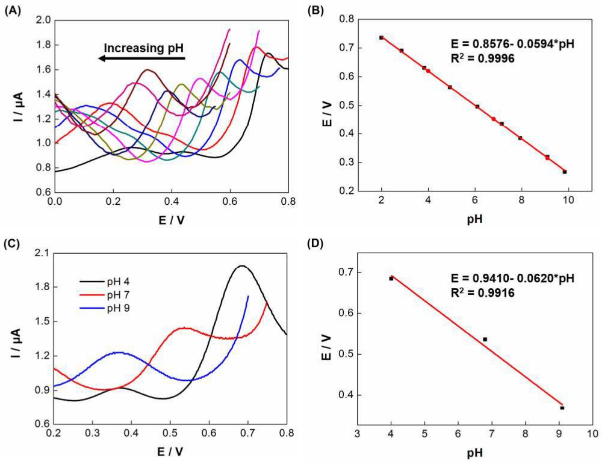


Figure 3. Square wave voltammetric (frequency = 25 Hz, step potential = 2 mV, amplitude = 0.02 V) responses of the polymeric wave associated with (A) salicylaldehyde when placed in Britton-Robinson buffer and the pH varied from 2 to 10 (black squares) and IUPAC buffers (pH 4, 7 and 9) (red dots) and (B) the corresponding plot of oxidative peak potentials as a function of pH; (C) the polymeric wave with salicylic acid when paced in IUPAC buffers (pH 4, 7 and 9) and (D) the corresponding plot of oxidative peak potentials as a function of

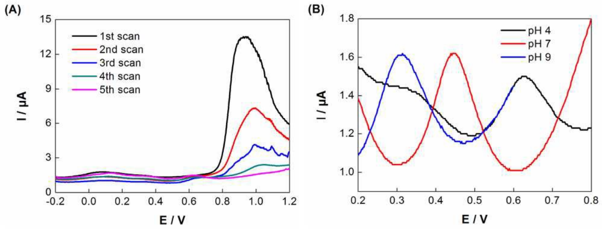


Figure 4. (A) Repetitive square wave voltammetric (frequency = 25 Hz, step potential = 2 mV, amplitude = 0.02 V) responses of salicylaldehyde under stirred conditions. (B) Square wave voltammetric response of the newly formed species associated with the oxidation of salicylaldehyde when placed in IUPAC buffers (pH 4, 7, 9).

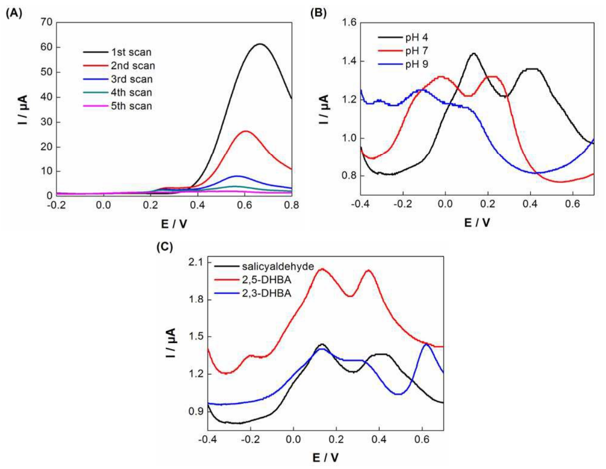


Figure 5. (A) Repetitive square wave voltammetric (frequency = 25 Hz, step potential = 2 mV, amplitude = 0.02 V) responses of 2,3-dihydroxybenzaldehyde. (B) Square wave voltammetric responses of the newly formed species associated with the oxidation of 2,3-dihydroxybenzaldehyde when placed in IUPAC buffers (pH 4, 7 and 9); (C) Comparison of the square wave voltammetric waves (frequency = 25 Hz, step potential = 2 mV, amplitude = 0.02 V) associated with the oxidation products of 2,3-dihydroxybenzaldehyde (2,3-DHBA), 2,5-dihydroxybenzaldehyde (2,5-DHBA) and salicylaldehyde when placed in pH 4 buffer solution.

in standard pH 4, 7, 9 buffers. It can be clearly seen that as the pH is increased the redox wave shifts to lower potentials with well-defined waves being observed at each pH value. The plot of peak potential shift as a function of pH was found to be linear with a slope of 62 mV per pH unit consistent with the n electron n proton redox process (figure 3D). It should be noted that similar results were obtained for the oxidation products of 2-hydroxybenzylalcohol and 2-hydroxypropiophenone. These results suggest that the newly formed species attributed to the oxidation of salicylic acid, 2-hydroxybenzylalcohol, 2-hydroxypropiophenone and salicylaldehyde are similar in structure.

To understand the stability and nature of the new redox species experiments were conducted under forced convection conditions; it can be envisaged that if the product is water soluble stirring the solution would have a dramatic effect on its response. Figure 4A details the repetitive square wave voltammetric response of the species when the salicylaldehyde modified electrode was placed in stirred pH 4 solution. The response is consistent with that of figure 1, in which a large oxidative wave is observed at +0.97 V on the first scan and subsequent scanning generates a new redox wave at +0.63 V. This is an important result as it shows that stirring of the solution has negligible impact on the voltammetric response, and the redox wave emerging at +0.63 V is due to species absorbed onto the electrode surface; under stirred conditions the emergence of this wave may expect to be hindered if the species were soluble. Figure 4B highlights the square wave voltammetric response when the resulting layer formed under stirred conditions was placed in various pH buffers, well defined waves are observed in each case. A comparison of the results shown in figure 3A and figure 4B suggest that under stirred conditions an increased voltammetric peak resolution is observed. The corresponding plot of peak potential as a function of pH is overlaid (diamonds) on figure 3B.

It has previously been shown that the electrochemical oxidation mechanism of substituted phenols can follow an ECE reaction process in which the phenol is oxidized by a 1-electron 1-proton transfer, generating a radical species. This radical species can then undergo attack by water to form the dihydroxyquinone structure which can then be oxidized and reduced at potentials lower than that of phenol. In the case of salicylaldehyde it can be envisaged that two species could be formed should this ECE reaction take place, namely 2,3-dihydroxybenzaldehyde and 2,5-dihydroxybenzaldehyde. In the following the voltammetry of these molecules is assessed over a wide range of pH values 4-9, to aid understanding of the oxidation mechanism of the compounds detailed above.

Figure 5A details repetitive square wave voltammograms for 2,3-dihydroxybenzaldehyde. The voltammetric response was recorded in pH 4 buffer solution. It can be clearly seen that on the first scan a large oxidation wave is observed at +0.65 V which decreases dramatically upon repetitive scans, and new oxidative features occur at lower potentials namely at +0.40 V and +0.15 V. This is shown in more detail in figure 5B which shows the response of the resulting electrode after oxidation in pH 4 solution in various pH buffered solutions (4, 7 and 9).

At each pH two well defined waves are observed, it should be noted that the wave at higher oxidation potential produced a Nernstian response with pH of 62 mV per pH unit, whilst the wave at lower potentials produced a value of 51.5 mV/pH unit. Analogous responses to those obtained for 2,3-dihydroxybenzaldehyde were recorded for 2,5-dihydroxybenzaldehyde. These results suggest that the dihydroxy species polymerizes on the electrode surface, through a 1,4-Michael addition reaction[32]. To understand if the new electrochemical wave which has been the subject of interrogation for the various derivatives of phenol *vide supra*,

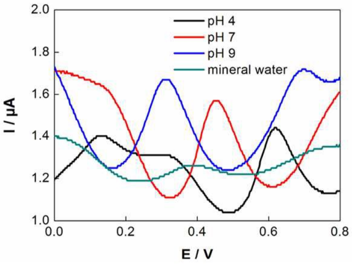


Figure 6. Square wave voltammetric (frequency = 25 Hz, step potential = 2 mV, amplitude = 0.02 V) responses of the new redox wave associated with oxidation salicylaldehyde when placed in IUPAC buffers (pH 4, 7, and 9). Overlaid is the reponse when the modified electrode was placed in mineral water (black line).

Table 1. A comparison of the measured mineral water pH using the glass electrode with that determined using the redox active system. Also detailed is the gradient of the calibration line.

Compound	Measured pH	Determined pH	Error (%)	Sensitivity (mV/pH)
Salicylic acid	7.65	7.68	0.392	62.0
Salicylaldehyde	7.65	7.69	0.522	59.4
2-Hydroxybenzylalcohol	7.65	8.02	4.84	58.7
2-Hydroxypropiophenone	7.30	7.30	0.00	57.6
2,3-Dihydroxybenzaldehyde	7.50	8.10	8.00	62.1
2,5-dihydroxybenzaldehyde	7.50	7.56	0.800	61.5

is due to the formation of dihydroxybenzaldehyde polymeric based layer on the surface, the response of each of the layers, 2,3-dihydroxybenzaldehyde, 2,5-dihydroxybenzaldehyde and salicylaldehyde were compared in pH 4 buffer solution. The resulting three square wave voltammograms are overlaid in figure 5C (note the current's scale for each response has been offset for clarity). It can be clearly seen that the 2,3-dihydroxybenzaldehyde and 2,5-dihydroxybenzaldehyde produce similar responses after undergoing oxidation. In the case of the oxidation products of salicylaldehyde similar voltammetric features are observed to that of the dihydroxybenzaldehydes, suggesting that the oxidized phenol undergoes attack by water to form the dihydroxy species, which once formed, immediately polymerize on the surface of the electrode. However, in addition to these waves there is an additional wave formed at +0.59 V, which as highlighted above, and undergoes a Nernstian response over a wide pH range. This suggests that this product is not due to the oxidation of the dihydroxy adducts.

Comparison of the voltammetric resolution of the three waves for salicylaldhyde shows that the feature, not associated with the dihydroxybenzaldehyde polymers, is well resolved and will be used for further interrogation for use within a pH sensor.

Determination of pH in unbuffered media

Having understood the voltammetric response of the newly formed layer and showing that the oxidation of salicylic acid, 2-hydroxybenzylalcohol, 2-hydroxypropiophenone and salicylaldehyde produce new redox active layers, which are both insoluble in water but also undergo n-electron n-proton redox process, the ability of each species to determine the pH of unbuffered media was assessed. It has been shown previously that the use of 1,2-dihydroxyanthraquinone is capable of accurately determining the pH of unbuffered media due to the formation of hydrogen bonds between the two oxygen moieties in close proximity. Analysis of the structure suggests that this could be the case for salicylic acid, 2-hydroxybenzylalcohol, 2-hydroxypropiophenone and salicylaldehyde. However, unlike the dihydroxyanthraquinones and 5,8-dihydroxy-1,4-naphoquinone, the oxygen which would promote hydrogen bonding is attached to a carbon atom which has free rotation and therefore hydrogen bonding would align the two oxygen moieties into a planar geometry analogous to the 1,4-dihydroxyanthraquinone species.

Figure 6 details the voltammetric response of the salicylaldehyde redox layer, after initial oxidation in pH 4 solution, when placed pH 4, 7 and 9 solutions (dashed response). The result is as predicted, similar to that shown in figure 3B. Also overlaid is the response of the electrode when placed in a commercial mineral water sample (solid line). A well-defined wave is observed between pH 7 and pH 9. Using the trend in peak potential with pH, the pH of the mineral water was found to be 7.69 which is in excellent agreement with that stated on the bottle of 7.7 and measured with a commercial glass pH electrode, 7.65.

Analogous experiments were conducted with salicylic acid, 2-hydroxypropiophenone and 2-hydroxybenzylalcohol, and the resulting data is summarized in table 1. This compares the measured mineral water pH using the glass electrode and that determined using the redox active system and highlights the gradient of the calibration line. Also shown in the table 1 is the data obtained when using the redox wave associated with the oxidation of 2,3-dihydroxybenzaldehyde and 2,5-dihydroxybenzaldehyde in unbuffered media.

The data in table 1 shows that the error of measuring the pH of mineral water by salicylic acid, salicylaldehyde and 2-hydroxypropiophenone are all smaller than 1%, indicating their suitability to be used within a pH sensor for bufferless sensing, whilst 2-hydroxybenzylalcohol is not suitable. For 2-hydroxybenzylalcohol it suggests that the hydrogen bonding between the two alcohol groups is not strong enough to facilitate efficient proton transfer between the molecule and the aqueous media. In addition to the polymeric layers formed, oxidation of 2,3-dihydroxybenzaldehyde and 2,5-dihydroxybenzaldehyde was found to produce good correlation with that of measured pH, however the definition of the waves was not as pronounced with these molecules compared with salicylaldehyde. The results above show the importance of having a group within the proximity of the moiety to be oxidized or reduced which can promote hydrogen bonding and hence proton transfer between the solvent and the molecule.

Conclusions

A novel pH sensor utilizing a group of electro-polymerized substituted-phenols has been developed. The electrochemical responses of the polymers based on salicylic acid, salicylaldehyde, 2-hydroxybenzylalcohol, 2-hrdroxypropiophenone, 2,3-dihydroxybenzaldehyde, and 2,5-dihydroxybenzaldehyde in both buffered (pH 2 – 10) and unbuffered media have been studied. The voltammetric responses for all the modified electrodes show similar results which agree with the Nernst equation in buffered solutions, and the salicylic acid, salicylaldehyde and 2-hydroxybenzylalcohol show reliable capability of measuring pH or unbuffered media. In addition, the electro-polymerization mechanism for the substituted phenols has also been discussed by comparing the electrochemical performance of different substituted phenols.

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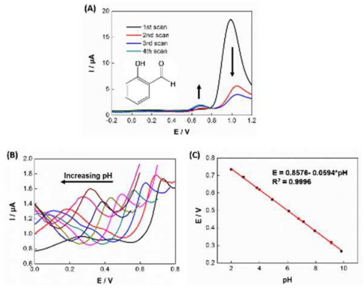

Polymeric waves associated with the electrochemical oxidation of salicylaldehyde and its derivatives exhibit Nernstian responses to pH variations in both buffered and unbuffered media.