*Int. J. Electrochem. Sci.*, 13 **(2018)** 5850 – 5859, doi: 10.20964/2018.06.64

**International Journal of ELECTROCHEMICAL SCIENCE**
www.electrochemsci.org

# Spectroelectrochemical Studies of Interactions between Vitamin A and Nanocolloidal Silver

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*Received:* 28 January 2018 / *Accepted:* 26 March 2018 / *Published:* 10 May 2018

The electrochemical stability of retinyl palmitate (RP) known as Vitamin A in mixed water/ethyl alcohol solutions containing NaCl or $NaNO_3$, in the absence and presence of silver nanoparticles (nAg) was investigated by cyclic voltammetry (CV) recorded on platinum electrode. The chemical interaction between retinyl palmitate and silver nanoparticles was also studied using UV-Vis spectrophotometry applied on the above mentioned media. The experimental results obtained from UV-Vis spectrophotometry showed that in the presence of $NO_3^-$ ions, weak RP-nAg interaction takes place, while in the presence of chloride ions a significant change in environment composition has been highlighted due to the occurrence of instantaneous RP-nAg interaction. The cyclic voltammetry displayed different shapes of cyclic voltammograms recorded on platinum electrode in water/alcohol solutions containing RP and RP/nAg in the presence of $NO_3^-$ ions compared to those recorded in $Cl^-$ presence due to the specific interaction RP-nAg depending on the anion type. Thus, $NO_3^-$ addition leads to mainly electrochemical interaction compared to $Cl^-$ presence that favors chemical RP-nAg interaction. Based on the cyclic voltammetry results obtained in the presence of $NO_3^-$ ions, the electrochemical decomposition mechanism of Vitamin A was proposed.

**Keywords:** Retinyl palmitate; Silver nanoparticles; Cyclic voltammetry; UV-Vis spectroscopy.

## 1. INTRODUCTION

Vitamin A, or generally referred to as retinoids, is the base compound of the naturally occuring compounds retinol, retinyl palmitate, retinaldehyde and retinoic acid. These retinoids are biologically important for the cellular division, differentiation, growth, health and viability not only in the case of skin cells [1-3]. Vitamin A (all-trans retinoid) is sensitive to physio-chemical conditions such as heat, UV-light, Vis-light or oxygen and isomerizes to different cis-isomers with lower bioactivity [4]. In vitro studies showed that retinyl palmitate can generate reactive oxygen species under UV-A radiation

and also in these conditions can present photomutagenicity to some human skin cells [4]. Clinical in vitro and in vivo studies of formulations containing octocrylene, octyl methoxycinnamate, benzophenone and retinyl palmitate did not indicate any phototoxic potential [5].

Photoirradiation of retinyl palmitate generated a series of photodecomposition products and reactive oxygen species involved in lipid peroxidation [6, 7]. Photodecomposition, photomutagenicity and photocitotoxicity tests indicated that retinyl palmitate is not mutagenic under He-Ne laser photoirradiation and can be used before photodynamic therapy to enhance its effect [8]. In vivo studies on mice showed that retinyl palmitate can be used as a cytoprotectant, especially for damaged cells by anticancer drugs [9].

Scientific Committee on Consumer Safety has established the safe concentration for exposure to retinyl palmitate and retinyl acetate via body lotion (0.05 %) and via hand cream, face cream (0.3 %) [10].

The dermatologic use of vitamin A is limited due to its adverse effects and its chemical stability to oxidation, heat, light, moisture or acids. Solid lipid nanoparticles, nanoemulsions and liposomes for retinyl palmitate were studied in order to improve the photostability and biocompatibility [11, 12].

A reverse-phase high performance liquid chromatography method with ultraviolet detection was developed for the quantification of retinyl palmitate, retinol and retinoic acid in cosmetic products [13]. Many methods have been developed for the analysis of fat soluble vitamins (vitamins A, D, E and K) in pharmaceutical supplements, infant formula, adult nutritionals [14-17].

Endogenous levels of retinoids (retinyl esthers, retinol, retinal) were quantified in order to reveal their homeostasis in diseases such as cancer, Alzheimer`s diseas, diabetes or obesity [18-19].

Electrochemical methods have also shown their efficient applicability to the analysis of biologically active compounds [20-26] including retinol [27, 28].

Nanoparticles exhibits special physico-chemical properties different from their bulk dissolved forms and have been gaining increasing attention in the applied and fundamental research [29-33]. Nanocolloidal/ionic silver presents high antimicrobial activity against fungi, bacteria or microbes and represents one of the components of pharmaceutical and cosmetic formulations [34-37].

The vitamins and colloidal silver can be found as active ingredients in different pharmaceutical or naturist supplements used as tonics, revitalizing and detoxifying as well as in cosmetics. Retinyl palmitate (RP) is the main storage form of retinoid (vitamin A) in humans and animals. Due to its biological effects, it is found in various commercial products such as: drugs, cosmetics and foods. Moreover, silver nanoparticles (nAg) are also used as adjuvants in different supplements due to its antiviral activity. The interactions that may occur between vitamins and colloidal silver nanoparticles should be known, especially if the commercial products containing these compounds are used in chloride media or stored for a long time.

This study provides information on specific interactions between retinyl palmitate (RP), known as Vitamin A and silver nanoparticle (nAg). To investigate RP-nAg chemical interaction, the UV-Vis spectrophotometry was performed for mixed solutions (water/ethylic alcohol) containing $Cl^-$ or $NO_3^-$ ions and RP, in the absence and presence of nAg. The cyclic voltammetry recorded on platinum electrode in NaCl and $NaNO_3$ alcoholic solutions containing RP, without and with silver nanoparticles

(nAg) with was used to study the electrochemical stability of mixtures. The RP electrochemical decomposition mechanism was proposed.

## 2. MATERIALS AND METHODS

### *2.1. Materials*

Pure vitamin A (retinyl palmitate) as yellowish oil was obtained from Merck. Other chemicals used in this study e.g. NaCl and $NaNO_3$ were also supplied by Merk, Germany. A $10^{-4}$ mol·L$^{-1}$ retinyl palmitate stock alcoholic solution was prepared and stored in a refrigerator (< 10 °C) in dark environment. 1.0 mol·L$^{-1}$ NaCl and 1.0 mol·L$^{-1}$ $HNO_3$ stock solutions were prepared and used as supporting electrolyte. The working electrolyte solution ($5.0 \cdot 10^{-6}$ mol·L$^{-1}$ retinyl palmitate, $10^{-1}$ mol·L$^{-1}$ NaX; X = Cl, $NO_3$) was prepared by appropriate dilution. The powder of silver nanoparticles was purchased from Sigma. The working electrolyte solutions were prepared using bidistilled water. The molecular structure of vitamin A is presented in Fig. 1.

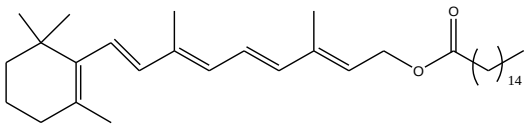



**Figure 1.** Molecular structure of [(2E,4E,6E,8E)-3,7-Dimethyl-9-(2,6,6-trimethyl-1-cyclohexenyl)nona-2,4,6,8-tetraenyl] hexadecanoate; (retinyl palmitate - RP).

Platinum plate were purchased from Merck (purity higher than 99.9 %), cut in the form of plates with 1x3 cm size. The electrodes had a 2 cm$^2$ active surface. $10^{-1}$ mol·L$^{-1}$ $H_2SO_4$ and $10^{-1}$ mol·L$^{-1}$ NaOH solutions were used for ultrasonically cleaning of platinum electrodes for 5 min.. An Ag/AgCl,$KCl_{sat}$ reference electrode was employed in all cyclic voltammetry measurements.

### *2.2. Methods*

The cyclic voltammetry was performed in a standard electrochemical cell with three electrodes: two identical platinum electrodes, each having an active area of 1 cm$^2$, were used as working electrode and auxiliary, respectively. The Ag/AgCl,$KCl_{sat}$ electrode was used as reference electrode.

The cyclic voltammetry measurements were carried out using a VoltaLab 40 potentiostat with VoltaMaster 4 software. The cyclic voltammograms were recorded in mixed water/ethylic alcohol solutions containing NaCl or $NaNO_3$ and Vitamin A (RP), in the absence and presence of silver nanoparticles (nAg) with a potential scan rate of 100 mV·s$^{-1}$, in a dynamic regime, the stirring rate being of 300 rot·min$^{-1}$.

The UV-Vis spectra were recorded by a Varian Cary 50 spectrophotometer (Cary Win UV software) equipped with a spectrophotometric quartz cell having dimensions of 10x10x45 mm .

## 3. RESULTS AND DISCUSSION

### *3.1. UV-Vis Spectrophotometry results*

Figure 2 shows the UV-Vis spectra of RP blank alcoholic solution and RP alcoholic solution containing $Cl^-$ ions or $NO_3^-$ without and with nAg. The UV-Vis spectrophotometric scans of the electrolyte solutions were recorded in the wavelength range of 200 nm and 800 nm.

As shown Figure 2a, two peaks of retinyl palmitate (RP spectrum) were identified; one well defined peak with absorbance maximum around 325 nm and one split peak with high absorbance value, at 250 nm. There is observed a significant effect of chloride ions on RP (RP_NaCl spectrum), both peaks becoming very broad with low absorbance maximum values. The UV-Vis spectral scan of mixture containing RP, $Cl^-$ and silver nanoparticles (curve RP_NaCl_nAg) shows a strong interaction between all the species; the peak recorded at 400 nm corresponding to silver nanoparticles is split and shifted to higher absorbance values; the peaks attributed to RP ($\lambda_{max}$ = 325 nm and $\lambda_{max}$ = 250 nm) disappear; at wavelength values lower than 300 nm, an absorbance gradual increase was recorded, due to the formation of intermediate species between RP and silver nanoparticles and/or ionic silver.

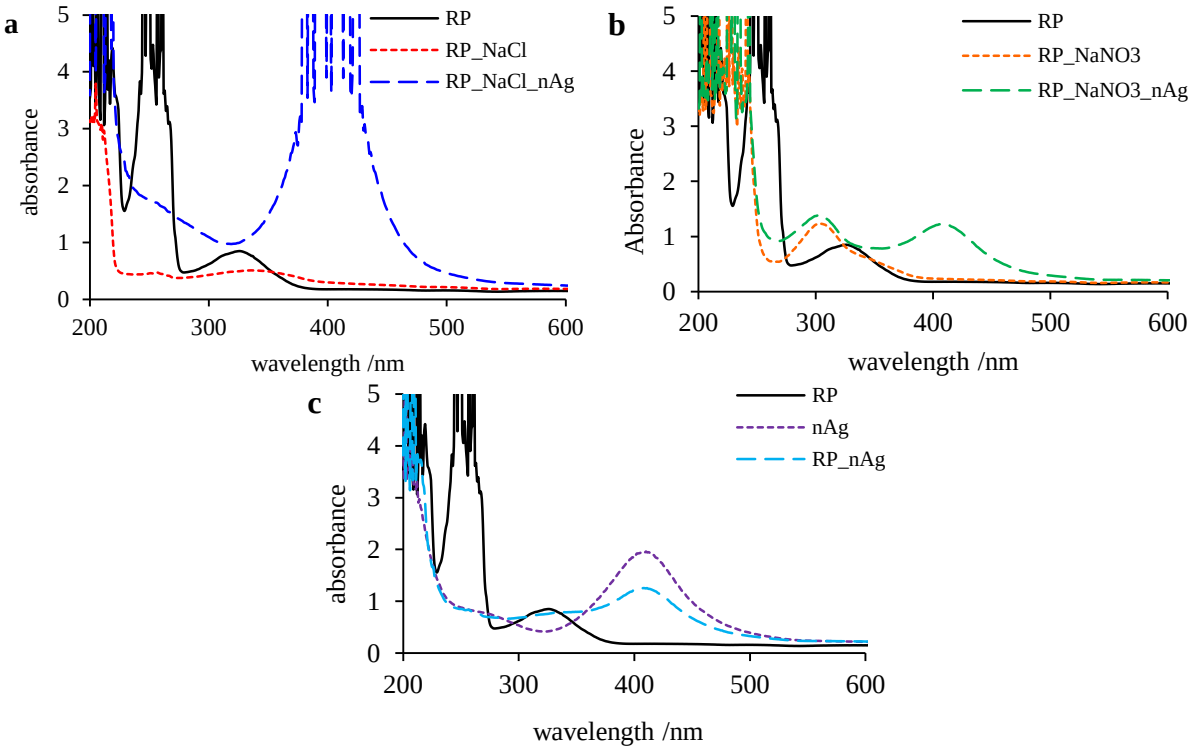



**Figure 2.** UV-Vis spectrophotometric scans of: i) $5 \cdot 10^{-6}$ mol·L$^{-1}$ RP in alcoholic solution; ii) $5 \cdot 10^{-6}$ mol·L$^{-1}$ RP, $10^{-1}$ mol·L$^{-1}$ $NaNO_3$; iii) $5 \cdot 10^{-6}$ mol·L$^{-1}$ RP, $10^{-1}$ mol·L$^{-1}$ $NaNO_3$, 500 mg·L$^{-1}$ nAg; iv) $5 \cdot 10^{-6}$ mol·L$^{-1}$ RP, $10^{-1}$ mol·L$^{-1}$ NaCl; v) $5 \cdot 10^{-6}$ mol·L$^{-1}$ RP, $10^{-1}$ mol·L$^{-1}$ NaCl, 500 mg·L$^{-1}$ nAg in hydro-alcoholic (9:1) solution.

In Figure 2b, it can be observed the effect of nitrate ions and silver nanoparticles on the RP UV-Vis spectrum. In the presence of nitrate ions (RP_$NaNO_3$ spectrum) the two peaks of RP were shifted to wavelength lower values: $\lambda_{max}$ = 300 nm and $\lambda_{max}$ = 230 nm. After addition of silver nanoparticles (RP_$NaNO_3$_nAg spectrum), other peak at 400 nm corresponding to nAg was registered.

Figure 2c presents the UV-Vis comparative spectra of RP in mixed water/alcoholic solution, aqueous suspension of silver nanoparticles and their mixture. The UV-Vis scan of nAg suspension (nAg spectrum) shows a peak with absorbance maximum at 400 nm corresponding to silver nanoparticles and broad absorption peak with low intensity, corresponding to ionic silver [25]. In the presence of nAg (RP_nAg spectrum), the peak at 250 nm completely disappears and two peaks at 400 nm and 320 nm occur corresponding to nAg and RP-nAg complexes, respectively.

It has been reported that vitamins interact with silver nanoparticles, as an example being the interaction between vitamin C and silver nanoparticles studied by cyclic voltammetry and UV-Vis spectrophotometry [25].

In our previous study the electrochemical behavior of vitamin C in $10^{-1}$ mol·$L^{-1}$ NaCl solution, in the absence and presence of silver nanoparticles was investigated [25]. The kinetics of zero order reaction was computed for Vitamin C degradation in the absence and presence of silver nanoparticles, the reaction rate constant reaching a double value in the presence of nAg [25].

Consequently, nAg has an electrocatalytic effect on the Vitamin C degradation, at constant current density of 20 mA·$cm^{-2}$, indicating that after electrolysis time of 4.0 min the Vitamin C electrodegradation reaction is very fast due to the silver ions formation, that leads to the vitamin C rapidly oxidation to ascorbate radical [25]. In contrast, the interaction between Vitamin A and silver nanoparticles is instantaneous in NaCl solution, as shown Figure 2a through overlapping multiple interferences highlighted at 400 nm. Consequently, the electrolysis performing is unnecessary, under these conditions the reaction kinetics is difficult to evaluate and the interaction between nAg and Vitamin A can be assimilated to an instantaneous chemical transformation reaction in RP_nAg complexes.

### *3.2. Electrochemical behavior of RP in the presence of $NaNO_3$ supporting electrolyte*

Figure 3 shows typical cyclic voltammograms of platinum electrode in water/alcoholic 9:1 (v/v) solutions: i) $10^{-1}$ mol·$L^{-1}$ $NaNO_3$; ii) $10^{-1}$ mol·$L^{-1}$ $NaNO_3$, $5\cdot10^{-6}$ mol·$L^{-1}$ RP; iii) $10^{-1}$ mol·$L^{-1}$ $NaNO_3$, $5\cdot10^{-6}$ mol·$L^{-1}$ RP, 500 mg·$L^{-1}$ nAg.

On the anodic scan, many oxidation processes are identified in working electrolyte solutions ($E_o^1 = -0.9\ V$, $E_o^2 = -0.25\ V$, $E_o^3 = 0.25\ V$, $E_o^4 = 0.8\ V$). The RP molecules showed an irreversible behaviour, with successive small anodic peaks of current density on Pt electrode. The anode peaks can also be attributed to various electrode processes of nitrate ion (Fig. 3b) at the metal/electrolyte solution interface. On the cathodic scan, two reduction peaks can be observed ($E_r^1 = \sim 0.0\ V$, $E_r^2 = -0.5\ V$).

A significant decrease in the potential value of 0.2 V was obtained on platinum electrode for retinyl palmitate under experimental conditions due to the presence of silver nanoparticles. The relationship between the oxidation currents on working electrode for both electrolytes (presence / absence of nAg) proves the interaction of retinyl palmitate with silver nanoparticles and indicates that

nAg has an electrocatalytic effect. From the experimental results, it is clearly observed that retinyl palmitate produces significantly higher voltammetric signals compared to those recorded in the absence of silver nanoparticles.

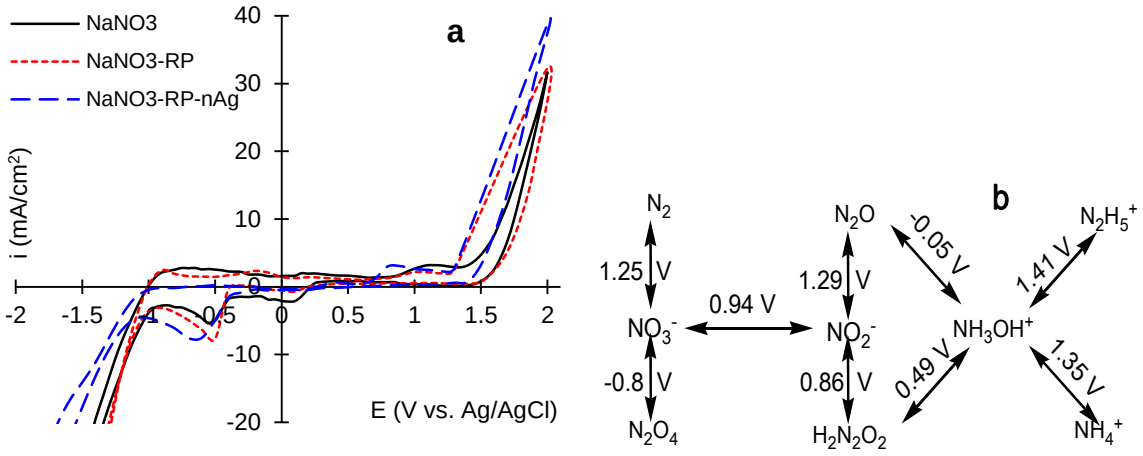
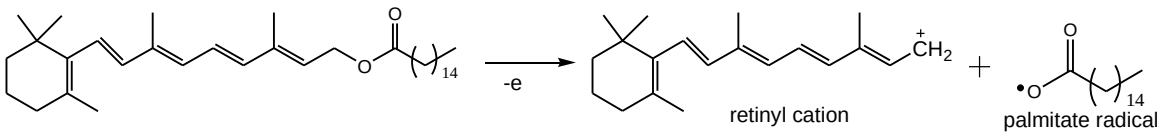



**Figure 3.** Cyclic voltammograms of i) $10^{-1}$ mol·L$^{-1}$ $NaNO_3$; ii) $10^{-1}$ mol·L$^{-1}$ $NaNO_3$, $5\cdot10^{-6}$ mol·L$^{-1}$ RP; iii) $10^{-1}$ mol·L$^{-1}$ $NaNO_3$, $5\cdot10^{-6}$ mol·L$^{-1}$ RP, 500 mg·L$^{-1}$ nAg, hydro-alcoholic 9:1 (v/v) solutions, platinum electrode.

Retinyl palmitate contains five conjugated double bonds (>C=C<) which explains its high susceptibility to oxidation. Retinyl palmitate undergoes electrochemical transformations at the electrode surface to highly oxidation state intermediates. According to Scheme 1, the initial ester molecule cleaves oxidatively with formation of the retinyl cation and the palmitate radical [7].

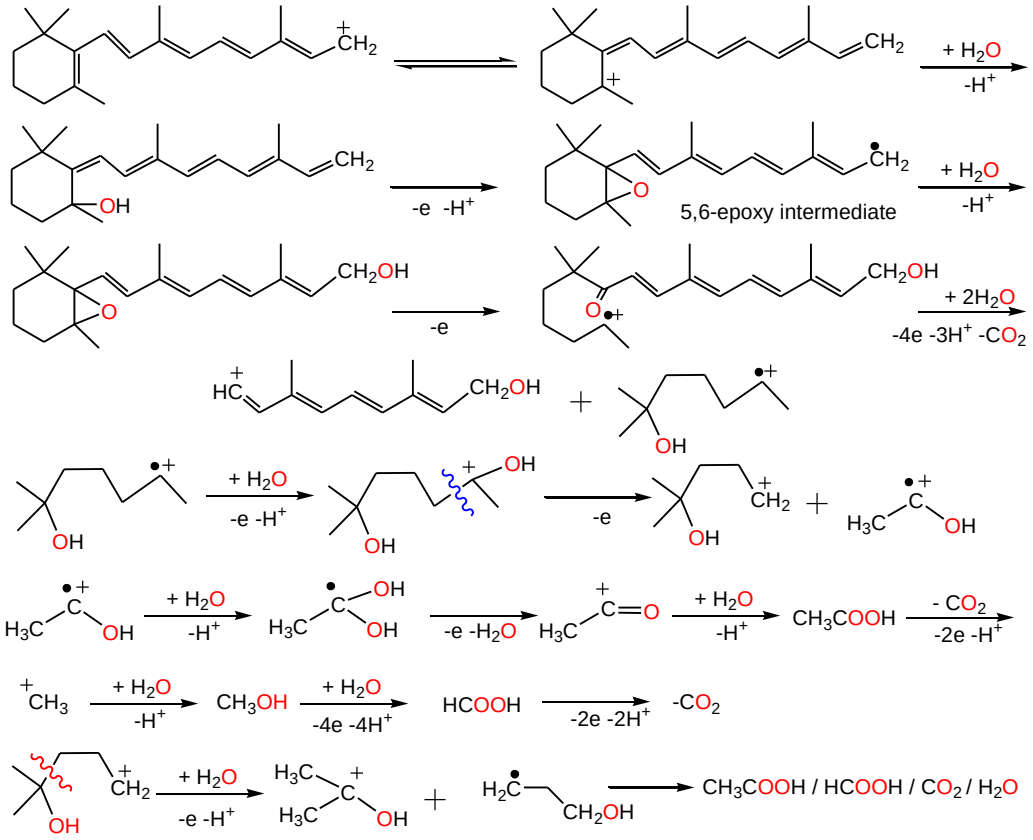



**Scheme 1.** Electrochemical degradation of retinyl palmitate.

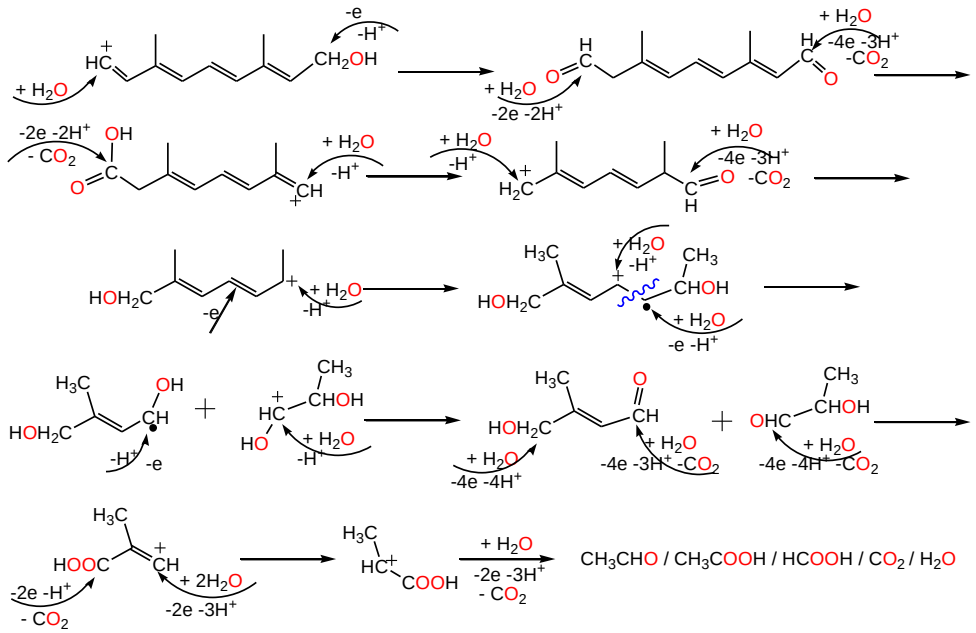
Also, the retinyl cation may form retinol in the presence of hydroxyl ions. The process of retinyl cation degradation (Scheme 2) initiates with the formation of cyclohexene derivatives at the conjugated π system such as epoxide derivatives. Epoxy structures have also been identified as intermediates in vitamin A degradation [6, 7].

As the intermediates passed through the double layer, they cleaved to hydroxi-, keto-enol, aldehyde/ketone, carboxylic acid and/or bifunctional structures of these. The various acid-base equilibria or the equilibria between the mesomere structures which can form along the electrochemical degradation mechanism could be influenced by the acidity of the solution, the value of the working electrode potential and / or the current density. The overall electrochemical mechanism involves several steps. When hydroalcoholic solution of RP was exposed to higher overpotentials, many electrochemical degradation products were formed. All the electrodegradation products (ionic and/or

radical) are electrochemicaly unstable. Thus, upon higher polarization, the underproducts further decompose into inorganic products.




**Scheme 2.** Decomposition products of retinyl cation formed through an electrochemical mechanism.




**Scheme 3.** Decomposition products of nonatetraene intermediate formed through an electrochemical mechanism.

The first cleavage of the carbon chain leads to the generation of a nonatetraene cation intermediate with high reactivity due to the four double bonds from its structure. The presence of delocalized π electrons can lead to the electrochemical degradation mechanism through different paths; a possible degradation pathway is shown in Scheme 3. The palmitate radical can easily stabilize to palmitic acid. The molecular structure of palmitic acid contains only carbon atoms having sp3 hybridization, its electrochemical degradation requires much higher overvoltages. A greater stability of palmitic acid can explain its accumulation in the system, knowing that is one of the products identified in the degradation of retinyl palmitate [7].

### *3.3. Electrochemical behavior of RP in the presence of NaCl supporting electrolyte*

Figure 4a shows the cyclic voltammogramms recorded on platinum electrode, between -2.0 V and +2.0 V at 0.1 $V \cdot s^{-1}$, in NaCl blank solution and in mixed water/alcohol solutions containing NaCl and RP, in the presence and in the absence of nAg. Figure 4b displayed the electrochemical processes, the oxychloride active species that can be formed and the values of the corresponding potentials.

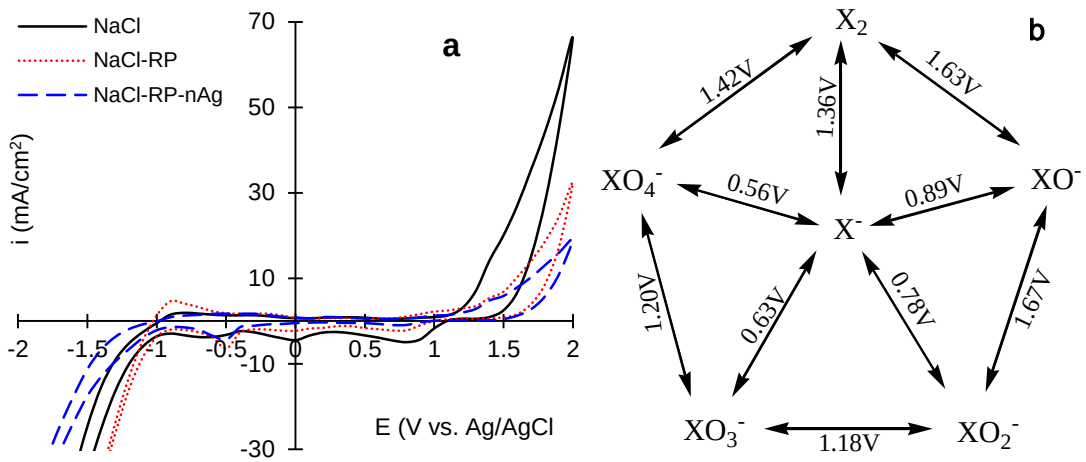



**Figure 4.** Cyclic voltammograms of i) $10^{-1}$ $mol \cdot L^{-1}$ NaCl; ii) $10^{-1}$ $mol \cdot L^{-1}$ NaCl, $5 \cdot 10^{-6}$ $mol \cdot L^{-1}$ RP; iii) $10^{-1}$ $mol \cdot L^{-1}$ NaCl, $5 \cdot 10^{-6}$ $mol \cdot L^{-1}$ RP, 500 $mg \cdot L^{-1}$ nAg, water/alcoholic 9:1 (v/v) solutions, platinum electrode.

An irreversible voltammetric behaviour of platinum electrode in aqueous solution of supporting electrolyte was observed corresponding to chloride ion oxidation and reduction of oxychloride species at the electrode surface [25, 26]. Once formed in the solution, the hypochlorite ion due to its high oxidizing action may lead to homogeneous processes such as oxidation of retinyl palmitate in the bulk electrolyte.

The sharp increase of anodic peak at around -0.9 V when retinyl palmitate is added to supporting electrolyte solution corresponded to RP adsorption on the electrode surface [28]. In the presence of silver nanoparticles, this peak becomes very broad and its intensity decreases which prove the interaction of retinyl palmitate with silver nanoparticles.

After adsorption of retinyl palmitate on the working platinum electrode, cyclic voltammogram shows a well-defined anodic peak at +1.0 V which may correspond to a partial electrochemical degradation of retinyl palmitate [27].

The cyclic voltammogram shape changes after the silver nanoparticles addition, indicating the the chemical/electrochemical interaction occurrence of the type RP-nAg.

Both anodic peaks (-0.9 V and +1.0 V) attributed to retinyl palmitate adsorption and electrochemical partial degradation, respectively disappeared in the presence of silver nanoparticles, while the current density values corresponding to cathodic peaks decreased.

## 4. CONCLUSIONS

The supporting electrolytes cause chemical and physical changes on the platinum electrode surface, and thereby also a different electrochemical response. This study provides information regarding reactivity and of the reactive intermediates generated by chemical/electrochemical reactions of retinyl palmitate and silver nanoparticles.

UV-Vis spectrophotometry indicated a strong interaction between retinyl palmitate molecules and silver nanoparticles, in the presence of $Cl^-$ ions and low interaction in the presence of $NO_3^-$ ions.

The experimental results obtained from cyclic voltammetry reveal that, the addition of nAg in solution leads to a considerable decrease in the current density, followed by a significant hysteresis shape modification due to the interaction of Vitamin A with silver nanoparticles.

ACKNOWLEDGMENTS
The funding of this work was supported by the research grants awarded by the University of Craiova, Romania, in the competition “The Awards of Research Results-ISI Articles”, April 2017.

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