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The Effect of the Buffering Capacity of the Supporting Electrolyte on the Electrochemical Oxidation of Dopamine and 4-Methylcatechol in Aqueous and Nonaqueous Solvents

Shanshan Chen, Kah Yieng Tai, and Richard D. Webster*[a]

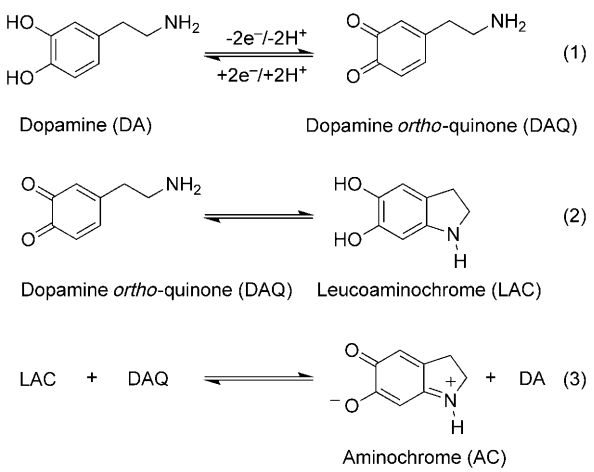
Abstract: Dopamine was electrochemically oxidized in aqueous solutions and in the organic solvents *N,N*-dimethylformamide and dimethylsulfoxide containing varying amounts of supporting electrolyte and water, to form dopamine *ortho*-quinone. It was found that the electrochemical oxidation mechanism in water and in organic solvents was strongly influenced by the buffering properties of the supporting electrolyte. In aqueous solutions close to pH 7, where buffers were not used, the protons released during the oxidation process were able to sufficiently change the localized pH at the electrode surface to reduce the deprotonation rate of dopamine *ortho*-quinone, thereby slowing the conversion into leucoaminochrome. In *N,N*-dimethylformamide and dimethylsulfoxide solutions, in the absence of buffers, dopamine was oxidized to dopamine *ortho*-quinone that survived without further reaction for several minutes at 25 °C. The voltammetric data obtained in the organic solvents were made more complicated by the presence of HCl in commercial sources of dopamine, which also underwent an oxidation process.

Keywords: chromophores · cyclic voltammetry · oxidation · reduction · UV/Vis spectroscopy

Introduction

4-(2-Aminoethyl)benzene-1,2-diol, also known as dopamine (DA), is produced in the brain and functions as a neurotransmitter and neurohormone.[1] Owing to its catechol (*ortho*-hydroquinone) structure,[2–4] it can be oxidized in aqueous solution relatively easily in a two-electron and two-proton process transforming into the quinine (Q), which survives for at least several minutes at pH 1 (Scheme 1, reaction 1). The reaction in Scheme 1 is written as a $-2e^-/-2H^+$ process (concerted mechanism), but the individual electron-transfer steps could occur separately to the proton-transfer reactions (consecutive mechanism). At low pH, the amine group on dopamine ($pK_a = 8.92$) and dopamine *ortho*-quinone (DAQ) is protonated; however, as the pH increases the amine exists in its unprotonated form and dopamine *ortho*-quinone undergoes a cyclization reaction to form leucoaminochrome (Scheme 1, reaction 2).[5,6] Leucoaminochrome is oxidized at a less positive potential than dopamine; therefore, it reacts immediately with dopamine *ortho*-quinone to form aminochrome and dopamine (Scheme 1, reaction 3).[5,6] Aminochrome is itself not long lived and ultimately reacts to form neuromelanin, a polymeric material.

Detailed electrochemical experiments have established that the electrochemical behavior of dopamine is greatly influenced by the 1) electrode material and surface activity,



Scheme 1. Oxidation mechanism for dopamine.

[a] S. Chen, K. Y. Tai, Prof. Dr. R. D. Webster
Division of Chemistry and Biological Chemistry
School of Physical and Mathematical Sciences
Nanyang Technological University
Singapore 637371 (Singapore)
Fax: (+65) 6791-1961
E-mail: webster@ntu.edu.sg

2) pH, 3) solvent system, and 4) supporting electrolyte.[5–15] Because of dopamine's key involvement in neural processes, there is keen interest in in vivo voltammetric monitoring of dopamine in mammalian brains.[16] The voltammetric mechanism involves an adsorption/desorption process at carbon[17–24] and metallic electrodes,[21,25–28] which aids in the voltammetric detection limits. Pure carbon fibers give excellent detection limits,[17–21] and there have been extensive studies that use surface-modified electrodes to improve the detection of dopamine and reduce the interference from other biological molecules that are easily oxidized, such as ascorbic acid.[29–49] The oxidation of dopamine at the interface between aqueous and nonaqueous solvents has also been examined using liquid–liquid electrochemical techniques and 4-electrode potentiostats.[50–52]

The majority of electrochemical studies on dopamine have been performed in buffered aqueous solutions due to its low solubility in most organic solvents and because it exists biologically in an aqueous-phase environment rather than within bilayer lipid membranes. It has recently been shown that the buffering capacity of the electrolyte has a large effect on the electrochemical properties of dopamine, due to the protons released during the oxidation reaction affecting the environment at the electrode surface.[13] In this study, we were interested in examining the effect that the supporting electrolyte had on the oxidation of dopamine and 4-methylcatechol (MC) in water and in the nonaqueous solvents: *N*,*N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO), and whether the organic solvents could stabilize the dopamine *ortho*-quinone against the cyclization reaction.

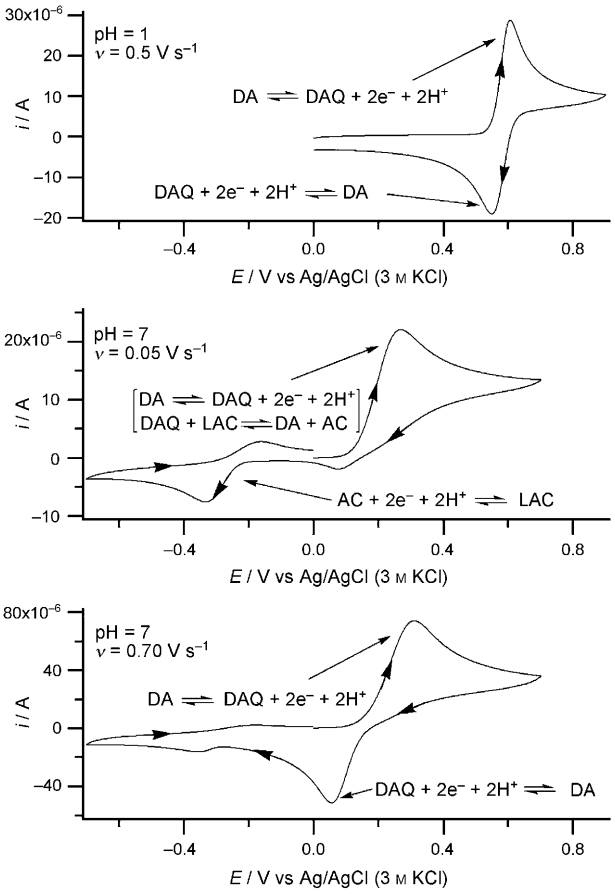


Figure 1. Cyclic voltammograms of dopamine in aqueous buffered solutions at pH 1 and pH 7 recorded at 22(±2)°C at a 3 mm diameter GC electrode and with a starting and finishing potential of 0 V vs. Ag/AgCl. The scan was commenced in the positive potential direction.

Results and Discussion

Electrochemistry in Buffered Aqueous Solutions

Figure 1 shows cyclic voltammetry (CV) data obtained in buffered aqueous solutions at pH 1 and pH 7 during the oxidation of dopamine. At pH 1, dopamine is oxidized in a chemically reversible two-electron, two-proton process to form dopamine *ortho*-quinone (Scheme 1, reaction 1). As the pH increases, the lifetime of dopamine *ortho*-quinone decreases due to the cyclization reaction of the amine group. At slow scan rates ($\nu = 0.05\ V\,s^{-1}$) at pH 7, dopamine was found to undergo oxidation to dopamine *ortho*-quinone which quickly reacted to form leucoaminochrome (Scheme 1, reaction 2). Because leucoaminochrome is more easily oxidized than dopamine, it is immediately oxidized to aminochrome (AC), which can then be detected as a reduction process on the reverse scan.[5,6] Aminochrome's structure is closer to that of a zwitterionic *para*-quinoneimine, than an *ortho*-quinone, which accounts for the large shift in reduction potential between aminochrome and dopamine *ortho*-quinone.[1] At pH 7, as the scan rate was increased to $0.7\ V\,s^{-1}$, the cyclization reaction of dopamine *ortho*-quinone was outrun and a chemically reversible two-electron, two-proton process was observed, similar to that observed at $\nu = 0.05\ V\,s^{-1}$ at pH 1. The rate constant for the cyclization reaction in pH 7 buffered solutions has been estimated by variable scan rate CV experiments to be approximately $0.2\ s^{-1}$ at 25 °C.[5,6]

It can be seen in Figure 1 that the oxidation process of dopamine shifts to more negative potentials as the pH increases. The oxidation potential (E_{obs}) of the process can be estimated from the midpoint of the oxidative (E_p^{ox}) and reductive (E_p^{red}) peaks, which vary according to the pH because protons are involved in the reduction reaction.[53–56] Hence, the measured E_{obs} is shifted from the formal potential (E_f^o) according to the Nernst equation:[57]

$$E_{obs} = E_f^0 + \frac{RT}{nF} \times \ln \frac{[DAQ][H^+]^2}{[DA]} \quad (1)$$

where n is the number of electrons transferred (2), R is the gas constant ($8.3143\ J\,K^{-1}\,mol^{-1}$), T is the temperature (in K) and F is the Faraday constant ($96485\ C\,mol^{-1}$). When [DA] = [DAQ], then $E_{obs} = E_{1/2}^f$ (the reversible half-wave potential).[57] According to Equation (1), at 25 °C, the $E_{1/2}^f$ optimally shifts by −59.2 mV per unit increase in pH (providing the $E_{1/2}^f$ does not significantly vary with the change in pH).

Equation (1) is valid for pH values between 1–7, whereas in more basic conditions, the acid dissociation constants of all the protonated compounds need to be incorporated into the Nernst equation.[54–56]

Electrochemistry in Pure *N*,*N*-Dimethylformamide and Dimethylsulfoxide

Figure 2 shows cyclic voltammograms of dopamine and 4-methylcatechol in *N*,*N*-dimethylformamide and dimethylsulfoxide. 4-Methylcatechol has a structure similar to dopamine but has a methyl group in place of the propylamine

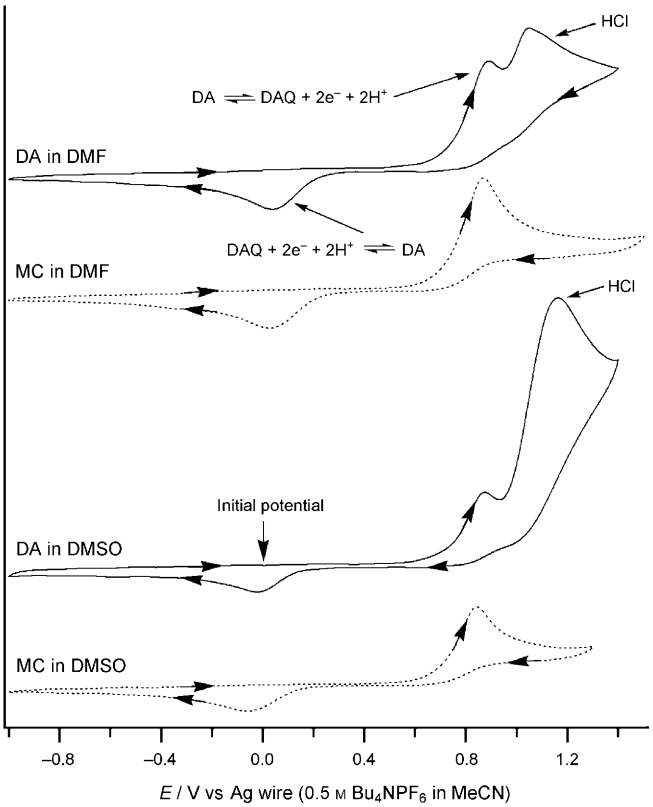


Figure 2. Cyclic voltammograms of 1 mM dopamine and 4-methylcatechol in DMF and DMSO with 0.2 M Bu_4NPF_6 recorded at 22(±2)°C at a 1 mm diameter GC electrode with a scan rate of 0.1 $V s^{-1}$. The starting and finishing potential was 0 V vs. Ag wire (0.5 M Bu_4NPF_6 in CH_3CN) with the scan commenced in the positive potential direction.

group, therefore, cannot undergo the cyclization reaction that dopamine *ortho*-quinone undergoes. The cyclic voltammetric results for dopamine obtained in the two solvents were similar but showed additional processes to those observed in aqueous solutions and small variations in the data existed between the platinum and glassy carbon (GC) electrode surfaces. Both dopamine and 4-methylcatechol displayed an oxidation process at approximately +0.8 V vs. Ag wire and a reverse reduction process at approximately 0 V vs. Ag wire when the scan direction was reversed. The reduction process at 0 V vs. silver wire was only evident if the scan was first performed in the positive potential direction, and was therefore associated with reduction of *ortho*-quinone that forms through the $-2e^-/-2H^+$ oxidation process (Scheme 1).

N,*N*-dimethylformamide and dimethylsulfoxide solutions containing dopamine displayed an additional oxidation process at approximately +1.1 V, which solutions containing 4-methylcatechol did not show (Figure 2). The process at +1.1 V was determined to be due to the oxidation of HCl, by a comparison of a cyclic voltammogram of a solution containing pure HCl in *N*,*N*-dimethylformamide and dimethylsulfoxide. Many compounds used for medicinal purposes are commercially only available combined with HCl because the hydrochloric acid is used to aid the adsorption of molecules in vivo. HCl is less dissociated in organic solvents (compared to in water) resulting in a number of complicated equilibria between the dissociated and nondissociated forms.[58] A detailed electrochemical study found that the electrochemical oxidation of HCl in dimethylsulfoxide involves the oxidized form reacting with the solvent.[58] At a platinum electrode, *N*,*N*-dimethylformamide and dimethylsulfoxide solutions containing HCl displayed an additional reduction process at negative potentials that was not observed on GC and is due to a surface-based process associated with the initial oxidation reaction. The HCl present in the dopamine solutions could partially be removed by adding an equal molar amount of $AgSbF_6$ to the dopamine solutions, thereby causing the Cl^- to precipitate as AgCl.

There is a very wide separation between the forward (E_p^{ox} = +0.8 V vs. Ag wire) and reverse (E_p^{red} = 0 V vs. Ag wire) processes in *N*,*N*-dimethylformamide and dimethylsulfoxide associated with dopamine and 4-methylcatechol converting into their respective *ortho*-quinones (Figure 2). There is no evidence, in the case of dopamine, of formation of the leucoaminochrome reaction product after the initial oxidation, as it occurs in pH 7 buffered aqueous solutions (Figure 1). Thus, the protons released during the oxidation process are sufficiently labile in *N*,*N*-dimethylformamide and dimethylsulfoxide to decrease the pH at the electrode surface and reprotonate the quinone during the reduction cycle to regenerate the hydroquinone. The reason for the large separation between the oxidation and reduction peaks most likely relates to the individual electron-transfer steps occurring in a consecutive manner, with each electron-transfer step having a unique redox potential. Scheme 2 shows the theoretical series of electron-transfer and proton-transfer reactions that are involved in the electrochemically induced conversion of the dihydroquinone (QH_2) into the quinone, in which the oxidation and reduction reactions occur through different pathways. In addition to the consecutive electron-transfer and proton-transfer steps, a concerted mechanism, in which the electron and proton-transfer steps simultaneously occur, is also possible and would occur by diagonal arrows in Scheme 2. The large potential separation between the forward and reverse processes in organic solvents has also been reported for the reversible $-2e^-/-H^+$

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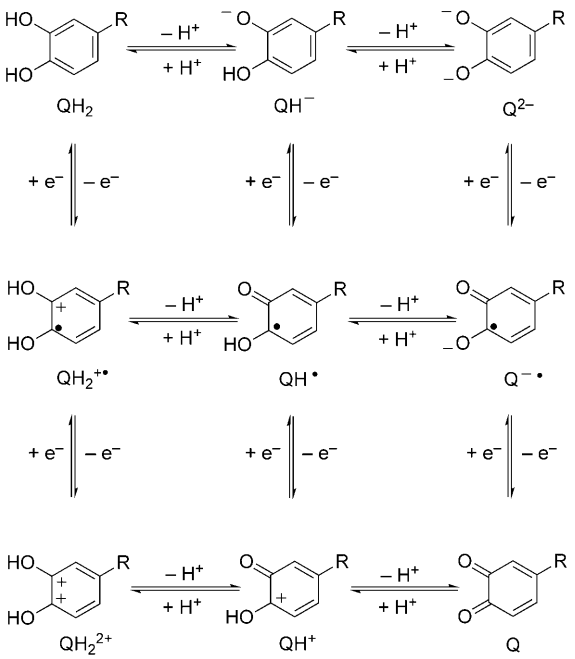

Scheme 2. Electrochemical square-scheme mechanism showing series of possible consecutive electron-transfer and proton-transfer reactions associated with the reversible transformation between *ortho*-hydroquinones and *ortho*-quinone in acidic conditions. Species QH_2 represents any *ortho*-hydroquinone, including DA and MC. One resonance structure is shown for each compound.

electrochemical transformations of the phenolic compound vitamin E into a diamagnetic cation.[59]

An alternative reason for the wide separation between the oxidation and reduction processes of DA/DAQ in *N*,*N*-dimethylformamide and dimethylsulfoxide, based on resistance effects of the solutions, is not supported by electrochemical experiments on other compounds. For example, cyclic voltammograms performed on ferrocene in *N*,*N*-dimethylformamide and dimethylsulfoxide, under the same conditions as the experiments on dopamine, resulted in a measured potential separation between the forward and reverse processes of 70 mV, close to the theoretically expected value for a electrochemically reversible one-electron transfer,[57] and considerably less than observed for dopamine and 4-methylcatechol (about 800 mV).

N,*N*-dimethylformamide and dimethylsulfoxide are both very hygroscopic solvents, thus the initial water concentrations of both solvents (containing 0.2 M Bu_4NPF_6) were calculated to be 25 ± 5 mM, based on the published experimental procedure where values of $|E_1-E_2|$ for a quinone were correlated with the amount of water present (E_1 and E_2 are the first and second reduction potentials of vitamin K_1).[55,56] Cyclic voltammetric experiments were also performed on 4-methylcatechol and dopamine in *N*,*N*-dimethylformamide in the presence of 3 Å molecular sieves, where the water content could be lowered to 2.5 mM. It was found that the voltammetric behavior was the same as observed at the higher water concentration shown in Figure 2, thus it is not believed that trace water has a large effect of the voltammetric properties of dopamine in *N*,*N*-dimethylformamide and dimethylsulfoxide.

In situ UV/Vis Spectroscopy of Oxidation Reaction

As dopamine *ortho*-quinone is known to be relatively short lived in pH 7 buffered solutions (Figure 1), we were interested in comparing how long lived the quinone was in pure *N*,*N*-dimethylformamide and dimethylsulfoxide solutions (containing Bu_4NPF_6), because the timescale of the cyclic voltammetric experiments shown in Figure 2 only indicate that the *ortho*-quinone has a lifetime of at least a few seconds. Figure 3 shows the in situ electrochemical UV/Vis spectra obtained during the oxidation of dopamine in an optically semitransparent thin layer electrochemical (OSTLE) cell at pH 1 in aqueous solution and in *N*,*N*-dimethylformamide and dimethylsulfoxide. At pH 1, the oxidized product shows a broad absorbance band at approximately 385 nm, which is associated with the two-electron oxidation product, dopamine *ortho*-quinone.[60] In both dimethylsulfoxide and *N*,*N*-dimethylformamide, the oxidized product also displays a broad absorbance band at 385 nm, similar to that observed

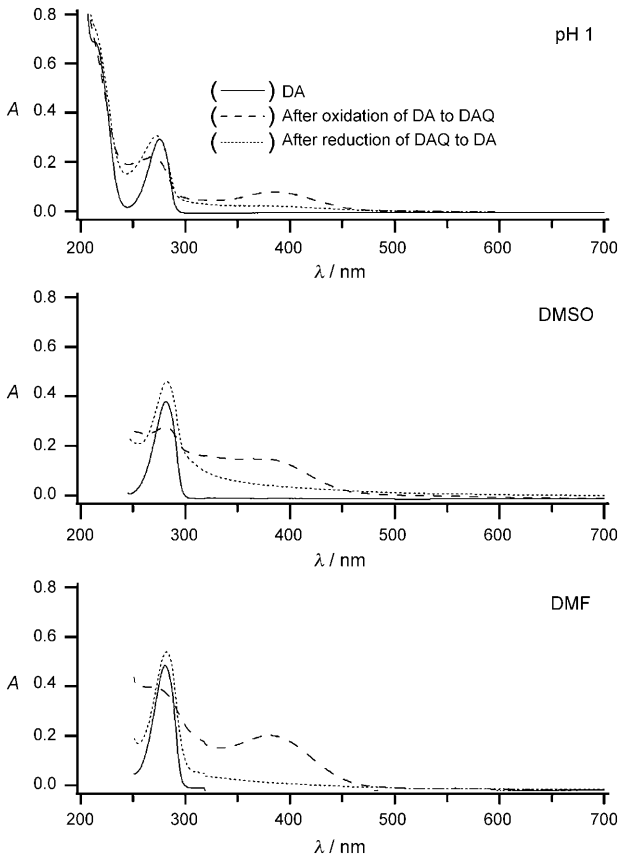

Figure 3. In situ electrochemical UV/Vis spectra obtained in an OSTLE cell during the oxidation of dopamine and reduction of the oxidized product at $22(\pm2)$ °C. Experiments in aqueous solution at pH 1 used sulfuric acid as the electrolyte, whereas 0.2 M Bu_4NPF_6 was used for experiments in DMSO and DMF.

in aqueous solutions at low pH. Previous UV/Vis experiments on oxidized products of dopamine in aqueous solutions at pH ≥ 7 have indicated that aminochrome has an absorbance maxima at higher wavelength (475 nm),[60,61] and it can form as a reaction product after the initial formation of dopamine *ortho*-quinone at 385 nm.[60] Therefore, the UV/Vis spectroscopic experiments in *N*,*N*-dimethylformamide and dimethylsulfoxide are consistent with the formation of dopamine *ortho*-quinone as a moderately stable product over the longer electrolysis timescales.

The UV/Vis data in Figure 3 indicate that the dopamine *ortho*-quinone can be reduced back to dopamine under electrolysis conditions, although the reaction is not completely chemically reversible and the UV/Vis spectra show residual absorbances above 300 nm possibly due to the formation of the polymeric reaction compound, neuromelanin.[60,61] Nevertheless, because the UV/Vis spectra shown in Figure 3 were collected over a period of 30 min, the partially reversible nature of the UV/Vis spectra indicate that the dopamine *ortho*-quinone survives for many minutes in dimethylsulfoxide and *N*,*N*-dimethylformamide, much longer than in pH 7 buffered aqueous solutions.

Chemical oxidation experiments were performed by reacting dopamine with 2 and 4 mol equivalents of $NOSbF_6$ in deuterated dimethylsulfoxide and studying the products by NMR spectroscopy. The NMR spectra of the reaction products were similar regardless of whether 2 or 4 mol equivalents of NO^+ was used as the oxidant, which suggests that the dopamine was undergoing a two-electron oxidation (and not being further oxidized on the long timescale synthetic experiments). NO^+ was used as the chemical oxidant because it is a sufficiently powerful oxidant for phenolic compounds and reacts cleanly to form $NO_{(g)}$ which is easily removed from solution.[62] The ^{13}C NMR spectra of the oxidized solution indicated the presence of several products, which were possibly caused by the reactions being performed at high concentrations to increase the signal-to-noise ratio of the NMR spectrum. Strong bands were detected at 178 and 182 ppm and assigned to the carbon atoms in the C=O bonds, which are expected for a quinone product.

Electrochemistry of Dopamine in Mixed Aqueous/Organic Solvents Containing Buffers

Figure 4 (bottom to top) shows the results that were obtained when water containing increasing ratios (v/v) of pH 7 buffer was added to *N*,*N*-dimethylformamide solutions containing dopamine. The nonaqueous reference electrode was used throughout the measurements in order to provide a better comparison with the potentials obtained in *N*,*N*-dimethylformamide and in *N*,*N*-dimethylformamide/water mixtures, although a junction potential unavoidably occurs (it was found that the potential difference between the aqueous and nonaqueous reference electrodes was < 100 mV).

At a *N*,*N*-dimethylformamide/water (buffer) ratio of 100:1, the reductive peak for the dopamine *ortho*-quinone (formed by initial oxidation of dopamine) decreased in intensity, and, when a ratio of 100:5 was reached, the peak for the reduction of dopamine *ortho*-quinone could not be detected. Furthermore, as soon as the aqueous buffer was added to the *N*,*N*-dimethylformamide solution, a new oxidative process was detected between +0.2 to +0.4 V, and the oxidation process at +0.9 V diminished in intensity. As more aqueous buffer was added to the solution, the process at +0.9 V progressively decreased in intensity, so that at a *N*,*N*-dimethylformamide/water (buffer) ratio of 100:30, only the oxidation process at +0.2 to +0.4 V occurred. The addition of water to the *N*,*N*-dimethylformamide solutions also resulted in the oxidation process of HCl moving to increasingly more positive potentials, so that at a *N*,*N*-dimethylformamide/water (buffer) ratio of 100:30, the oxidation peak of HCl was not detected within the potential window examined.

The results in Figure 4 can be interpreted based on the presence of the buffer in the aqueous solution neutralizing (or partially neutralizing) the protons released during the oxidation process and causing a shift in the E_p^{ox} towards more negative potentials, according to Equation (1). The observation that both the new oxidation peaks (at +0.2 to +0.4 V) and initial oxidation process (at +0.9 V) are evident at intermediate buffer ratios implies that the interactions with the buffer are complicated and a minimum concentration of buffer is needed in order to fully stabilize the localized pH at the electrode surface.

As the *N*,*N*-dimethylformamide/water (buffer) ratio increased above 100:10, a new reductive peak became evident at approximately −0.4 V, which is likely associated with the formation of aminochrome, due to the buffer decreasing the acid concentration at the electrode surface to allow the deprotonation of the dopamine *ortho*-quinone.

Electrochemistry of Dopamine in Mixed Aqueous/Organic Solvents Containing Inert Electrolyte, $LiClO_4$

Figure 5 (from bottom to top) shows cyclic voltammograms of dopamine in *N*,*N*-dimethylformamide containing 0.2 M Bu_4NPF_6 as increasing ratios (v/v) of aqueous solutions of 0.2 M $LiClO_4$ were added. As water (containing $LiClO_4$) was successively added to the *N*,*N*-dimethylformamide solution, the voltammograms in Figure 5 show that the potential gap between the E_p^{ox} and E_p^{red} peaks narrowed.

Figure 5 (top) shows voltammograms of dopamine and 4-methylcatechol in pure water containing $LiClO_4$, which had a measured pH of approximately 7. Whereas the forward process consisted of one peak (similar to in pure *N*,*N*-dimethylformamide or dimethylsulfoxide) in water containing 0.2 M $LiClO_4$, the reverse reductive process was split into two processes, which was likely due to the electron-transfer steps in the reduction reaction occurring sequentially (Scheme 2). In addition, the reductive peak at approximately −0.2 V associated with the cyclized reaction product, aminochrome, was much smaller than observed in pH 7 buffered aqueous solution (compare Figure 1), which indicated that the rate of the cyclization reaction was slower in aque-

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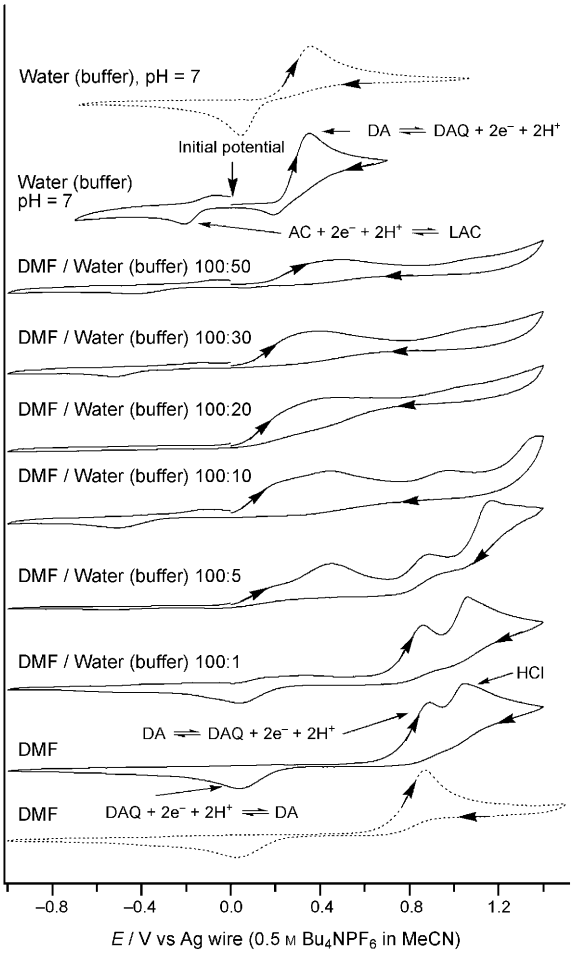
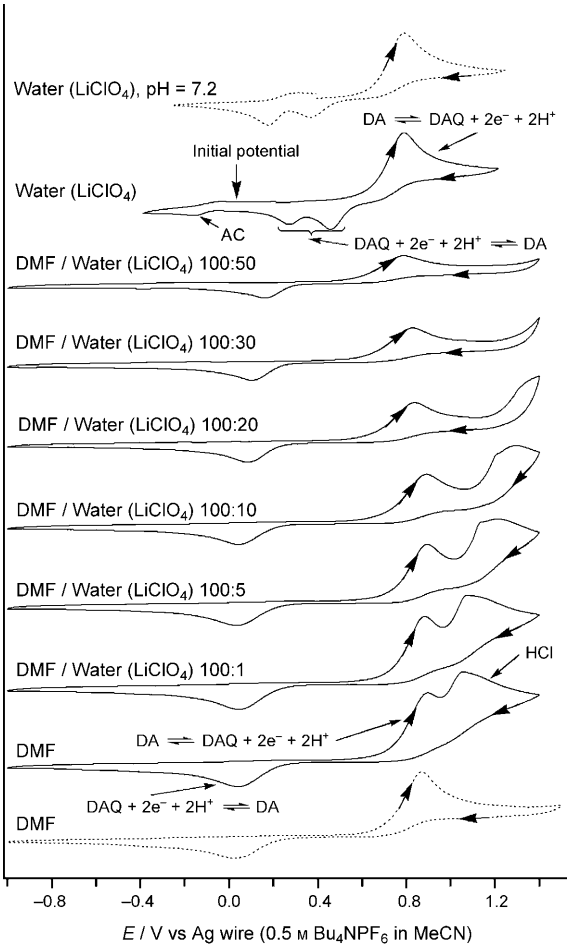


Figure 4. Cyclic voltammograms of 2 mM dopamine (solid lines) or 4-methylcatechol (dotted lines) recorded at 22(±2)°C at a 1 mm diameter GC electrode with a scan rate of 0.1 V s^{-1}, and a starting and finishing potential of 0 V vs. Ag wire (0.5 M Bu_4NPF_6 in CH_3CN). Voltammograms in pure DMF contained 0.2 M Bu_4NPF_6 whereas voltammograms in pure water contained pH 7 buffer. Voltammograms of mixed solutions of DMF and water were obtained by adding water (containing pH 7 buffer) to DMF solutions (containing 0.2 M Bu_4NPF_6) in the given volume ratio.



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ous solutions containing $LiClO_4$ compared to pH 7 buffered solutions (although the pH values of the bulk solution were the same). The reason for the difference between the data in Figures 4 and 5 is related to the buffering properties of the electrolytes, because in non-buffered solutions the protons released during the oxidation reaction are able to decrease the pH at the electrode surface, thereby reducing the rate of the cyclization reaction of dopamine *ortho*-quinone.

The data in Figure 4 and 5 indicated that the addition of water to organic solvents has a much smaller effect on the electrochemistry of dopamine, compared to the buffering properties of the electrolyte. Figures 4 and 5 show that there was a substantial shift in the oxidation peak potential (E_p^{ox}) of dopamine in aqueous solutions containing $LiClO_4$ (Figure 5) and aqueous solutions containing the pH 7 buffer (Figure 4), although the pH values of the bulk solutions were the same. The cyclic voltammogram of dopamine in water containing 0.2 M $LiClO_4$ had an $E_p^{ox} = +0.8$ V vs. Ag wire compared to dopamine in pH 7 buffered water with $E_p^{ox} = +0.4$ V vs. Ag wire. The shift to more positive potentials of dopamine in water containing $LiClO_4$ implied that dopamine experienced a more acidic environment at the electrode surface compared to the buffered solution.

Conclusions

Dopamine was electrochemically oxidized in *N*,*N*-dimethylformamide or dimethylsulfoxide (containing an inert electrolyte such as Bu_4NPF_6 or $LiClO_4$) in a chemically reversible $-2e^-/-2H^+$ process to form dopamine *ortho*-quinone. The separation between the forward (E_p^{ox}) and reverse (E_p^{red}) peaks was large (i.e., 0.8–0.9 V), which was significantly greater than in aqueous solutions. In situ electrochemical-UV/Vis spectroscopy confirmed that dopamine *ortho*-quinone survives for at least several minutes in dimethylsulfox-

ide and *N*,*N*-dimethylformamide at 22(±2)°C (with Bu_4NPF_6), compared to in pH 7 buffered aqueous solutions in which the half-life is several seconds. Whereas the addition of water (containing $LiClO_4$) to the *N*,*N*-dimethylformamide or dimethylsulfoxide solutions had a relatively small effect on the voltammetric behavior, the addition of pH 7 buffered water to the *N*,*N*-dimethylformamide or dimethylsulfoxide solutions resulted in a shift in the oxidation peak to more negative potentials and a loss in the reduction process associated with dopamine *ortho*-quinone.

The electrochemical oxidation of dopamine in unbuffered aqueous solutions at pH 7 resulted in the formation of dopamine *ortho*-quinone, which survived longer than in pH 7 buffered solutions. The reason for the increased lifetime of the dopamine *ortho*-quinone in pH 7 unbuffered solutions was most likely due to the protons released during the oxidation process, which changed the pH in the vicinity of the electrode thereby stabilizing the dopamine *ortho*-quinone against deprotonation (and slowing the following reaction to form leucoaminochrome). Therefore, the lifetime of dopamine *ortho*-quinone in a biological medium (produced by oxidation of dopamine) may be significantly longer than in ideally buffered pH 7 solutions under laboratory conditions.

Experimental Section

Chemicals

3-Hydroxytyramine hydrochloride (dopamine-HCl; >98.5%) was obtained from Fluka and 4-methylcatchol (96%) was from Alfa Aesar. ACS grade DMSO and DMF (Tedia) were used as received, Bu_4NPF_6 was prepared by reacting tetrabutylammonium hydroxide with hexafluorophosphoric acid, and lithium perchlorate (anhydrous, 99%) was from Alfa Aesar. Water, with a resistivity ≥18 MΩ cm from an ELGA Purelab Option-Q was used for the experiments at different pH values. Sulfuric acid was used for experiments at pH 1. Citric acid-phosphate buffered solution (pH 7) was prepared from disodium hydrogen phosphate (Merck) and citric acid (Amresco).

Electrochemical Measurements

Cyclic voltammetry experiments were conducted with a computer controlled Eco Chemie Autolab III potentiostat. Working electrodes were 1 mm and 3 mm diameter planar Pt or GC disks, used in conjunction with a Pt auxiliary electrode. For nonaqueous experiments, an Ag wire reference electrode was connected to the test solution through a salt bridge containing 0.5 M Bu_4NPF_6 in CH_3CN. An Ag/AgCl reference electrode containing 3 M KCl was used for experiments in aqueous systems. KF titrations were conducted with a Mettler Toledo DL32 coulometer using (Riedel-deHaën) HYDRANAL-coulomat CG for the cathode compartment and HYDRANAL-coulomat AG for the anode compartment.

In Situ UV/Vis Spectroscopy

A Perkin–Elmer Lambda 750 spectrophotometer was used in conjunction with an OSTLE cell (pathlength = 0.05 cm) using a Pt mesh working electrode.[63,64] The cavity of the spectrometer was purged from the atmosphere with a high volume flow of nitrogen gas.

Acknowledgements

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