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Voltammetric Determination of Stability Constants of Lead Complexes with Vitamin C*

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Interactions between lead and ascorbic acid were investigated by polarography and voltammetry. The following techniques were applied: sampled polarography, differential pulse anodic stripping voltammetry, and square-wave voltammetry. Measurements were performed in perchlorate aqueous solutions under physiological ionic strength (0.15 mol dm^{-3}). Electrochemical reaction of the lead(II) ascorbate complex was studied in various electrolyte compositions to find the optimal measurement conditions for determination of the corresponding stability constants ([Pb^{2+}] = 4×10^{-7} mol dm^{-3}, pH = 5.5; total concentration of ascorbic acid between 10^{-5} and 10^{-1} mol dm^{-3}). Determination of stability constants of labile lead(II) ascorbate complexes was based on the DeFord-Hume methodology, and they were calculated from the dependence of the shift of Pb$^{\mathrm{II}}$ peak potential on the free ascorbate ion concentration. The computed stability constants were: $\log \beta_1 = 9.3 \pm 0.2$ and $\log \beta_2 = 18.0 \pm 0.1$.

INTRODUCTION

Vitamin C is the term frequently used to refer to L-ascorbic acid in a nutritional context and it also encompasses its oxidation product, dehydroascorbic acid. L-ascorbic acid is found naturally in a wide variety of plants and animals. The human body does not produce it and its only source is from diet.[1] A fundamental feature of the chemistry of L-ascorbic acid is its redox behaviour. In an excellent paper on the complex redox behaviour of L-ascorbic acid, Creutz[2] pointed out that the oxidation and reduction reactions of L-ascorbic acid and its redox companions are complicated by the intervention of simultaneous proton transfer reactions. Of particular interest in the context of transition metal chemistry is the fact that L-ascorbic acid will form chelate complexes with transition metal ions.[3] In most cases, the structures of these species have been deduced from spectroscopic studies of one sort or another and it is generally believed that such complexes are formed to produce a five-member ring with the enediol part of the molecule.[4]

It has been suggested that the presence of the ascorbate anion plays a key role in assisting many factors involved in host resistance to acquired immune deficiency syndrome (AIDS) and it has been found that germanium(IV) sodium ascorbate (GeNaA) retards manifesta-

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* Dedicated to the memory of the late Professor Marko Branica.

** Author to whom correspondence should be addressed. (E-mail: gbranica@mimi.imi.hr) tion of AIDS symptoms.[5] Apart from biological activity of ascorbic acid, applications of its metal complexes in biology and medicine have been subject of numerous investigations.

Redox reactions of L-ascorbic acid are of fundamental importance. The vast majority of the reductions of metal ions by ascorbic acid have been carried out in the pH range 2–8. Creutz has pointed out that under these conditions, ascorbic acid itself may exist as H_2A or HA^-. A one-electron oxidation will produce either $HA^\bullet$ or $A^{-\bullet}$ and a two-electron oxidation will produce dehydroascorbic acid. The majority of studies of ascorbic acid oxidation by metal ions have proposed the formation of an ascorbate free radical in the rate-determining step. In all cases, the overall product is assumed to be dehydroascorbic acid. The nature of the products is generally deduced from the stoichiometry of the reaction and the visible absorbance of the reduced metal ion. Only occasionally have direct analytical techniques demonstrated the nature of the oxidation of ascorbic acid by metallic ions.[6–8]

Lead is a ubiquitous environmental toxin that induces a broad range of physiological, biochemical, and behavioural dysfunctions. Recent studies have shown that lead causes oxidative stress by inducing generation of reactive oxygen species, reducing the antioxidant defence system of cells. It is plausible that impaired oxidant/antioxidant balance can be partially responsible for the toxic effects of lead. Although oxidative conditions contribute to lead-induced toxicity, restoration of the cell's antioxidant capacity appears to provide a partial remedy. Several studies have been done to determine the effect of antioxidant supplementation following lead exposure. Ascorbic acid as antioxidant alone and in combination with thiamine was found to be effective by increasing urinary elimination of lead. Thiamine alone, however, showed no beneficial effects. This beneficial role of ascorbic acid was attributed to its ability to form complexes with lead(II).[9] Simon and Hudes reported a population-based study that indicated an inverse relation between the serum ascorbic acid and blood lead levels among Americans.[10] The authors suggest that higher intake of ascorbic acid may be effective in preventing lead toxicity if a causal relationship is confirmed.

The present study was inspired by literature reports, which have shown that antioxidants may play an important role in abating some hazards of lead and may have protective effects in lead toxicity. Data suggest that some antioxidants can function as chelators as well, and this dual benefit makes them strong candidates for treating lead poisoning.[11]

Labile metal forms have been shown to be the species most likely to penetrate a cell membrane, and are therefore considered predominant bioavailable species.[12] The system investigated by voltammetry has been shown to be electrochemically labile. The kind of metal species that can be measured with a mercury electrode depends on thermodynamic and kinetic aspects, as well as the diffusion coefficient of each complex species.[13] Lingane[14] and DeFord and Hume[15] introduced the polarographic techniques of speciation of labile metal complexes. These speciation techniques are performed at a fixed pH and various total ligand L_t to total metal M_t concentration ratios. The shift observed in the half-wave potential was related to excess of the ligand in a solution. The former speciation technique[14] allows studying a single labile metal complex. The latter[15] focuses on the investigation of several consecutive ML_j labile species. Lability of metal complexes was determined by the ratio of the time-scale of the polarographic experiment (drop life time) to the rate of association and dissociation processes, in relation to a metal complex under investigation. The DeFord and Hume technique seems to be one of the most frequently used in the speciation studies of labile metal species by different modes of voltammetry.[16–18]

After thorough inspection of the available stability constants databases and published papers,[23–27] only one paper[27] was found that reported the value of the stability constants of lead(II) and vitamin C. However, no data based on the electrochemical procedure were found. It was decided that it was worth getting data for a better understanding of the interactions between a well-known antioxidant such as ascorbic acid and a widespread metal toxin such as lead. In this work, the interaction of L-ascorbic acid and Pb^{II} ions was studied in aqueous solution using voltammetry and it yielded the values of apparent stability constants for lead ascorbate complexes. Consecutive stability constants for the formation of complexes between Pb^{II} and ascorbate species were determined. The basic model applied to the data from square-wave voltammetry (free ligand concentration, shift of peak potential) was the DeFord-Hume equation with a least-square treatment and a non-linear (weighted Levenberg-Marquardt) fit of F_0 implemented in the Sigma Plot software.

EXPERIMENTAL

Chemicals and Solutions

The following chemical reagents were used for all voltammetric experiments: HCl (Sigma), NaOH (Sigma), $NaClO_4$ (Sigma), L-ascorbic acid (Fluka) and $Pb(NO_3)_2$ (Fluka). All the chemicals used in voltammetric measurements were of analytical grade. Stock solutions were prepared with deionized water (Millipore, Bedford, Mass., USA). The stock solution of L-ascorbic acid (2 mol dm^{-3}) was prepared by dissolving the analytical grade chemical in deionized water, which had been previously degassed with nitrogen for 30 minutes. The solution was kept in darkness at 4 °C and was found to be stable over a period of several weeks. Diluted solutions of ascorbic acid were prepared from the stock just prior to analysis. Pure nitrogen (99.99 %) was used to deaerate the solutions.

Instrumentation

Electrochemical experiments (sampled direct current polarography; Sampled d.c., square wave voltammetry, SWV; and cyclic voltammetry, CV) were carried out using a computerized multipurpose system consisting of a µ-AUTOLAB (EcoChemie, Utrecht, The Netherlands), a personal computer (486 DX2-80 MHz 32 Mb RAM) and a Static Mercury Drop Electrode Assembly (SMDE) PAR 303A (Princeton Applied Research, Princeton, USA) with a homemade holder of electrode components. A three-electrode system consisting of a static mercury drop electrode as the working electrode, a platinum wire counter electrode and an Ag/AgCl (sat. NaCl) reference electrode was used. The electrochemical instrument was controlled by a computer with the following software packages: EAS (Electro Analytical System) and GPES 4.5 (General Purpose Electrochemical System). Hydrogen ion activities were measured with an Orion Research pH meter.

Experimental Procedure

Electrochemical measurements were performed in the solutions (50 mL) of physiological ionic strength (0.15 mol dm^{-3} $NaClO_4$ as the supporting electrolyte). The adjusted pH was maintained constant during the measurements. The pH values were measured in the voltammetric cell prior to and at the end of each experiment. The solutions (50 mL) were purged with nitrogen for at least 15 minutes prior to each experiment and the nitrogen atmosphere was maintained thereafter.

Computations

The basis for interpreting the SWV data was the well-known De Ford-Hume relation:

$$\Delta E(c_{\text{Pb}}) = E([\text{L}]) - E([\text{L}]_{\to 0}) = (RT/2F)\ \ln \alpha_0 \quad (1)$$

where E stands for a half-wave or a peak potential, whichever is appropriate, and α_0 stands for the fraction of non-ligated lead. The ratio of the diffusion currents of a ligated and a non-ligated lead was omitted because it was not readily calculable from the SWV data, and because the E_p value has a greater effect on the calculated stability constants than the variation in the height of lead peak. In terms of Leden's function F_0, the final mathematical model can be written as:

$$F_0 = 1 / \alpha_0 = 1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \ldots \quad (2)$$

If only one labile complex is present, the shift of the peak potential can be expressed as:

$$\Delta E_p = RT \ln(1+ \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \ldots + \beta_n[\text{L}]^n)/2F \quad (3)$$

where L stands for the ligand and β_n are the corresponding cumulative stability constants.

Equation (2) was solved for β_n by weighted multilinear regression. The statistical weights were estimated initially according to Momoki *et al.*[19] and subsequently refined iteratively by fitting the method based upon the weighted nonlinear regression of Eq. (2), and using the Levenberg-Marquardt minimizing routine.

The free-ligand concentrations [L] were computed by solving the following mass-balance equation, written for all the forms of a ligand and lead involved in the complex formation:

$$[\text{L}] = C_\text{L} / \{1 + [\text{H}] \times K^{\text{H}}_1 + [\text{H}]^2 \times K^{\text{H}}_1 K^{\text{H}}_2\}; \quad (4)$$

where C_L and [H] are total concentrations of the ligand and protons. The latter were determined from the solution pH value, whereas the acidity constants of ascorbic acid were taken from literature.[20] Consequently, the hydrolysis of ascorbate is given by the following constants ($\log K^{\text{H}}_1 = 11.35$, $\log K^{\text{H}}_2 = 4.02$). The cumulative stability constants were calculated according to:

$$\beta_n = [\text{ML}_n] / [\text{M}] \times [\text{L}]^n \quad (5)$$

RESULTS AND DISCUSSION

The behaviour of lead ions in aqueous solution can be affected by a variety of competing reactions, such as hydrolysis, complexation, precipitation/dissolution, oxidation/reduction, and sorption/desorption at the surface of particles. Since these reactions change the speciation of lead ions, they control to a large extent both their toxicity and mobility in a natural system. Speciation is therefore of central importance when studying any metal ion behaviour in natural aquatic environments, in which these reactions can all occur simultaneously, but to highly different extents under different conditions.[21] To calculate the valuable stability constants of Pb^{II} complexes with vitamin C, thoroughly picked experimental conditions were chosen to avoid any changes in input conditions of the system under investigation that could be foreseen.

Voltammetric Characteristics of Pb^{II} Hydroxide Complexes

Figure 1 shows a set of square-wave anodic stripping voltamograms (SWASV) of the electrolyte containing 10^{-8} mol dm^{-3} Pb^{II}, 0.15 mol dm^{-3} $NaClO_4$ while solution pH was varied from 4.34 to 9.88. The single voltammetric peak of Pb^{II} shifted to lower (more negative) potentials ($\Delta E_p = -94$ mV) with increasing the pH value. This is a consequence of the formation of labile, lead hydroxide complexes. From the dependence of the shift of the peak potential (ΔE_p) on the increasing concentration of hydroxide ions (Figure 2), it can be seen that at pH = 5.5 there are no hydroxide complexes present in the measured system. Hence, this pH value was chosen for further investigations.

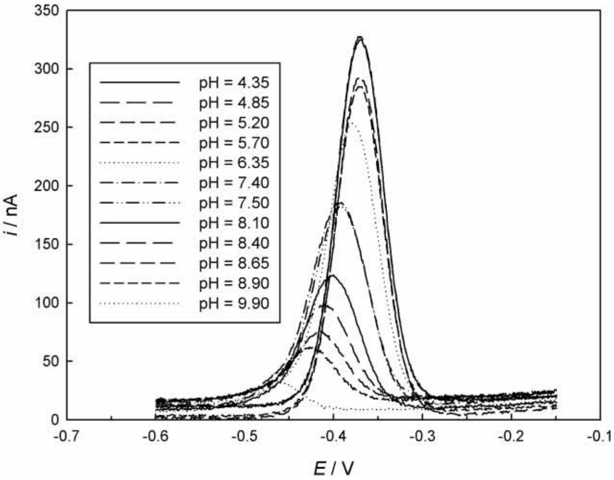

Figure 1. A set of SWAS voltamograms of 1×10^{-8} mol dm^{-3} Pb^{II} in 0.15 mol dm^{-3} NaClO$_4$ at increasing pH values. SWASV parameters: f = 100 Hz, t_{dep} = 120 s, E_A = 25 mV.

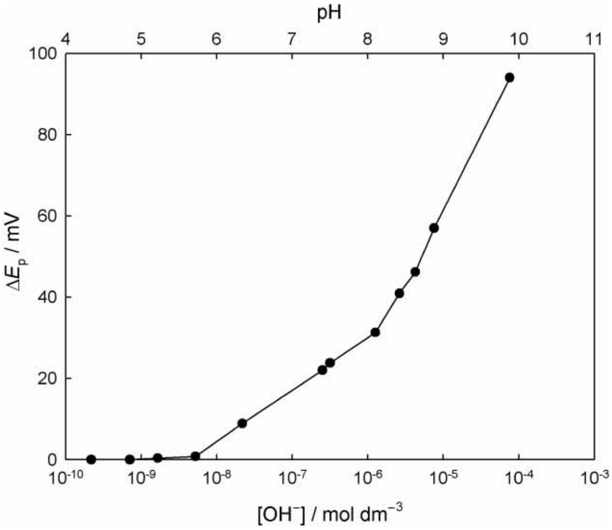

Figure 2. Dependence of the peak potential shift on the solution pH values. Data obtained from the SWAS voltamograms of Figure 1.

Voltammetric Characteristics of Pb^{II} Ascorbate Complexes

The curves in Figure 3 are the sampled direct current polarograms of 10^{-5} mol dm^{-3} [Pb^{2+}] with increasing amounts of L-ascorbic acid (from 10^{-5} to 10^{-1} mol dm^{-3}) in the supporting electrolyte (0.15 mol dm^{-3} NaClO$_4$; pH = 5.5), measured with a drop time (t_{drop}) of one second on SMDE. Figure 3 shows the relationship between the limiting current, the half-wave potential and the added ligand concentration (L-ascorbic acid). The curves of d.c. polarograms evidence a diminution of the limiting current as the ligand concentration is increased. Additionally, there is a shift to more negative potential. All this indicates that the Pb^{II} species involve quite stable complexes. The slope of the waves changes with the increase in L-ascorbic acid concentration. In addition, the increase of ligand concentration produces a post-wave at more negative values. Both effects could be explained by the formation of quite stabile Pb^{II} ascorbate complexes.

Figure 4 shows square-wave voltamograms of the system. All these measurements were performed at 100 Hz. Like in the case of d.c. polarograms, the increment in ligand concentration produces a shift of the peak potential towards more negative values and the appearance of the second peak. According to the shape of curves, both effects should be produced by the formation of quite stable complexes of lead(II).

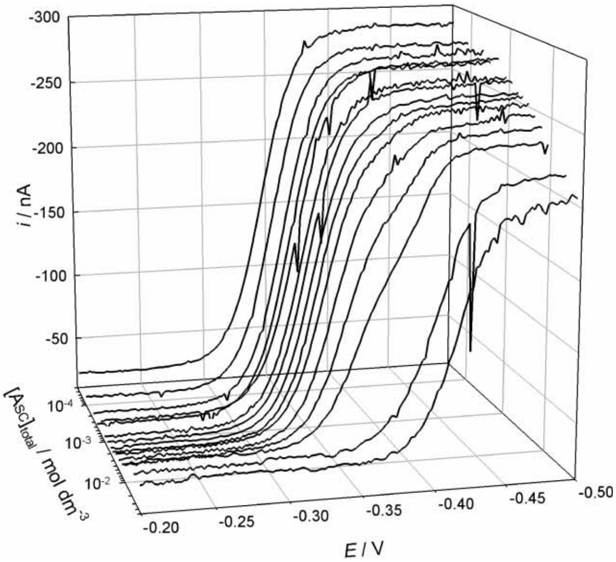

Figure 3. Sampled d.c. polarograms of 2×10^{-5} mol dm^{-3} Pb^{II} in 0.15 mol dm^{-3} NaClO$_4$ (pH = 5.5) with increasing concentration of L-ascorbic acid. Sampled d.c. parameters: t_{drop} = 1 s.

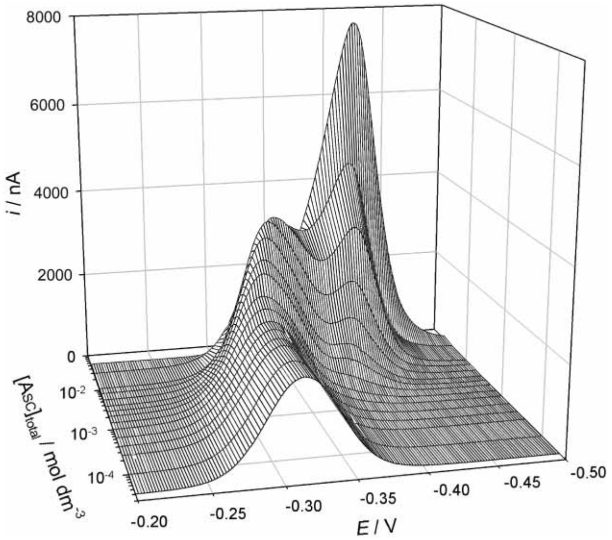

Figure 4. SW voltamograms of 2×10^{-5} mol dm^{-3} Pb^{II} in 0.15 mol dm^{-3} NaClO$_4$ (pH = 5.5±0.1) with increasing concentration of L-ascorbic acid. SWASV parameters: f = 100 Hz, E_A = 25 mV.

Figure 5 shows the dependence of normalized peak current and peak potential on the concentration of lead added in the solution (0.15 mol dm^{-3} NaClO$_4$; pH = 5.5; 0.01 mol dm^{-3} L-ascorbic acid, [Pb^{II}] between 2×10^{-7} and 4×10^{-4} mol dm^{-3}). It can be seen that at a concentration of 4×10^{-7} mol dm^{-3} of added lead there is no evidence of the second peak, but the second peak appears at higher concentration levels and then at [Pb^{2+}] > 4×10^{-4} mol dm^{-3} only one peak is present but at potentials more positive than that of the expected complex. After all these measurements, appropriate conditions were known under which voltammetric experiments for determination of the conditional stability constants of Pb^{II} complexes with vitamin C in aqueous solution would be done. These conditions are: 0.15 mol dm^{-3} NaClO$_4$ as supporting uncomplexing electrolyte; pH = 5.5 throughout the measurement; [Pb^{2+}] = 4×10^{-7} mol dm^{-3}; L-ascorbic acid concentration range: 2×10^{-5} mol dm^{-3} and 0.1 mol dm^{-3}.

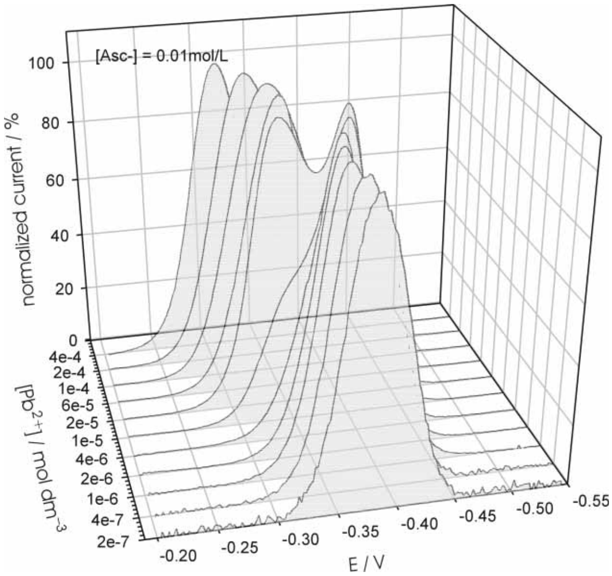

Figure 5. Normalized SW voltamograms recorded in 0.15 mol dm^{-3} NaClO$_4$ and 0.01 mol dm^{-3} L-ascorbic acid (pH = 5.5±0.1) with increasing concentrations of Pb^{II} ions. SWASV parameters: f = 100 Hz, E_A = 25 mV.

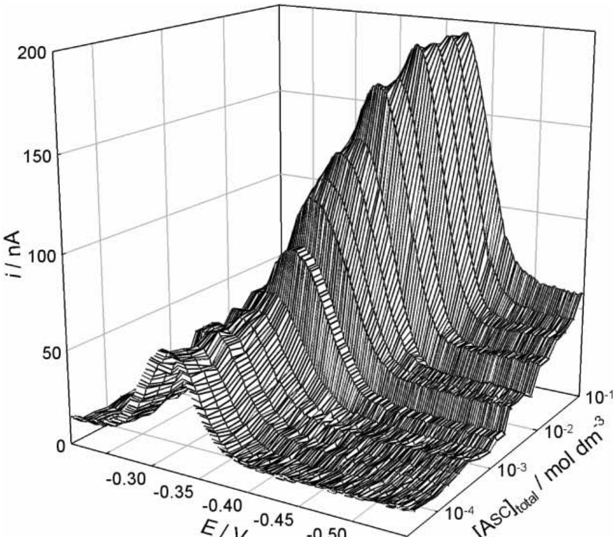

Figure 6. A set of Pb^{II} SW voltamograms recorded in a solution containing 4×10^{-7} mol dm^{-3} Pb^{II} and L-ascorbic acid added subsequently in the range between 2×10^{-5} to 0.1 mol dm^{-3} (pH = 5.5±0.1) and ionic strength of 0.15 mol dm^{-3} in NaClO$_4$ as supporting electrolyte; SWV parameters: f = 100 Hz, E_A = 25 mV.

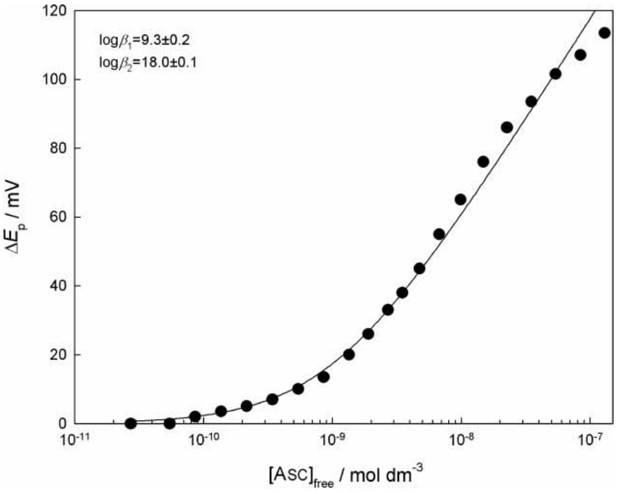

Figure 7. Shift of the Pb^{II} SW voltammetric peak potential as a function of the free ligand concentration (L-ascorbic acid) at a constant ionic strength (0.15 mol dm^{-3}, pH = 5.5 ± 0.1). Solid curve was computed using the following stability constants: $\log\beta_1$ = 9.3 ± 0.2 and $\log\beta_2$ = 18.0 ± 0.1.

Stability Constants of Pb^{II} Ascorbate Complexes

Figure 6 illustrates a typical set of voltamograms obtained from a solution containing 4×10^{-7} mol dm^{-3} Pb^{II}, 0.15 M NaClO$_4$ at pH = 5.5, with an increasing concentration of added L-ascorbic acid (between 2×10^{-5} mol dm^{-3} and 10^{-1} mol dm^{-3}). The systems investigated exhibited a labile character, having a single, reversible SWV peak that shifted towards more negative potential values with an increase in the ligand concentration, and some changes in the peak height. Figure 7 presents voltammetric data of the shift of the peak potential (ΔE_p) *vs.* increasing concentration of the free ligand (L-ascorbic acid). The solid line in Figure 7 was calculated using stability constants (β values) derived from the SWV data. The free ligand concentration was calculated according to Eq. (4) and the shift of the peak potential was calculated according to Eq. (3). Since the most lead(II) complexes generally have a 1:2 composition,[22] the complex formation equilibrium of the lead(II) ion with L-ascorbic acid in a dilute aqueous solution is assumed to be established by the consecutive two-step reactions:

$$\mathrm{M} + \mathrm{L} \leftrightarrow \mathrm{ML}$$

$$\mathrm{ML} + \mathrm{L} \leftrightarrow \mathrm{ML_2}.$$

Computations of the stability constants, under the assumption of a series of mononuclear complexes (ML_n; $n = 1,2…$) estimated by voltammetry, yielded the values: $\log \beta_1 = 9.3 \pm 0.2$ and $\log \beta_2 = 18.0 \pm 0.1$, in the pH range where lead(II) hydroxide complexes were negligible.[20] Voltammetric data were tested by several polynomials of different degrees, the best fit selected, and the coefficients of the polynomial were assumed to be the conditional stability constants of the complexes. The best-fitting polynomial was $\beta_1[L] + \beta_2[L]^2$ for L-ascorbate lead complexes. In mathematical terms, the assumed model is a square polynomial of the general form of Eq. (3). The goodness of fit can be judged from the coefficient of determination (R^2), *i.e.*, the fraction of the total variance explained by the model. Its complement, $1–R^2$ (a fraction of residual variation), was low (*ca.* 1 %), indicating that these data were in very good agreement with the square polynomial model of Eq. (3). Our values of apparent stability constants of lead(II) ascorbate complexes disagree with those previously reported,[27] possibly because of the method of calculation (our data were calculated using the free ligand concentration, compared to the total ligand concentration used in other papers)[27] and experimental conditions (pH, lead(II) concentration, *etc.*).

CONCLUSION

Electrochemical investigations of lead and L-ascorbic acid were performed using sampled d.c. polarography and square wave voltammetry (direct and anodic stripping mode). At pH ≤ 5.5 there is no evidence of lead hydroxides. The chosen pH for establishing the stability constants was 5.5. At higher concentrations of lead ($>10^{-6}$ mol dm^{-3}) and ascorbate ($>5\times10^{-3}$ mol dm^{-3}), adsorption effects were observed on the working electrode, yielding the post-wave. It was found that the electrode reaction of lead(II) (4×10^{-7} mol dm^{-3}) is reversible in 0.15 mol dm^{-3} $NaClO_4$ and that lead(II) ascorbate complexes are electrochemically labile up to the L-ascorbic acid total concentration of 10^{-2} mol dm^{-3}, which were the conditions in the solution used for the determination of the stability constants by square-wave voltammetry. Stability constants were computed from the data obtained (the peak potential shift in dependence on the free ascorbate concentration) by applying non-linear regression of the DeFord-Hume F_0 function after the Levenberg-Marquardt fit implemented in the Sigma Plot software. Computations of the apparent stability constants, under the assumption of a series of mononuclear complexes (ML_n, $n = 1,2...$), yielded the following values for lead ascorbate complexes: $\log \beta_1 = 9.3 \pm 0.2$ and $\log \beta_2 = 18.0 \pm 0.1$.

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SAŽETAK

Voltametrijsko određivanje konstanta stabilnosti kompleksa olova sa C-vitaminom

Gina Branica, Mirjana Metikoš-Huković i Dario Omanović

Međudjelovanje olova i askorbinske kiseline (C-vitamina) istraživano je polarografskim i voltametrijskim metodama. Rabljene su sljedeće tehnike mjerenja: polarografija s linearnom promjenom potencijala, diferencijalna pulsna voltametrija s anodnim otapanjem i pravokutnovalna voltametrija. Mjerenja su izvođena u vodenim otopinama perklorata, fiziološke ionske jakosti 0,15 mol dm^{-3}. Elektrokemijska reakcija askorbinato kompleksa olova(II) proučavana je u različitim eksperimentalnim uvjetima. Utvrđeni su optimalni uvjeti za određivanje pripadajućih konstanta stabilnosti proučavanih kompleksa ([Pb^{2+}] = 4×10^{-7} mol dm^{-3}, pH = 5,5; ukupna koncentracija askorbinske kiseline između 10^{-5} i 10^{-1} mol dm^{-3}). Određivanje konstanta stabilnosti labilnih kompleksa olova sa C-vitaminom temeljeno je na metodi DeFord-Hume-a, a konstante su izračunate iz ovisnosti pomaka potencijala redukcije olova o koncentraciji slobodnih iona askorbinata. Izračunate su sljedeće konstante stabilnosti: $\log \beta_1 = 9{,}3 \pm 0{,}2$ and $\log \beta_2 = 18{,}0 \pm 0{,}1$.