Sonovoltammetric Behavior of Ascorbic Acid and Dehydroascorbic Acid at Glassy Carbon Electrodes: Analysis Using Pulsed Sonovoltammetry

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Abstract
The effect of power ultrasound on the voltammetric behavior of ascorbic acid and dehydroascorbic acid at a glassy carbon electrode is described. The voltammetric characteristics of both compounds were found to be modified by ultrasonically formed radicals. In the case of dehydroascorbic acid the single sweep voltammogram shows an anodic signal in the presence of ultrasound which probably results from the formation of an oxidizable radical known to be an intermediate of ascorbic acid oxidation. In the case of ascorbic acid pulsed sonovoltammetry is applied and characterized regarding the time dependence of the current decay and the reliability of its analytical performance. The utility of pulsed sonovoltammetry is demonstrated analyzing a pain killer tablet regarding the ascorbic acid content.

Keywords: Voltammetry, Ultrasound, Ascorbic acid, Dehydroascorbic acid

1. Introduction

The application of power ultrasound in combination with voltammetric methods is attracting the growing interest of various research groups [1–4]. This is due to the following features of ultrasound assisted voltammetry amongst other possibilities.

(a) The mass transport to and from the electrode surface is tremendously enhanced. (b) The mechanism of chemical and electrochemical reactions can be altered by the generation of radicals or other high-energy species formed as a result of cavitation. (c) Adsorption processes can be modified and (d) a continuous in-situ activation of the electrode surface is possible. However, the phenomena observed during sonovoltammetric experiments need to be discussed with respect to the individual properties of the electrochemical system under investigation. Or, in other words, not all of the mentioned beneficial effects of ultrasound operate in all experimental situations.

The studies presented in this article deal with the electrochemical oxidation of ascorbic acid at glassy carbon electrodes. It is known from the literature [5–7] that this electrochemical reaction proceeds very irreversibly at unactivated glassy carbon. Moreover voltammograms obtained from rotating disk electrode experiments often do not reach a diffusion controlled current plateau region [5]. This makes quantitative evaluation difficult.

A variety of procedures for the pretreatment of glassy carbon electrodes have been proposed which result in activated electrode surfaces. Among them, electrochemical [5], laser radiation [8], vacuum heat [9] treatments and dispersion of metal oxide particles on the glassy carbon surface [10] have been shown to improve the voltammetric characteristics of the electrooxidation of ascorbic acid. However, regarding the mechanism of ascorbic acid oxidation at activated/deactivated glassy carbon electrodes some controversy exists in the literature. Wightman and co-workers [6] attributed the activation and deactivation of glassy carbon electrodes to the change in hydrophilicity while Hu and Kuwana [7] suggested that charge transfer at a glassy carbon electrode can occur through several types of sites such as "pristine" carbon resulting from vacuum heat treatment, quinoidal surface functionalities and blocked sites. In the latter argumentation the explanation for activity changes produced by different electrode treatments is based on the assumption of heterogeneity in charge transfer sites.

The present article seeks to characterize the effects of power ultrasound in the modification of the voltammetric reactivity of ascorbic acid and dehydroascorbic acid at glassy carbon electrodes. The formation of radicals in the presence of ultrasound and the voltammetric behavior in the post-ultrasound period are discussed with respect to the their possible analytical utility.

2. Experimental

The sonovoltammetric cell used in this work has been described previously [11]. Briefly, the working electrode was introduced into a Pyrex cell reservoir from the bottom facing the titanium tipped horn (13 mm diameter) which was positioned between 1 mm and 40 mm above the working electrode surface. The sonic horn employed for the sonovoltammetric measurements was a Model VCX 400 (Sonics & Materials, USA) which operates at 20 kHz and provides power levels up to 55 W cm^{-2}. Thermostating of the cell was accomplished by means of a stainless steel cooling coil inserted in the solution through which water was circulated from a constant-temperature bath. The electrochemical cell was completed employing a saturated calomel reference electrode (SCE) and a graphite rod serving as counter electrode. The solution was thoroughly purged of oxygen prior to the voltammetric experiments by outgassing with argon.

The working electrode used for the sonovoltammetric experiments was a glassy carbon disk electrode (Bioanalytical Systems, West Lafayette, IN) with geometrical surface area of 0.071 cm^2. In addition, a platinum microdisk electrode ($d = 25\,\mu m$) and a carbon fiber microdisk electrode ($d = 10\,\mu m$) were prepared as described previously [12] and used for steady-state voltammetry in quiescent solutions. All electrodes were carefully polished using alumina suspensions of decreasing particle size ranging from 60 μm to 0.05 μm.

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Voltammetric measurements were carried out using an Oxford potentiostat. In the case of microelectrode experiments the potentiostat was combined with a current amplifier.

Aqueous solutions were made up using Elgastat (High Wycombe, Bucks, UK) UHQ grade water (18 MΩ cm). Solutions of ascorbic acid (99.7%, BDH, Anala R) and dehydroascorbic acid (Aldrich) were prepared just before the experiment. The dissolution of dehydroascorbic acid was found to be facilitated by the application of ultrasound. All other chemicals were of analytical-reagent grade and used as received. Phosphate buffer solutions (PBS) were prepared using potassium dihydrogen orthophosphate and the pH was adjusted with potassium hydroxide.

3. Results and Discussion

3.1. Electrooxidation of Ascorbic Acid in the Absence of Ultrasound

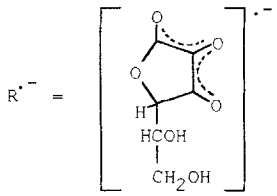
The oxidation mechanism of ascorbic acid (H_2A) at glassy carbon electrodes has been reported previously [7, 13] and is as follows:

$$\text{(I)} \quad HA^- \leftrightharpoons R^{\cdot -} + H^+ + e^-$$

$$\text{(II)} \quad R^{\cdot -} \leftrightharpoons DHAA + e^-$$

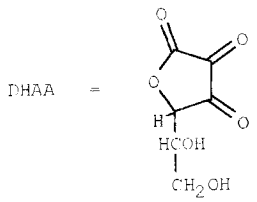
$$\text{(III)} \quad DHAA + H_2O \rightarrow Hy$$

In neutral solutions the electroactive species is ascorbate (HA^-) according to the reported pK values ($pK_1 = 4.17$, $pK_2 = 11.57$) [14]. In the first electron transfer step a radical $R^{\cdot -}$ is formed which has been identified by means of electron paramagnetic resonance [15] (see Scheme I).

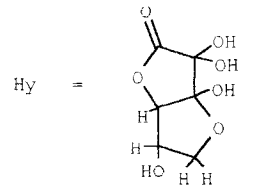


Scheme I.

The second electron transfer step results in the initial form of dehydroascorbic acid (DHAA, see Scheme II) with three carbonyl groups which finally yields in aqueous solution the hydrated bicyclic species Hy (see Scheme III).



Scheme II.



Scheme III.

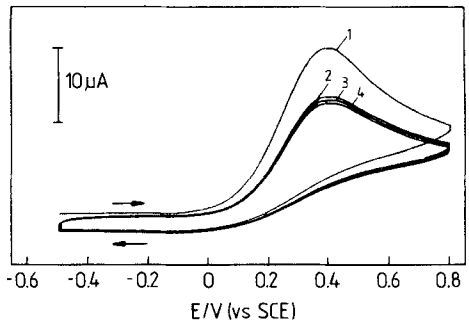


Fig. 1. Cyclovoltammogram of 2.84 mM ascorbic acid in 0.15 M PBS (pH 7.00) recorded with 20 mV/s using a polished glassy carbon electrode. Voltammograms 1–4 correspond to subsequently recorded scans.

Figure 1 shows a cyclic voltammogram for the oxidation of ascorbic acid in neutral solution which was obtained using a polished glassy carbon electrode.

The irreversibility of the reaction was indicated by an anodic shift of the peak potential (E_p) for increasing scan rates (ν). According to the relation $dE_p/(d \lg \nu) = 29.6[\text{mV}]/(\alpha \cdot n_a)$ where α is the transfer coefficient and n_a is the number of electrons transferred in the rate-determining step (rds) a value of $\alpha \cdot n_a = 0.54$ was obtained suggesting that the first electron transfer is the rds [7].

As illustrated in Figure 1 the peak current i_p decreased during successive recordings and reached usually a stable value after the fourth or fifth scan. A waiting period in the potential range from −1 V to 0 V (vs. SCE) results in an increase in i_p for a subsequent recorded single sweep or cyclovoltammogram. This probably reflects the influence of adsorption processes. From the point of view of batch analysis where the electrode is in steady contact with the analyte such behavior is disadvantageous with respect to the reliability of the analytical measurements.

3.2. Sonovoltammetry of Ascorbic Acid and Dehydroascorbic Acid

In the presence of power ultrasound, single sweep votammograms for ascorbic acid were obtained as illustrated in Figure 2. The current was more than a magnitude of order larger compared to that in quiescent solutions. However, no limiting current was observed in the accessible potential range. In this respect the situation was worse, the slope in the expected "limiting current"

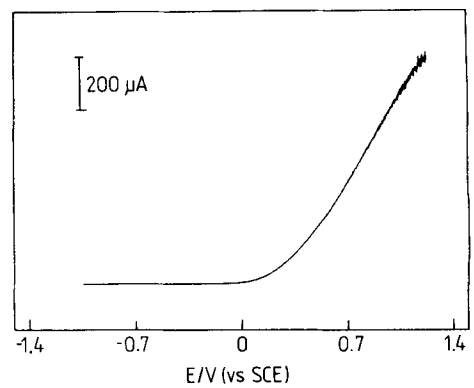


Fig. 2. Sonovoltammogram obtained with a scan rate of 20 mV/s using a glassy carbon electrode continuously exposed to power ultrasound (20 kHz, 20% power setting). The solution composition is the same as in Figure 1 and the distance between the electrode surface and the sonic horn is 3 mm.

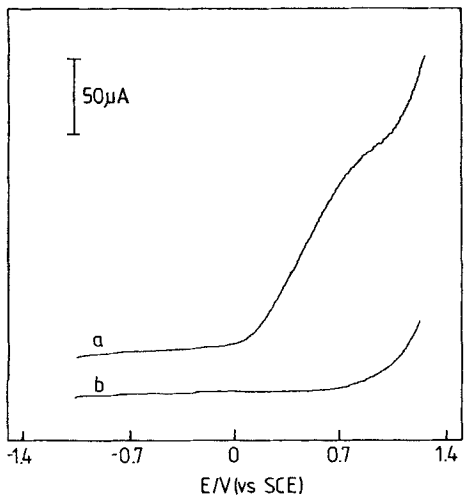


Fig. 3. Voltammograms recorded with 20 mV/s using a glassy carbon electrode (a) in the presence of power ultrasound (20 kHz, 20% power setting) and (b) without ultrasound. The solution contains 2 mM dehydroascorbic acid dissolved in 0.2 M PBS (pH 7.00). The distance between the electrode surface and the sonic horn is 1.5 mm.

region was higher when shorter distances between the electrode surface and the tip of the sonic horn were employed.

For dehydroascorbic acid at concentrations lower than or equal to 2×10^{-3} M no cathodic signals were obtained with or without the application of ultrasound. This observation is in agreement with studies of Brezina et al. [16] using platinum electrodes. Ruiz et al. [17] observed a cathodic wave at the dropping mercury electrode using highly concentrated solutions ($c = 0.04$ mol/L). However this was found to be approximately 500 times less sensitive than the corresponding oxidative wave for ascorbic acid. Note that the rate of step (III), in which DHAA transforms into Hy, is 1.3×10^3 s^{-1} [18]. Hence Hy is the species present in solutions of DHAA.

Figure 3 shows voltammograms for dehydroascorbic acid recorded in the presence and absence of ultrasound. Clearly when applying ultrasound an anodic wave can be observed but this was only slightly dependent on the concentration of dehydroascorbic acid. It was however, very dependent on the electrode–horn tip distance and the selected power level. The oxidizable species is probably the radical $R^{\cdot -}$ which can be generated by reduction of dehydroascorbic acid by atomic hydrogen H$^{\cdot}$ [19] known to be formed ultrasonically from water [20]. This observation could also explain the sonovoltammetric behavior of ascorbic acid described above assuming that the anodically formed dehydroascorbic acid is immediately transformed to $R^{\cdot -}$ leading to a complex amplification of the signal. In addition, $R^{\cdot -}$ can be generated from ascorbic acid via attack by the OH$^{\cdot}$ radical also formed by the sonolysis of water [20].

3.3. Characterization and Application of Pulsed-Ultrasound Voltammetry

In order to circumvent the problems associated with the determination of ascorbic acid in the presence of ultrasound we studied the current behavior when the ultrasound was applied in a pulse mode during recording the voltammograms. The current traces in the "pulse off" interval were evaluated. Surprisingly, very well-defined voltammograms with a well-defined current plateau were obtained at waiting times between 0.3 s and 2.0 s as illustrated in Figure 4.

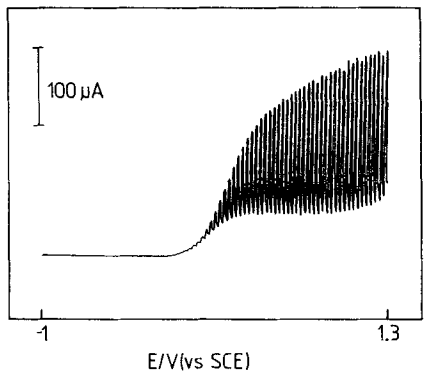


Fig. 4. Sonovoltammogram recorded with 20 mV/s using a glassy carbon electrode exposed to pulsed ultrasound (20 kHz, 30% power setting, pulse sequence: 0.5 s pulse duration, 1 s pulse off). The solution composition is 2.5 mM ascorbic acid in PBS (0.15 M, pH 6.8) and the distance between the electrode surface and the sonic horn is 5 mm.

Table 1. Dedendence of the limiting current i_l of the pulsed ultrasound voltammetric wave on the distance d between the electrode and the sonic horn. Experimental conditions are as follows: 5 mM ascorbic acid in 0.3 M PBS (pH 6.8) ; 20% power setting, pulse duration, 0.1 s; pulse off, 0.8 s and a scan rate of 20 mV/s was used.

d [mm]	1	2.5	15	35
i_l [μA]	160	165	160 ± 5	175 ± 15

The limiting current of the pulsed ultrasound wave for typical waiting times of between 0.5 s and 1 s was found to be almost independent of the power level used and of the electrode–horn tip distance which is shown in Table 1.

At shorter d (equal to or smaller than 3 mm) the pulsed ultrasound voltammograms exhibit a higher precision, however the current signal in the "pulse on" interval is much higher compared to that at larger distances (>10 mm).

Further, the current decay was investigated quantitatively. It was found using a concentration of ascorbic acid of 5 mM that the current decreases with the inverse square root of time according to the following empirical equation:

$$i_l[\mu A] = 141.91 t^{-1/2}[s^{-1/2}] - 9.5[\mu A] \quad (1)$$

The time interval ranged from 0.3 s to 2 s and the regression coefficient was 0.9996.

This result is suggested of the Cottrell equation describing the current response of a potential step experiment under semi-infinite planar diffusion:

$$i = \frac{nFA\sqrt{Dc}}{\sqrt{\pi t}} \quad (2)$$

where n is the number of transferred electrons, F the Faraday constant, A the electrode area, c the bulk concentration of the electroactive species and D its diffusion coefficient. The diffusion coefficient of ascorbate under the experimental conditions used was found to be 4.7×10^{-6} cm^2 s^{-1} on the basis of steady-state voltammetry in quiescent solution by using a 25 μm platinum microdisk electrode and a 10 μm carbon fiber microdisk electrode. This gives values from Equation 2 in agreement with these reported in Equation 1 if a surface roughness of 1.7 is assumed. A rather high surface roughness was also found by Zhang and Coury Jr. [1] after ultrasonic irradiation of glassy carbon electrodes in aqueous solution.

From the results given above it can be concluded that once the ultrasound is switched off the solution near the electrode surface

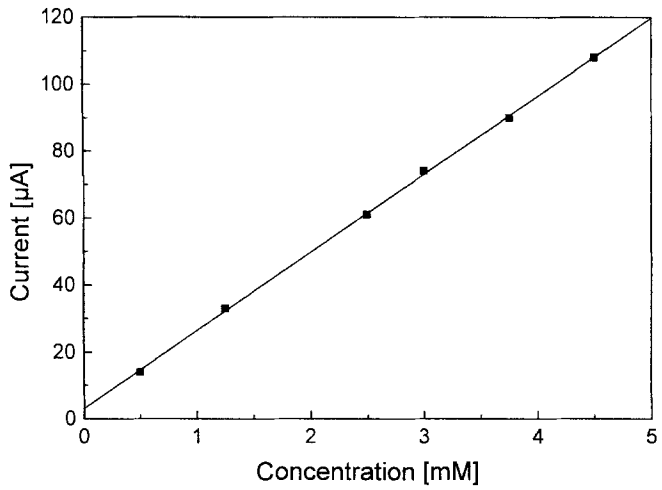


Fig. 5. Calibration plot for ascorbic acid determination via pulsed sonovoltammetry. Experimental conditions are as follows: Pulsed power ultrasound (20 kHz, 20% power setting, sequence: 0.5 s pulse duration, 1 s pulse off). Voltammograms are recorded as in Figure 4. The distance between the glassy carbon electrode and the sonic horn is 1.5 mm. The supporting electrolyte is a 0.2 M PBS (pH 7.00).

rapidly becomes quiescent and approximately Cottrell transport is rapidly resumed.

The concentration dependence of the pulsed ultrasound voltammetric wave was found to be linear within the investigated concentration range between 5×10^{-4} M to 5×10^{-3} M as illustrated in Figure 5.

It is important to note that during repetitive concentration determinations no influence of different waiting periods between the recordings was observed. For example, immediately repeated recordings in the presence of pulsed ultrasound gave the same wave height as obtained after a waiting period of up to several minutes before recording the voltammogram. Consequently using the pulsed ultrasound mode problems with undefined adsorptive accumulation prior to the measurements could be avoided. This is one great value of pulsed sonovoltammetry for analytical purposes, at least in the context of ascorbic acid.

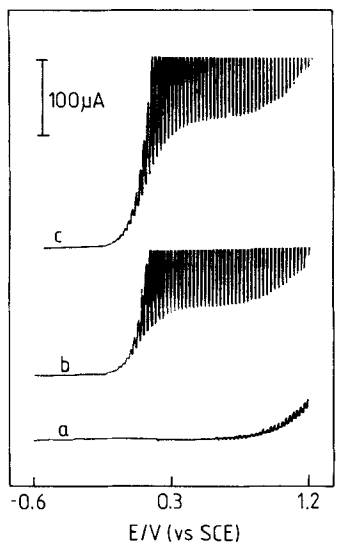


Fig. 6. Ascorbic acid determination by means of pulsed sonovoltammetry. The voltammograms are recorded with a scan rate of 20 mV/s using a glassy carbon electrode. Experimental conditions are as follows: Pulsed power ultrasound (power setting, 20%; pulse duration, 0.5 s; pulse off, 0.8 s; distance between the electrode and the horn tip, 2 mm). The voltammogramms are recorded (a) in 200 ml PBS (0.2 M, pH 7.00); (b) after addition of 0.7285 mg of a painkiller tablet and (c) after further addition of 50.7 mg ascorbic acid. The upper current traces in voltammograms (b) and (c) are truncated.

In order to demonstrate the practical utility of the method a painkiller (ASPIRIN plus C, Bayer, Germany) was investigated with respect to its ascorbic acid content. Figure 6 shows the pulsed sonovoltammograms for an aliquot of the tablet added to the buffer solution and after the addition of a weighted amount of ascorbic acid. The evaluation via the standard addition technique yielded a content of 245 mg per tablet which is close to the manufacturers data (active substances: 400 mg acetylsalicylic acid, 240 mg ascorbic acid).

4. Conclusion

It has been shown that power ultrasound modifies the voltammetric behavior of ascorbic acid and dehydroascorbic acid via the formation of radicals. Studies of the pulsed ultrasound current response were presented which show that the current decay approximately follows the Cottrell equation. The reliability of pulsed ultrasound recordings suggest its analytical application in cases where the continuous application of ultrasound complicates the overall electrode process. Even for uncomplicated reactions pulsed sonovoltammetry has some advantageous in comparison with continuously applied ultrasound during recording the voltammograms. First the mass transport is more precisely defined and, secondly, the distance between the electrode surface and the sonic horn tip has only negligible effects on the limiting current. However, the mass transport efficiency is lower in the case of pulsed sonovoltammograms.

Particularly, in the present work we have shown that reliable determinations of ascorbic acid could be performed via pulsed sonovoltammetry using polished glassy carbon electrodes without any other time consuming or sophisticated pretreatment procedures. The recorded pulsed sonovoltammograms show an extended transport controlled current plateau. No adsorption problems occured in batch analysis where the analyte is in steady contact with the electrode.

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6. References

[1] H. Zhang, L.A. Coury Jr., *Anal. Chem.* **1993**, *65*, 1552.
[2] R. G. Compton, J. C. Eklund, S. D. Page, G. H. W. Sanders, J. Booth, *J. Phys. Chem.* **1994**, *98*, 12410.
[3] R.G. Compton, J.C. Eklund, S.D. Page, T.O. Rebbitt, *J. Chem. Soc., Dalton Trans.* **1995**, 389.
[4] J. Klíma, C. Bernard, C. Degrand, *J. Electroanal. Chem.* **1994**, *367*, 297.
[5] N. Cenas, J. Rozgaite, A. Pocius, J. Kulys, *J. Electroanal. Chem.* **1983**, *154*, 121.
[6] M.R. Deakin, P.M. Kovach, K.J. Stutts, R.M. Wightman, *Anal. Chem.* **1986**, *58*, 1474.
[7] I.-F. Hu, and T. Kuwana, *Anal. Chem.* **1986**, *58*, 3235.
[8] E. Hershenhart, R.L. Mc Creery, R.D. Knight, *Anal. Chem.* **1984**, *56*, 2256.

[9] D. Fagan, I.-F. Hu, T. Kuwana, *Anal. Chem.* **1985**, *57*, 2759.
[10] J. Zak, T. Kuwana, *J. Chem. Soc.* **1982**, *104*, 5541.
[11] R.G. Compton, J.C. Eklund, S.D. Page, *J. Phys. Chem.* **1995**, *99*, 4211.
[12] F.-M. Matysik: *Ph. D. Thesis*, University of Leipzig, Leipzig, Germany **1994**.
[13] G. Dryhurst, K.M. Kadish, F. Scheller, R. Renneberg, *Biological Electrochemistry*, Vol. 1, Academic Press, New York **1982**, pp. 256–277.
[14] *Merck Index*, 11th ed., Rahway, NJ, USA **1989**, p. 858.
[15] A. Aldaz, A.M. Alquic, *J. Electroanal Chem.* **1973**, *47*, 532.
[16] M. Brezina, J. Koryta, T. Loucka, D. Marsiková, *J. Electroanal. Chem.* **1972**, *40*, 13.
[17] J.J. Ruiz, J.M. Rodríguez-Mellado, M. Domínuez, A. Aldaz, *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1567.
[18] S.P. Perone, W.J. Kretlow, *Anal. Chem.* **1966**, *38*, 1760.
[19] B.H.J. Bielski, D.A. Comstock, R.A. Bowen, *J. Amer. Chem. Soc.* **1971**, *93*, 5624.
[20] T.J. Mason, *Practical Sonochemistry*, Ellis Horwood, Chichester, UK **1991**, p 26.