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Voltammetric and FTIR Spectroscopic Studies of the Oxidation of Retinyl Propionate at Pt Electrode in Non-Aqueous Media

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The electrooxidation of vitamin A was investigated at a platinum electrode in non-aqueous solution. The process of electrooxidation and its kinetics were investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Cyclic voltammograms for retinyl propionate showed three oxidation peaks. The process was adsorption controlled. The parameters of retinyl propionate electrooxidation, i.e., electron transfer coefficient and rate constant were calculated. Structural investigations of retinol propionate and its oxidation products were conducted using FTIR spectroscopy. Theoretical calculations of retinyl propionate, electronic properties like highest occupied molecular orbital (E_{HOMO}) were calculated using with HyperChem software by AM1 semi-empirical method. Voltammetry and FTIR spectroscopy, are faster and less expensive methods for analysis than chromatographic methods, which often require large amounts of toxic solvents and long times for analysis. The voltammetric methods are environmentally friendly and can be successfully used for to study the antioxidative activity of compounds.

Keywords: cyclic voltammetry; differential pulse voltammetry; FTIR spectroscopy; Pt electrode; retinyl propionate

1. INTRODUCTION

Vitamins are essential organic molecules that an organism depends on for survival. An essential organic molecule becomes a vitamin if the organism cannot synthesise it and must obtain the molecule from its diet [1-2]. A key feature of vitamin biology is that vitamin status is heavily influenced by the environment. In addition to diet, other environmental factors may also influence vitamin status. Vitamin A is arguably the most multifunctional vitamin in the human body and is

essential for human survival at every point from embryogenesis to adulthood [3-4]. The range of cellular activities it participates in is overwhelming, and more are still being discovered. The molecular mechanism of vitamin as physiological function was first elucidated for vision [5-6]. Decrease in vitamin A consumption causes mortality in children [7-8]. Vitamin A and its metabolites play important roles in cell differentiation, growth, reproduction, and vision [9-10]. Due to its antioxidant properties, vitamin A can prevent many illnesses, including cancer [11]. It is also useful for the growth and reproduction of our body as its different forms are able to play multiple functions [12-13]. There are several major forms of vitamin A: retinol, retinal, retinoic acid, retinyl acetate, retinyl palmitate, retinyl propionate and β-carotene [14-16]. Vitamin A is available from animal sources in the form of preformed vitamin A or retinol (as retinyl esters) and from plant sources, particularly vegetables and fruits, in the form of provitamin A carotenoids (predominantly β-carotene) [17]. As liposoluble compounds, all of the forms of vitamin A are naturally absorbed and stored in the fat cells in the body where the various individual reactions of interest will occur. As reported in some studies, different vitamin A species exist and are stored in different parts of the human body [18-19]. The conversion from one form to another will depend on the needs of the body and often involves redox transformation.

Therefore, we are interested in electrochemically studying these compounds to establish a probable reaction mechanism. Electrochemical methods are an important class of diagnostic techniques that were widely used for the investigation of the biological properties of electroactive species [20-23] including flavonoids and vitamins [24-30]. Electrochemical measurements are necessary for the determination of the fundamental physico-chemical parameters of the compounds in this study [31-33]. One of the bioactive Vitamin A compounds is retinyl propionate.

The aim of the investigations described in this paper was the determination of the retinyl propionate electrochemical behaviour in the electrooxidation process at a platinum electrode. Experiments were conducted in non-aqueous media. Structural investigations of retinol propionate and its oxidation products were conducted using FTIR spectroscopy.

2. EXPERIMENTAL

2.1. Reagents

Pure retinyl propionate [(2E,4E,6E,8E)-3,7-dimethyl-9-(2,6,6-trimethylcyclohexen-1-yl)nona-2,4,6,8-tetraenyl] propanoate, $C_{23}H_{34}O_2$) was obtained from Sigma-Aldrich (Germany) and used as received. The solvent were acetonitrile (CH_3CN) pure p.a. was obtained from Sigma-Aldrich (Germany), and tetrabutylammonium perchlorate ($(C4H_9)_4NClO_4$) from Fluka (Germany) was used as a supporting electrolyte. The non-aqueous solutions of retinyl propionate were prepared by dissolving the substrate in 0.1 mol L^{-1} $C_4H_9)_4NClO_4$ in acetonitrile. The concentration substrate solutions was in the range from 0.23×10^{-2} mmol L^{-1} to 3.33×10^{-2} mmol L^{-1}. All reagents used were of analytical grade. The experiments were carried out at room temperature.

2.2. Measurement methods

Electrochemical measurements were recorded with an Autolab PGSTAT30 potentiostat, controlled by GPES 4.9 electrochemical software from EcoChemie, Untrecht, The Netherlands), coupled with a conventional three-electrode cell. The three-electrode cell system consisted of platinum working electrode (Pt), a ferricinium/ferrocene (Fc^+/Fc) reference electrode and a Pt wire as the counter electrode. Prior to the measurements, all of the solutions were degassed with argon. During the measurements, an argon blanket was maintained over the solution. The effect of the scan rate on the electrooxidation of vitamin A in an non-aqueous medium was assessed.

3. RESULTS AND DISCUSSION

3.1. The electrochemical behaviour of retinyl propionate

The reactions characterising the electrochemical oxidation of retinyl propionate at a platinum electrode were studied by cyclic (CV) and differential pulse voltammetry (DPV). Sensitivities in differential pulse voltammetry (DPV) are better than other techniques of voltammetry [34-36]. Selected cyclic and differential pulse voltammograms of the electrooxidation of retinyl propionate and the supporting electrolyte are shown in Figure 1. The half-wave potential of the electrode reaction, as investigated by cyclic voltammetry, corresponds to the peak potential from the differential pulse voltammetry. Within the potential range where the compound oxidation peaks appear, the supporting electrolyte (0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ in acetonitrile shows no characteristic peaks, (Fig. 1, curve 3) [20, 28].

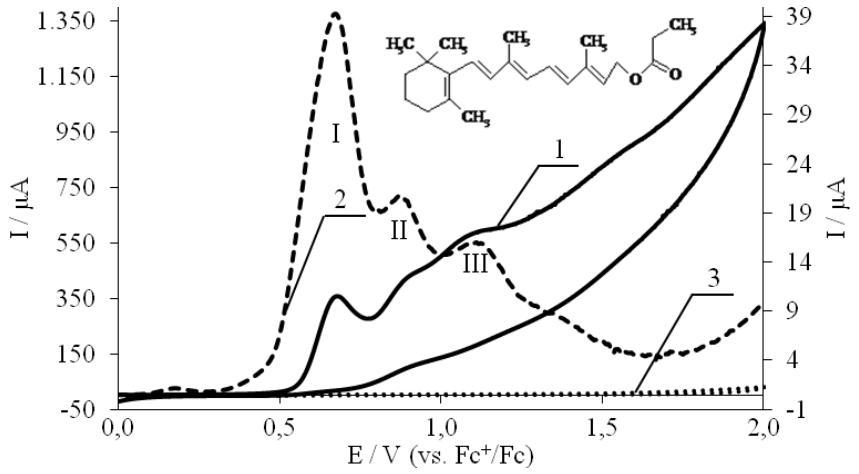


Figure 1. Voltammograms of retinyl propionate electrooxidation at a Pt electrode; curve 1 – cyclic voltammogram 2 – differential pulse voltammogram, 3 – cyclic voltammogram recorded in the supporting electrolyte; c = 0.55 x 10^{-5} mol L^{-1} in 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ in acetonitrile, v = 0.05 V s^{-1}.

From Fig. 1 (curves 1 and 2), it follows that retinyl propionate is oxidised in at least three steps at potentials lower than the electrolyte decomposition potential. The half-wave potential ($E_{1/2}$) of the first step of retinyl propionate oxidation, as determined by cyclic voltammetry, is 0.63 V; this value corresponds to the peak potential from the differential pulse voltammetry measurements. The half-wave potentials ($E_{1/2}$) of the second and third steps are 0.86 V and 1.09 V, respectively.

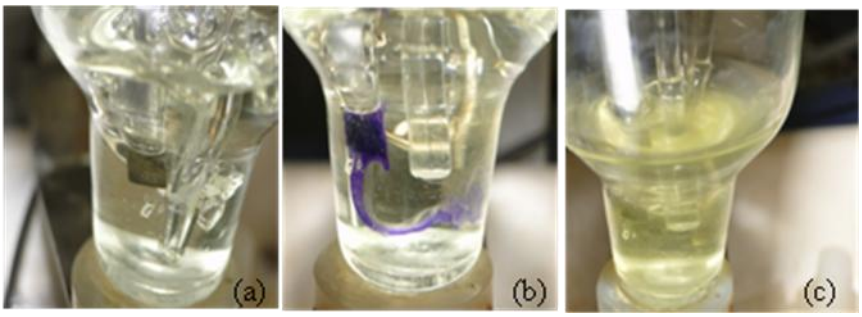


Figure 2. The change in the colour of retinyl propionate during electrooxidation on a Pt electrode: (**a**) before electrooxidation, (**b**) electrooxidation, and (**c**) after electrooxidation.

When conducting the cyclic voltammetry experiments, the formation of a blue product was observed on the Pt electrode at the beginning of the first oxidation stage at 0.65 V (Fig. 2). As the electrode potential increased, the blue product diffused into the solution. After changing the direction of the electrode polarisation, the blue colour of the product disappeared, indicating the formation of a transient species. This observation suggests the formation of a retinyl propionate radical during the first step of the electrooxidation in which the first electron is exchanged.

3.2. The effect of the scan rate and retinyl propionate concentration on substrate electrooxidation

The effect of the polarisation rate on the electrooxidation of retinyl propionate was investigated using cyclic voltammetry with scan rates of 0.01 to 0.20 V s^{-1} (Fig. 3). The peak potential and current were determined for the first step of the electrode reaction of retinyl propionate oxidation, whereas only the peak potential was measured for the second step. When scanning negative potentials, only fluctuations in the current are perceptible, and the accurate localisation of the potential peaks is not evident.

Two approaches widely used to study the reversibility of electrochemical reactions and to determine whether a reaction rate is controlled by adsorption or diffusion are the analyses of i_p on $v^{1/2}$ and of ln i_p on ln v curves. Figure 3 shows these plots for the first oxidation peak of retinyl propionate in acetonitrile. For reversible or irreversible systems without kinetic complications, i_p varies linearly with $v^{1/2}$ and intercepts the origin. However, the plot of i_p on $v^{1/2}$ deviations from linearity and presents a value other than zero for the linear coefficient if the electrode process is preceded by a homogeneous chemical reaction.

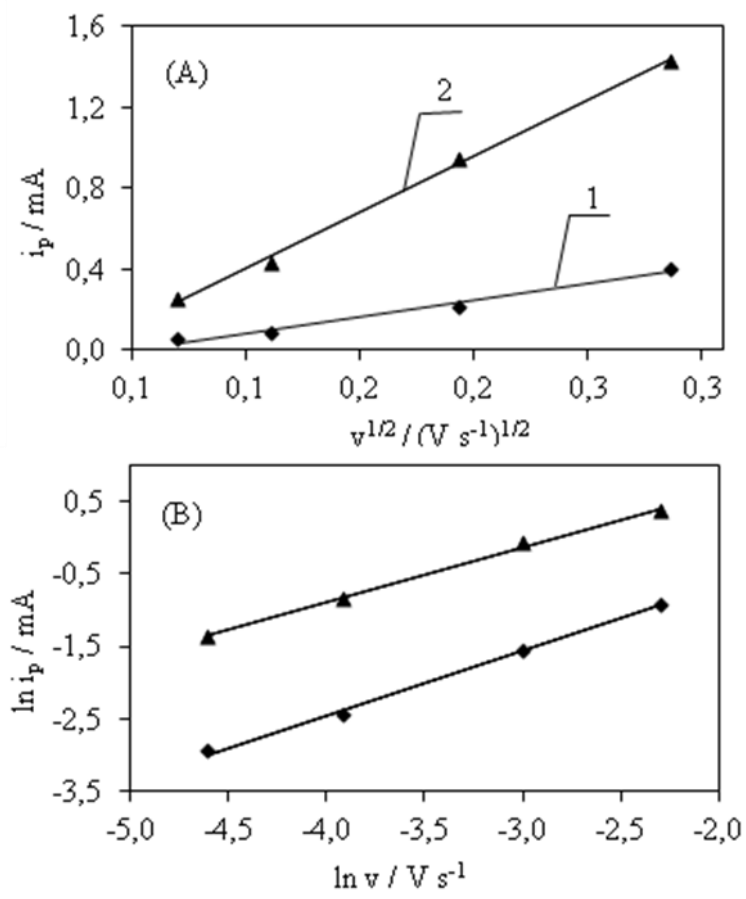


Figure 3. (**a**) Dependence of the peak anodic current (i_p) on the square root of the potential scan rate (v). (**b**) Dependence of peak anodic current on the potential scan rate in double logarithm coordinates for the oxidation of retinyl propionate at a Pt electrode in 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ in acetonitrile; curve 1 – c = 0.23×10^{-5} mol L^{-1}, 2 – c = 3.33×10^{-5} mol L^{-1}.

Over the scan rate range from 0.01 to 0.2 V s^{-1}, the electrooxidation peak current depends linearly on the square root of the polarisation rate and is described by the following equations:

$i_p = \{1.465\ [v\ (V\ s^{-1})]^{1/2}\}$ mA - 0.108 mA, $R^2 = 0.992$ for c = 0.23×10^{-5} mol L^{-1},

$i_p = \{5.539\ [v\ (V\ s^{-1})]^{1/2}\}$ mA - 0.318 mA, $R^2 = 0.998$ for c = 3.33×10^{-5} mol L^{-1}.

This dependence does not cross the origin (Fig. 3a). This fact suggests that the electrooxidation of retinyl propionate can be controlled by absorption or diffusion preceded by a chemical reaction. On the other hand, the dependence of ln ip on ln v is linear (Fig. 3b) and described by the following equations:

$\ln i_p = \{0.895\ \ln v\ (V\ s^{-1})\}$ mA + 1.119 mA, $R^2 = 0.998$ for c = 0.23×10^{-5} mol L^{-1},

$\ln i_p = \{0.909\ \ln v\ (V\ s^{-1})\}$ mA + 2.351 mA, $R^2 = 0.999$ for c = 3.33×10^{-5} mol L^{-1}.

The average slope of this fit is 0.854±0.05, close to the theoretical value of 1.0, which indicates that the process is mainly controlled by adsorption. A slope close to 0.5 is expected for diffusion-controlled electrode processes, and a slope close to 1.0 is expected for adsorption-controlled processes [37-41].

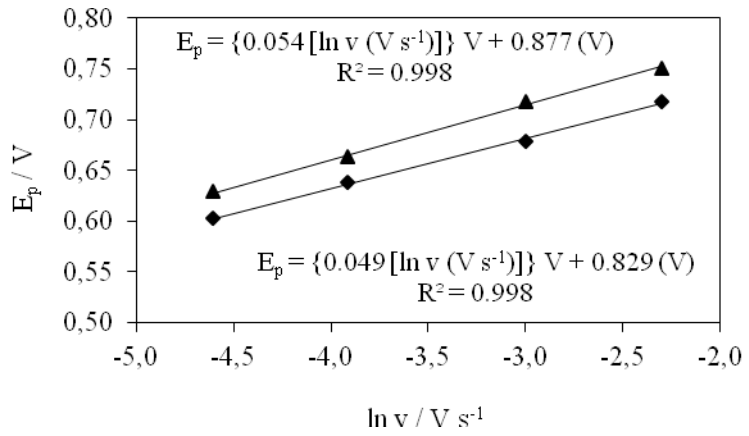


Figure 4. Relationship between the peak potential, E_p, and the logarithm of the scan rate, ln v, for the oxidation of retinyl propionate at a Pt electrode in 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ in acetonitrile.

The E_p of the oxidation peak was also dependent on the scan rate. The plot of E_p versus log υ was linear with a correlation coefficient of 0.998 (Fig. 4), and the relationship between the peak potential and logarithm of scan rate can be expressed by the following equations:

E_p = {0.054 [ln v (V s^{-1})]}V + 0.877 (V) $R^2 = 0.998$ for c = 0.55×10^{-5} mol L^{-1}

E_p = {0.049 [ln v (V s^{-1})]}V + 0.829 (V) $R^2 = 0.998$ for c = 3.33×10^{-5} mol L^{-1}.

For an adsorption-controlled and irreversible electrode process, according to Laviron [42], E_p is defined by the following equation:

$$E_p = E^0 + \frac{RT}{\alpha nF}\ln\frac{RTk^0}{\alpha nF} + \frac{RT}{\alpha nF}\ln v \qquad (1)$$

where α (alpha) is the transfer coefficient, k^0 is the standard heterogeneous rate constant of the reaction, n is the number of electrons transferred during the oxidation, v is the scan rate and E^0 is the formal redox potential, R is universal gas constant (8.314 J K^{-1} mol^{-1}), F is Faraday constant (96,487 C mol^{-1}), T is Kelvin temperature. Using the dependence of the peak anodic potential on the logarithm of the potential scan rate (Fig. 4), the value of the overall electron transfer coefficient (αn) was obtained as 0.49±0.2 for retinyl propionate electrooxidation.

According to Bard and Faulkner [38], α is found by the following equation:

$$\alpha = \frac{47.7}{E_p - E_{p/2}}mV \qquad (2)$$

where $E_{p/2}$ is the potential in which the current is half of the peak value. From this, we found the value of α to be 0.52. Furthermore, the number of electrons (n) transferred in the electrooxidation of retinyl propionate was calculated to be 1.

The equation for the formal rate constant (k_f) for the surface reaction of an irreversible system [1, 43] is given by the following equation:

$$E_p = E_{1/2} - (\frac{RT}{nF})[0.78 - \ln(\frac{k_f}{\alpha})^{1/2}] \qquad (3)$$

Substituting this value of α 0.49 in Eq. (3), the formal rate constant for the irreversible surface reaction, k_f, is calculated to be 52.58±0.5 s^{-1}.

The effect of the retinyl propionate concentration on the reaction of the substrate was investigated over the range from 0.23×10^{-2} mmol L^{-1} to 3.33×10^{-2} mmol L^{-1}. Cyclic voltammograms and the dependence of the oxidation peak current on the concentration are presented in Fig. 5a.

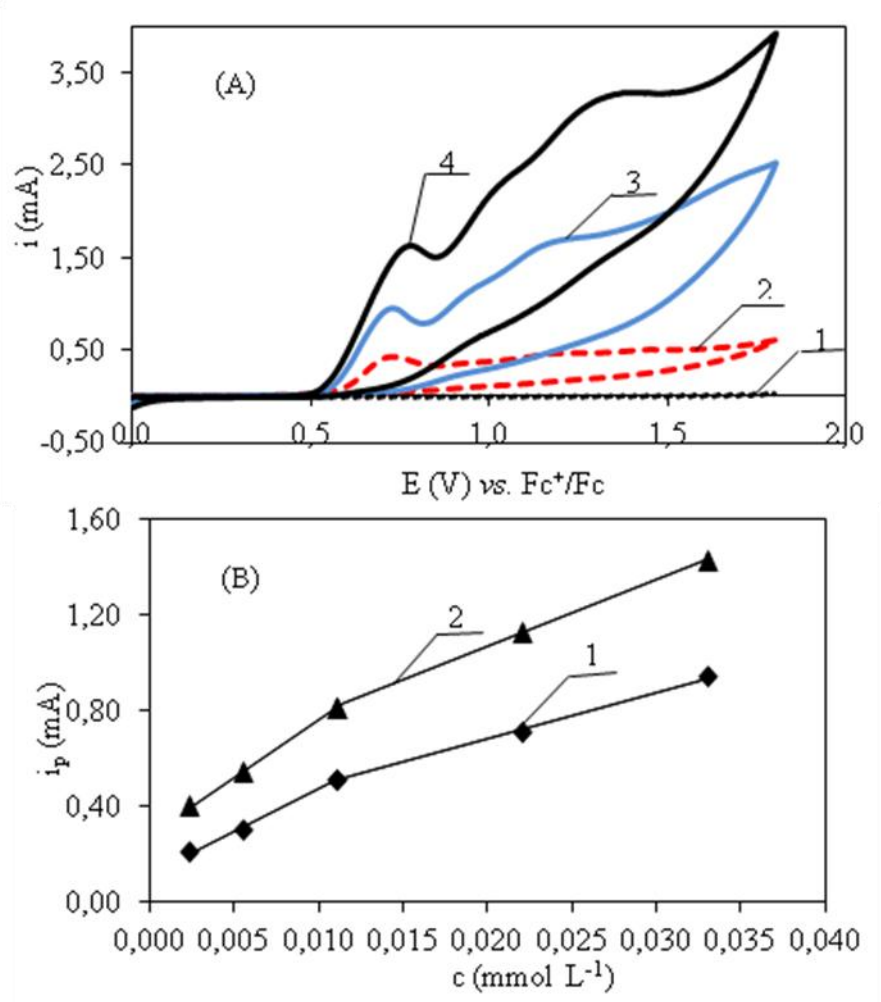


Figure 5. (**a**) Cyclic voltammograms of retinyl propionate oxidation at a Pt electrode; v = 0.1 V s^{-1} in 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ in acetonitrile for various concentrations; curve 1 – supporting electrolyte (0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ in acetonitrile), 2 – c = 0.55×10^{-2} mmol L^{-1}, 3 – c = 1.11×10^{-2} mmol L^{-1}, 4 – c = 3.33×10^{-2} mmol L^{-1} and (**b**) Dependence of the anodic peak current on the retinyl propionate concentration; curve 1 – v = 0.05 V s^{-1}, 2 – v = 0.1 V s^{-1}.

This dependence is linear at all concentration ranges, but there are two linear regions with different slopes. An increase in the concentration to 1.11 x 10^{-2} mmol L^{-1} causes a significant increase in the peak current. In the higher concentration region, the linear dependence of the slope is different and shows a slight increase in the peak current with the concentration (Fig. 5b). The peak dependence is linear up to a retinyl propionate concentration of 1.11 x 10^{-2} mmol L^{-1} and described by the following equations:

i_p = {34.929[c (mmol L^{-1})]}mA + 0.122 mA, R^2 = 0.996 for v = 0.05 V s^{-1},

i_p = {47.443[c (mmol L^{-1})]}mA + 0.286 mA,R^2 = 0.999 for v = 0.1 V s^{-1}.

The voltage dependence of the peak current on the retinyl propionate concentration up to 1.11 x 10^{-2} mmol L^{-1} is linear and described by the following equations:

i_p = {19.545[c (mmol L^{-1})]}mA + 0.291 mA, R^2 = 0.998 for v = 0.05 V s^{-1},

i_p = {28.182[c (mmol L^{-1})]}mA + 0.503 mA,R^2 = 0.999 for v = 0.1 V s^{-1}.

The linear dependence up to a retinyl propionate concentration of 1.11 x 10^{-2} mmol L^{-1} can be used to help determine the retinyl propionate concentration at Pt electrodes. Deviation from linearity was observed in the more concentrated solutions because of the adsorption of retinyl propionate or its oxidation products on the electrode surface.

3.3. Retinyl propionate oxidation processes

The electrode reaction kinetic parameters can be confirmed by quantum-chemical calculations. The distribution of the electron charges in a molecule, which determines the reactivity of the positions of a molecule, is not uniform for retinyl propionate [44-45]. The E_{HOMO} molecular orbital energies were calculated using the AM1 method with HyperChem software. The highest electron density in the retinyl propionate molecule is on the carbon atoms of the cyclic ring that are connected to alkyl groups, suggesting that these positions are easily oxidised. The calculated energy of the highest filled orbital (E_{HOMO} – ionisation potential) determines the ease of the electron release and indicates the sites most susceptible to oxidation. This energy (E_{HOMO}) for retinyl propionate is -8.929 eV (Fig. 6).

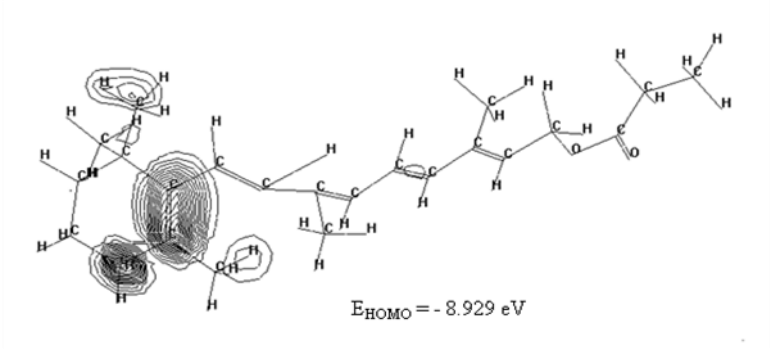


Figure 6. The electron density of retinyl propionate molecule sites likely to be susceptible to electrooxidation.

FTIR spectroscopy is used for the evaluation this type of compound [46-49]. The FTIR spectra of retinyl propionate before and after electrooxidation are shown in Fig. 7 as the dependence of radiation absorption on wave number. The FTIR analysis of retinyl propionate found the following functional groups: The frequency range from 2925-2875 cm^{-1} corresponds to aliphatic C-H stretching vibrations.

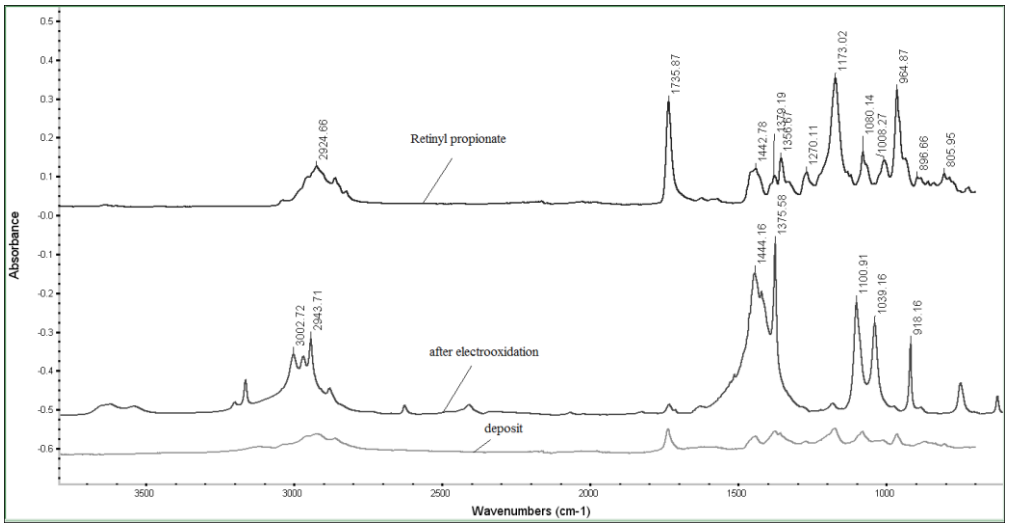
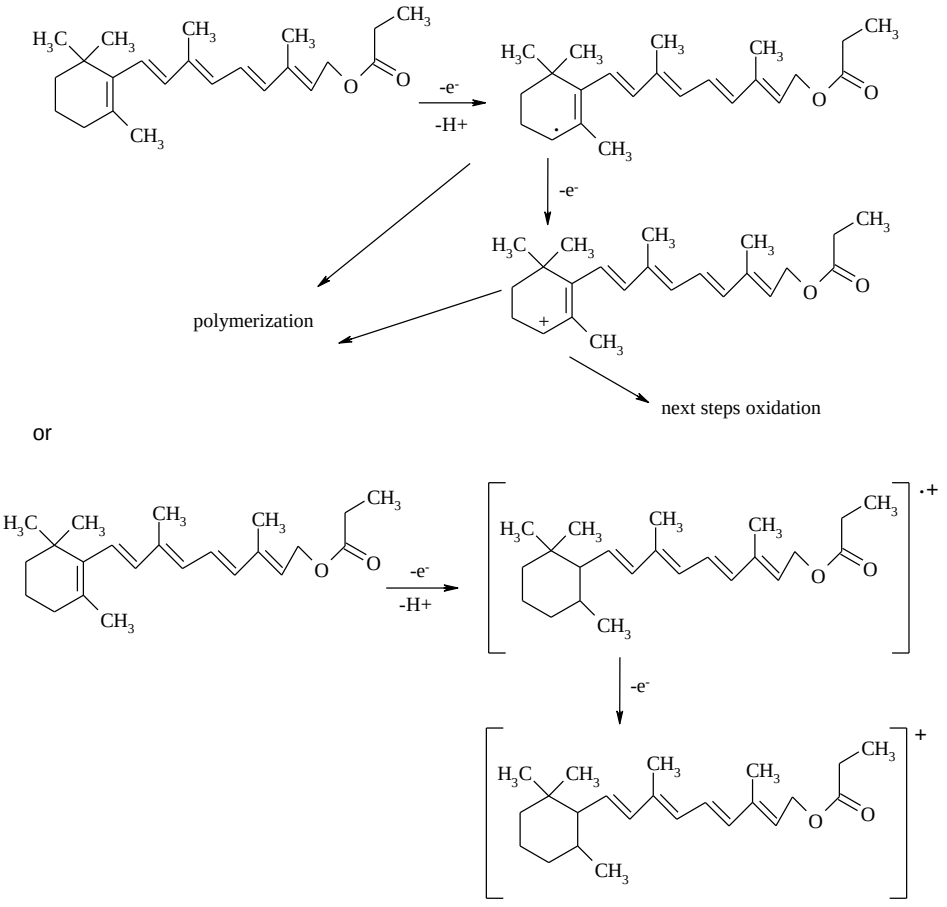


Figure 7. FTIR spectra of retinyl propionate before and after electrooxidation.



Scheme 1. Suggested mechanism of retinyl propionate electrooxidation.

The frequency range from 1435-1405 cm^{-1} peak corresponds to the CH_2 bending vibration. The frequency range from 1350-1260 cm^{-1} corresponds to C-O stretching and O-H bending in the presence

of alcohol. The peak at 964 cm^{-1} corresponds to the =C-H group and is visible only in the spectrum before oxidation. The frequency range from 1300-1250 cm^{-1} corresponds to the C-O asymmetric and C-O-C stretching in esters. The frequency range from 1120-1030 cm^{-1} corresponds to symmetric C-H stretching. The frequency range from 1750-1735 cm^{-1} corresponds to C=O stretching vibrations (ester), but after electrooxidation, this peak disappears. The infrared spectrum after oxidation shows a peak at 3164 cm^{-1}, which corresponds to a band with H, like C-H or O-H. The peaks in these spectra that arise from $-CH_3$ and $-CH_2$ scissoring vibrations (1377 and 1467 cm^{-1}) are visible both before and after the oxidation process.

Thus, based on electrochemical, quantum-chemical calculations and FTIR analysis, and the literature [50-52], one can suggest the following mechanism of retinyl propionate electrooxidation (Scheme 1).

4. CONCLUSIONS

Retinyl propionate is an important vitamin due to its antioxidant features. The electrooxidation behaviour of retinyl propionate was investigated at a Pt electrode. This compound is oxidised irreversibly in at least three electrochemical steps. The effect of the scan rate and retinyl propionate concentration was determined. The electrooxidation of retinyl propionate is adsorption controlled. In non-aqueous medium, the charge transfer coefficient (αn_α), transfer coefficient (α) and rate constant (k_f) were 0.49, 0.52 and 52.58 s^{-1}, respectively.

The linear dependence up to retinyl propionate concentration of 1.11 x 10^{-2} mmol L^{-1} can be applied to help determine the retinyl propionate concentration at Pt electrodes. Deviation from linearity was observed in the more concentrated solutions because of the adsorption of retinyl propionate or its oxidation products on the electrode surface.

In the first step of retinyl propionate oxidation, one electron was exchanged. The resulting product can further undergo oxidation or polymerisation processes. Structural investigations of retinol propionate and the oxidation products were conducted with FTIR spectroscopy. The electrochemical oxidation is highly sensitive and has reasonable selectivity and good precision.

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