Impact of redox potential electrochemical modification and storage conditions on the oxidation reaction prevention in dairy emulsion

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ORIGINAL PAPER

Impact of redox potential electrochemical modification and storage conditions on the oxidation reaction prevention in dairy emulsion

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Abstract Oxidation reactions in milk conclude to negative consequences such as lipid oxidation, undesirable flavors, degradation of vitamins, and changes in microbial flora of milk. The objective of the study was to investigate the effect of electroreduction and storage conditions on an oil/water emulsion made of canola oil and reconstituted skim milk. The electroreduction treatments were carried out at two different anode/cathode voltage differences (0 and 4 V) on a 2% stable oil/water emulsion made of canola oil and skim milk. After each electroreduction treatment, samples of electroreduced emulsion were placed in conditions of storage in regards to headspace (0%, 10%, and 50%), temperature (4 °C and 22 °C) and in the dark for 14 days. The results showed that the electroreduction treatment significantly reduced the redox potential of the emulsion samples to negative values (from +85 to −412 mV) and was also able to decrease their dissolved oxygen (DO) concentration (from 3.8 to 2.5 mg.L^{-1}). The storage conditions of headspace and temperature have had an important impact on the oxidation–reduction potential (ORP) value and the DO value. This study is the first to our knowledge to show that in storage conditions where the gaseous exchanges and especially the oxygen are limited, it is possible to maintain during 14 days a negative ORP in electroreduced oil–water emulsion.

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电化学改性和贮藏条件对防止乳体系氧化的作用

摘要 乳发生氧化反应会对乳的质量会产生负面影响, 如脂质氧化、不愉快风味物质的产生、维生素损失以及微生物菌群的改变。本文研究了电解还原和贮藏条件对以菜籽油/还原脱脂奶形成的水包油 (O/W) 型乳浊液的影响。电解还原反应是在以2%菜籽油/脱脂粉形成的水包油型乳浊液中通过不同阳极/阴极电压差 (0伏和4伏)来完成的。电解还原处理完后的乳浊液样品放在含有不同顶部空气体积 (0,10和50%) 的包装容器中, 在一定的温度(4和20 °C) 和避光条件下保藏14天。实验结果表明: 电解还原处理能够将乳浊液的氧化还原电位显著地降低到负值(从+85降低到-412 mV), 同时还能降低样品中溶解氧的浓度(从3.8降低到2.5 $mg.mL^{-1}$)。包装顶部的体积和贮藏的温度能够显著降低氧化还原电位 (ORP) 值和溶解氧 (DO)。本研究证明了在此贮藏条件下气体交换特别是氧气交换被限制, 在14天内贮藏过程中有可能使电解还原的水包油型乳浊液维持在负氧化还原电位的情况下。

Keywords Oil/water emulsion · Milk · Electroreduction · Redox potential · Dissolved oxygen · Storage

关键词 水包油型乳剂 · 乳 · 电解还原 · 氧化还原电位 · 溶解氧 · 贮藏

1 Introduction

In a complex fluid such as milk, many modifications arise during its processing and storage, whereas the oxidation–reduction reactions are dominantly the main reason for the degradation of milk (Jensen et al. 1991). These reactions result in the alteration of sensitive compounds. One of the main chemical transformations caused by oxidation–reduction reactions in milk is lipid oxidation. Phospholipids, the main fat on the milk fat globule membrane, are composed of polyunsaturated fatty acids and therefore are very sensitive to oxidative stress. As a consequence, undesirable oxidized/metallic flavors can develop in dairy products. It has also been shown that oxidation reduction reactions have a negative impact on the thermal stability of milk (Vahcic et al. 1992). Colorants and aroma concentrates added to products are also sensitive to oxidation (Borle et al. 2001).

Recently, a series of experiments have been done concerning the impact of the electroreduction process on milk. The evolution of the redox potential of electroreduced milk during treatment and storage has been shown by Bolduc et al. (2006) and Schreyer (2007). Bolduc et al. (2006) showed that as the anode/cathode voltage difference increases, reduction reactions take place in a faster rate and concluded that the decrease in the redox potential value is proportional to the different voltages used. Therefore, according to their results, 4 V was the optimal anode/cathode voltage difference to be applied for the electroreduction treatment of milk. Although negative redox values were reached during the treatment and the oxygen concentration decreased, the redox values were not stable and returned to positive values after 3 to 4 days of storage.

Although some research has been done to determine the efficiency of the electroreduction treatment for milk, no specific research has yet been carried-out to verify the impact of this procedure on the stability of milk containing lipids. In this current research, an oil/water model system of canola oil and skim milk powder was used. The specific objectives of this work were (1) to study the effect of an electroreduction treatment on an oil/water emulsion and (2) to

determine the impact of headspace and temperature during storage of electro-reduced and control samples of an oil/water emulsion.

2 Materials and methods

2.1 Material

The electroreduction treatments were carried out on a 2% stable oil/water emulsion made of canola oil and reconstituted skim milk (model system for the research). In order to make 4 L of a 2% stable oil/water emulsion alike milk, 196 g of skim milk powder (Agropur, Canada) was weighed and dissolved in 1,862 mL of warm water (54 °C) with agitation inside a thermostated water bath. After the powder had completely dissolved in water, the mixture was left to rest for 30 min. Then 41.44 g of canola oil (Merit Selection, Canada) was weighed while mixing was added to the reconstituted skim milk. Afterward, the warm (54 °C) oil/water emulsion was homogenized using an EF-C5 homogenizer (Avestin, Ottawa, ON, Canada) with pressure of 2,500 psi (17 MPa). Homogenization was repeated two times on each emulsion, and then the homogenized emulsion was placed at 4 °C in order to cool down to about 20 °C.

2.2 Method

2.2.1 Electroreduction system

The electroreduction system used is the same as the one used and described by Bolduc et al. (2006). This system is a dynamic cell divided into two different compartments by a cationic membrane (CMX-SB, Tokuyama Soda Corp, Tokyo, Japan). On one side of the membrane, the emulsion was in contact with a food-grade stainless steel cathode, and on the other side of the membrane, the electrolyte (0.1 $mol.L^{-1}$ H_2SO_4) was in contact with an anode. In order to have a continuous circulation during the treatment, each of the cell compartments was in contact with their own external tank. Both solutions were circulated by two centrifugal pumps (Iwaki Magnet Pump, Iwaki Co, Ltd., Tokyo, Japan), and their flows were controlled by two flow meters (Aalborg Instruments and Controls, Inc., Orangeburg, SC, USA) and were kept at 300 $mL.min^{-1}$.

2.2.2 Treatments

Using the electrolysis cell described above, two anode/cathode voltage differences were applied between the electrodes (0 and 4 V) which was supplied by an electrical power supply (Model HPD 30-10, Xantrex, Burnaby, BC, Canada). In this study, 0 V was used in order to investigate the modifications that take place on the emulsion just by passing through the electrolysis cell without having a potential difference. The 0-V voltage applied was obtained with the power supply plugged and set to "OFF".

Each electroreduction treatment was performed in triplicates using 300 mL of the oil/water emulsion and an equal volume of 0.1 M sulfuric acid. During each 60-min treatment, oxidation–reduction potential (ORP), dissolved oxygen (DO), pH,

conductivity, and the current intensity of milk were recorded at intervals of 30 s during the first 10 min and at intervals of 1 min thereafter.

2.2.3 Storage

The goal was to determine the storage conditions that have an effect on the modified parameters of the electroreduced oil/water emulsion. Two of the three most significant storage factors that impact the oxidative stability of lipids are oxygen and temperature that were studied on the electroreduced emulsion and control samples. After each electroreduction treatment, samples of electroreduced emulsion were poured in glass jars. Sodium azide (0.02%) was added to all modulated samples in order to prevent microbial growth during storage. They were placed in dark conditions of storage in regards to headspace and temperature for duration of 14 days in parallel with control nonelectroreduced milk. The ORP, DO, and pH of milk samples were recorded on days 0, 1, 2, 4, 8, and 14 at which analyses were performed on different jars of samples in order to prevent sample and headspace contamination. The experimental design used was a full-factorial one (2×2×3) for control and two treated samples at 0 and 4 V stored in the dark:

(a) Oxygen: The factor oxygen was demonstrated by the head space in the sample bottles. Three main head spaces were selected in portion to the volume of the sample bottles:

- 0%: no oxygen in the headspace of the sample
- 10%: typical volume of headspace in commercial milk
- 50%: presence of an important quantity of oxygen

(b) Storage temperature

- 4 °C: refrigerator temperature
- 22 °C: ambient temperature

2.3 Analytical methods

2.3.1 Oxidation–reduction potential measurement

The ORP was measured using a VWR Symphony platinum electrode (VWR Scientific Products, West Chester, PA, USA) with an internal Ag/AgCl reference electrode and filled with the recommended solution containing KCl and AgCl. This electrode was connected to a VWR Symphony portable SP20 pH/ISE meter. The electrode reading was verified with a homemade solution of potassium ferrocyanide and potassium ferricyanide having an ORP of +234 mV.

2.3.2 Dissolved oxygen measurement

The DO was measured using a VWR Symphony electrode (VWR Scientific Products) mounted with the specified membrane and filled with the supplied DO electrolyte solution. The electrode was connected to a VWR Symphony SP50D

portable DO meter. The electrode was calibrated every 2 h as described in the supplier's manual.

2.3.3 Conductivity measurement

The conductivity was measured with an immersible YSI probe (model 3417, K= 1 cm^{-1}, Yellow Springs Instrument, Yellow Springs, OH, USA) connected to an YSI 3232 adaptor to allow readings on the YSI 3100 conductivity meter of the same manufacturer. Since the conductivity varied proportionally with temperature and the values were not automatically compensated by the conductivity meter, all readings were corrected to 25 °C using the method described by Bazinet et al. (2004).

2.3.4 pH measurement

The pH was measured using a VWR Symphony electrode (VWR Scientific Products) equipped with an automatic temperature compensation device and connected to a VWR Symphony SR601C benchtop pH meter.

2.4 Statistical analysis

Data obtained during treatments and storage were subjected to multivariate analyses of variance using JMP IN software (Version 5.1, SAS Institute Inc., Cary, NC, USA).

3 Results

3.1 Electroreduction treatment of oil/water emulsion

During electroreduction, the anode/cathode voltage difference (P<0.0001), the time (P<0.0037), and the dual interaction time/voltage difference (P<0.0001) had a significant effect on the ORP value. The anode/cathode voltage difference of 0 V had no effect on the ORP value during treatment (P>0.1084). In this case, a voltage difference was not supplied by the electric power supply, but due to the presence of the emulsion and the electrolysis material, a small voltage difference was present. As expected, the voltage difference of 0 V did not decrease the ORP value, and this value was constant throughout the electroreduction treatment. On the contrary, the electroreduction treatment using the 4 V anode/cathode voltage difference performed on milk samples resulted in a significant exponential decrease of the ORP value as can be seen in Fig. 1. The general trend was that the redox potential decreased significantly in the first minutes of the treatment, to then stabilize at a constant value corresponding to a plateau. It was possible to decrease the ORP value to −412 mV after 60 min of treatment. Generally speaking, raw milk has an ORP between +200 and +300 mV under aerobic conditions (Morris 2000), while recently Bolduc et al. (2006) observed an average value of +182 mV for pasteurized skim milk. However, ORP values for the oil/water emulsion of canola oil and skim milk were not found in the literature. In this experiment, the mean initial ORP value for the oil/water emulsion used was +85±12 mV.

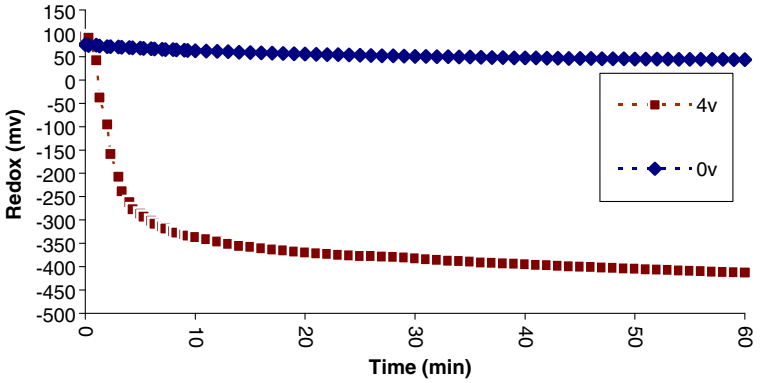

Fig. 1 Changes in the redox potential during treatment of oil/skim milk emulsions at 4 and 0 V

It appeared that the anode/cathode voltage difference ($P<0.0023$) and the dual interaction time/voltage difference ($P<0.0001$) had a significant effect on the evolution of the dissolved oxygen during the electroreduction treatment applying the voltage difference of 4 V (Fig. 2). The DO concentration was brought down from an averaged initial value of 3.8 to 2.5 mg.L^{-1} during the course of the electroreduction treatment at 4 V. Although the DO increased in the first few seconds, a decrease was seen in the DO value of the emulsion treated at 4 V while the DO concentration at 0 V remained stable throughout the treatment.

The repeated measure analysis of variance of the data showed that the anode/cathode voltage difference did not have a significant effect on the pH evolution during electroreduction treatment ($P>0.1084$). The mean initial pH value of the oil/milk emulsion in this study was 6.64. When milk was treated at 4 V, the pH decreased of 0.02 pH unit to reach 6.62 while the pH of the emulsion treated at 0 V remained constant throughout the treatment.

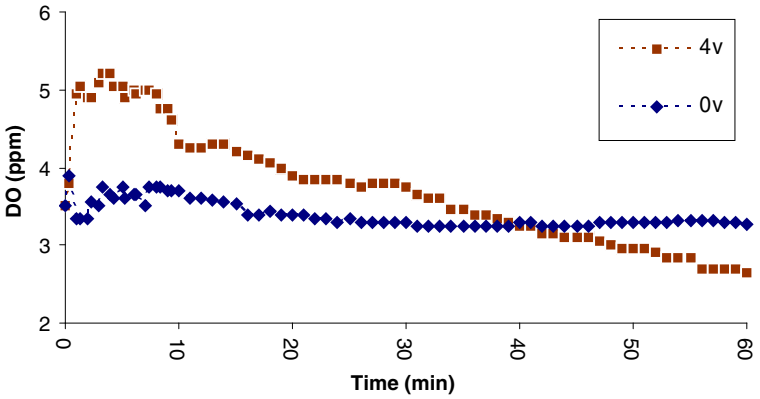

Fig. 2 Changes in the dissolved oxygen (*DO*) concentration during treatment of oil/skim milk emulsions at 4 and 0 V

There was not a significant difference between the changes of conductivity in all treatments ($P>0.2058$). The mean initial value of conductivity of the pasteurized milk used in this study was 4,493 $\mu S.cm^{-1}$ which remained constant throughout the 60 min of treatments at 4 and 0 V.

3.2 Storage of electroreduced oil/milk emulsion

According to the repeated measure analysis of variance, there was a significant effect of anode/cathode voltage difference ($P<0.0001$) and of the double interaction time/voltage ($P<0.0001$) on the ORP evolution during storage of electroreduced samples. The nonelectroreduced control samples and the electroreduced samples at 0 V presented the same evolution of ORP during the storage of 14 days. After an increase in the first day of storage in all conditions, their ORP values remained fairly constant throughout the storage period (Fig. 3b, c). Samples that were treated at 0 V maintained a positive ORP value, with a starting value similar to the values of control samples.

Electroreduced samples at 4 V had initial negative values and although a linear increase was seen for the samples with 10% and 50% at 4 °C and 20 °C: All samples maintained their negative values throughout the 14-day storage period (Fig. 3a). In the case of electroreduced samples at 4 V, the storage factor of headspace of the sample jars had a significant effect on the redox value after 14 days of storage. As shown on Fig. 3a, samples with more amount of headspace had a higher redox value compared to samples with less headspace in their sample jars. Furthermore, samples with 50% headspace had higher redox than samples with 10% headspace, and samples with no headspace had the lowest redox values throughout the storage period. On the contrary, the storage factor of temperature did not seem to have a significant effect on the redox value of the electroreduced samples. As shown in Fig. 3a, the samples with the similar headspace had similar redox values whether they were placed at 20 °C or 4 °C throughout the 14-day storage. In the case of electroreduced samples at 0 V and control samples (Fig. 3b, c), the storage factor of temperature had an important effect on the redox value during the storage period whereas samples stored in the same temperature had similar redox values. Also it was seen that samples stored in 20 °C had higher redox values than the redox values of samples stored at 4 °C.

Figure 4 presents the changes in dissolved oxygen concentration in the electroreduced samples at 4 V, samples electroreduced at 0 V, and control untreated samples during storage of 14 days. The repeated measure analysis of variance showed a significant effect of anode/cathode voltage difference ($P<0.0001$) and of time ($P<0.0001$) on the dissolved oxygen evolution during storage. In all cases, a decrease was observed at the end of the 14 days of storage which shows a consumption of the dissolved oxygen still present in the milk samples. Also, interactions of the storage factors of headspace and storage temperature seem to have an impact on the value of DO.

The anode/cathode voltage difference has no effect on the pH ($P>0.1063$) while time ($P<0.0001$) had a significant effect on the pH evolution during electroreduction treatment (Fig. 5). The mean initial pH value of the pasteurized milk used in this study was 6.63 which is in agreement with pH 6.6–6.8 reported in other articles (Amiot et al. 2002; White and Davies 1958).

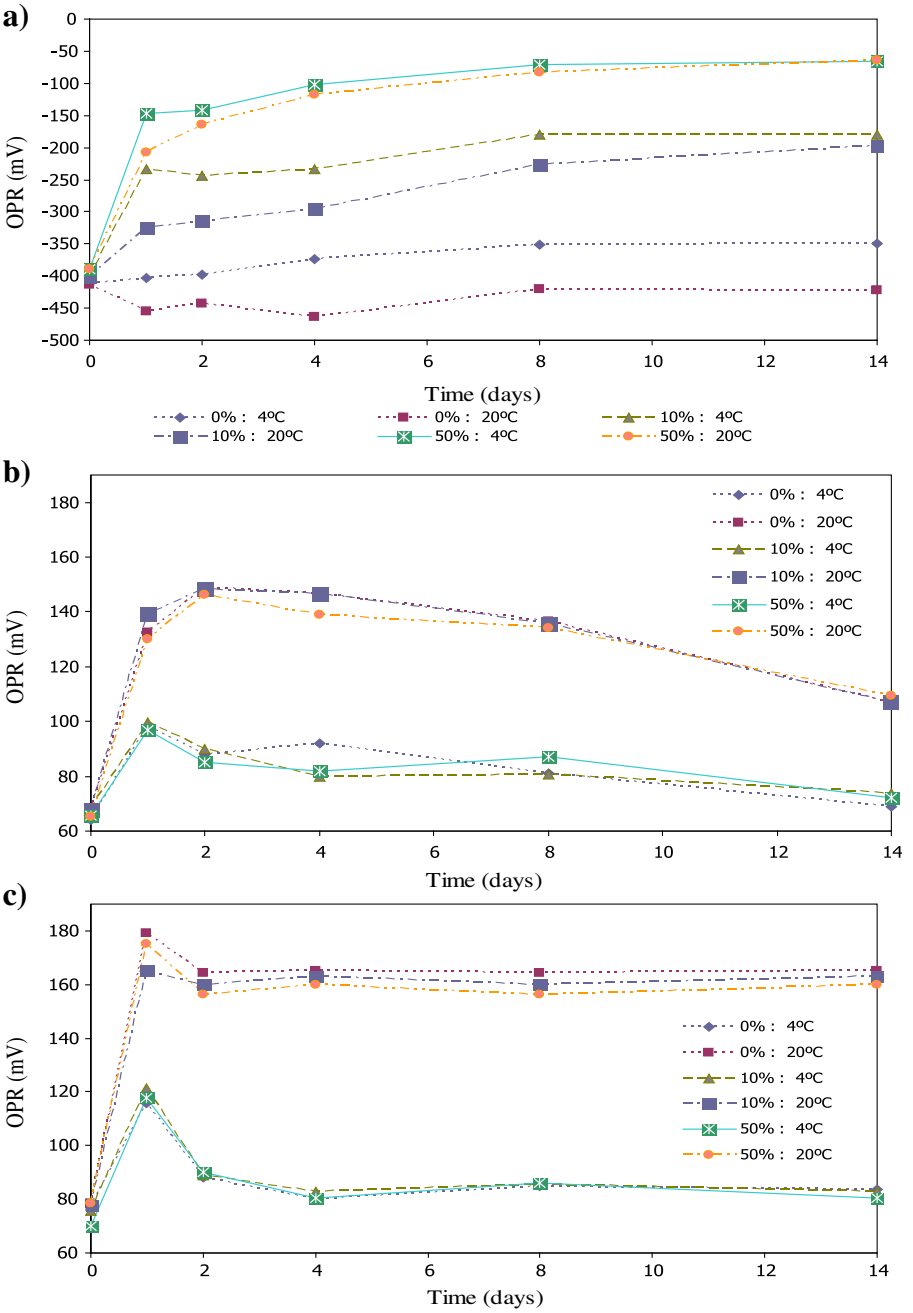

Fig. 3 Changes in the redox potential (*ORP*) value during storage of **a** electroreduced oil/skim milk emulsions at 4 V, **b** electroreduced oil/skim milk emulsions at 0 V, and **c** control oil/skim milk emulsions. Where 4 °C and 20 °C=temperature of storage; 0%, 10%, 50%=headspace of sample jars

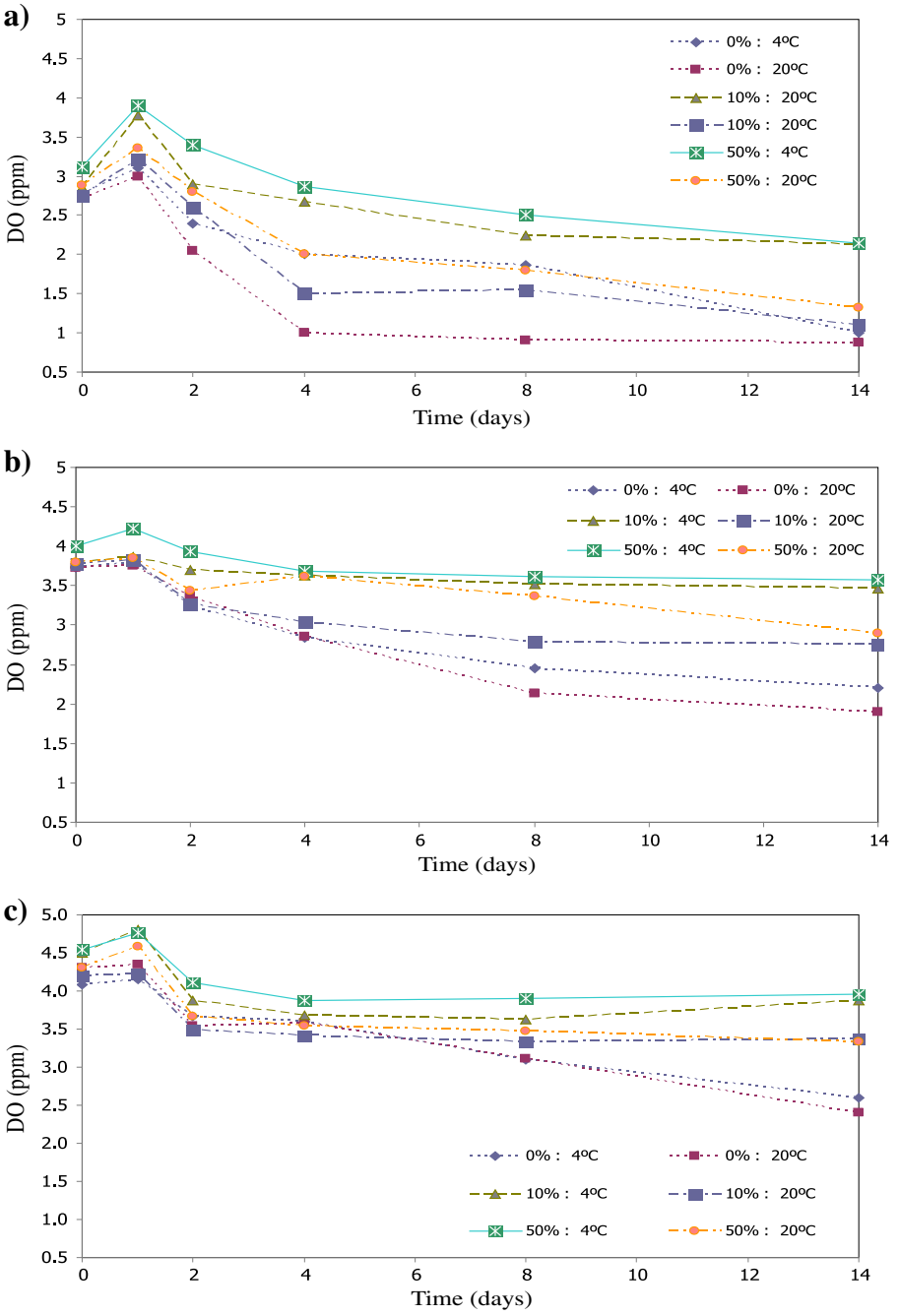

Fig. 4 Changes in the dissolved oxygen (*DO*) value during storage of **a** electroreduced oil/skim milk emulsions at 4 V, **b** electroreduced oil/skim milk emulsions at 0 V, and **c** control oil/skim milk emulsions. Where 4 °C and 20 °C=temperature of storage; 0%, 10%, 50%=headspace of sample jars

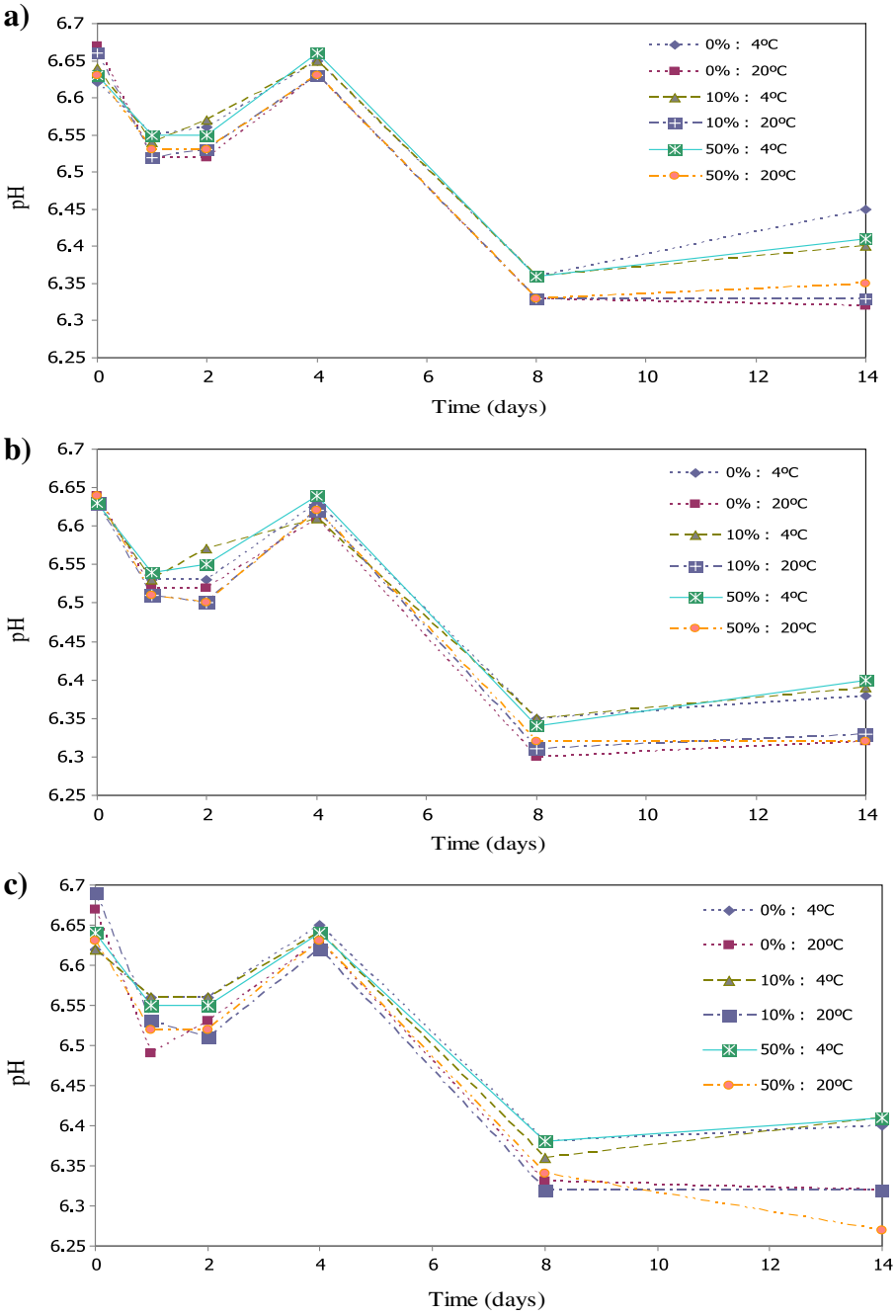

Fig. 5 Changes in pH during storage of **a** electroreduced oil/skim milk emulsions at 4 V, **b** electroreduced oil/skim milk emulsions at 0 V, and **c** control oil/skim milk emulsions. Where 4 °C and 20 °C= temperature of storage; 0%, 10%, 50%=headspace of sample jars

4 Discussion

4.1 Electroreduction treatment of oil/water emulsion

The electroreduction treatment reduced the redox potential quickly and decreased the dissolved oxygen concentration of the oil/water emulsion samples studied, without causing any major changes in their pH. This decline in the ORP can be explained by the fact that the operating principle of electroreduction is to generate the electrons needed to reduce electroactive species. This is emphasized by using a potential difference between the electrodes, which speeds up the transfer of electrons between electrodes (Tallec 1985). It appears from these results that the greater the anode/cathode voltage difference applied, the greater the number of electrons generated. As the anode/cathode voltage difference increases, electrons are transferred more rapidly from the cathode to the reducible species of milk. As a result, reduction reactions are taking place at a faster rate, which cause a faster decrease of the ORP value (Bolduc et al. 2006).

The increase of the DO concentration observed for 4 V treated samples may be due to the air that has remained in the tubes of the electrolysis cell. When the emulsion circulates through the cell compartments via the tubes, it may be exposed to the remaining air, and therefore, an increase of the oxygen concentration of the emulsion can be caused. The decrease in the concentration of oxygen is directly related to the reduction reactions taking place at the cathode: $½O_2+2\ H^+ + 2e^- \rightarrow H_2O$ (Tallec 1985). Electrons are transferred from the electric circuit to the cathode and then to the emulsion alike milk in which they are accepted by active species, one of them being oxygen. The protons necessary to this reaction would be provided by sulfuric acid from the anodic compartment which migrates through the cationic membrane to the milk cathodic compartment. These migrated protons would be consumed by dissolved oxygen to form water or would simply be reduced in dihydrogen according to the following equations:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

(Tallec 1985).

The very slight decrease of pH at 4 V could be due the presence of protons in the cathode section which had migrated through the cationic membrane from the anode compartment. The same results were observed by Bolduc et al. (2006) which the pH decreased of 0.2 and 0.15 U for electroreduction treatment carried out at anode/cathode voltage difference of 2 and 4 V, respectively.

Pastushenko et al. (2000) showed that the ORP increases with the fat content of milk. Furthermore, Schreyer et al. (2008) showed that pasteurized whole milk (3.25% fat) exhibits post-electroreduction variations in ORP that are lower than those for pasteurized skim milk and that the kinetics of ORP decrease for a given treatment were lower in the presence of milk fat. According to these authors, milk fat content has a significant effect on the decline in the ORP during electroreduction. A possible explanation, proposed by Schreyer et al. (2008) for this phenomena, is that the presence of fat on the surface of the stainless steel cathode would reduce the effectiveness of the process with regard to ORP and DO, since the quantity of

species reduced in contact with the cathode would be lower as would the formation of hydroxide, which impedes the migration of protons. In addition, the difference in ORP value for the canola oil/skim milk emulsion in the present study in comparison with the values for skim milk obtained by Bolduc et al. (2006) and Schreyer et al. (2008) was probably due to the type of lipids. The composition of canola oil and milk fat is completely different. All these results suggest that the electroreduction treatment did not change the electrolyte composition of the emulsion, and only the redox state of electroactive species present were changed.

4.2 Storage of electroreduced oil/milk emulsion

The increase in the ORP value of the different electroreduced milk products reflects the instability or reversibility of the changes in redox state of some milk species during electroreduction. The main electrochemically active species that determine the redox potential of milk are oxygen, ascorbate, and riboflavin, found in low concentrations in milk. However, exposed thiols and Maillard reaction conjugates produced by thermal process could affect the redox potential as well. According to Jacob (1970), dairy products profit from a capacity to buffering their ORP; it means that they are capable to counteract with any variation in their ORP.

Re-oxidation during storage may occur because the compounds that are electroreduced during electrolysis consume the dissolved oxygen still present in the milk. These results are consistent with those obtained by Bolduc et al. (2006) and Schreyer et al. (2008) for pasteurized 2% fat milk. In these previous studies, the ORP values of the electroreduced milk samples increased during storage to reach their initial value after less than 5 days of storage. Also, the milk samples were opened daily for taking measurements. The exposition to oxygen could be responsible in part for the increase in ORP values of these samples. In our study, glass jars were used instead of polypropylene jars and contained sodium azide as well as an anaerobic atmosphere was used until the last day of storage which allowed the elimination of the oxygen effect on the increase in ORP. In the absence of oxygen, the ORP of treated samples were stable during the 14 days of storage.

Samples electroreduced at 4 V maintained their negative redox values throughout the 14-day storage period, but a significant increase was seen at the end of storage period. The increase in the redox value may be due to the buffering capacity of dairy products which causes the changes in the redox state of the milk species during electroreduction (Jacob 1970). The rise in ORP during storage confirms the instability and reversibility of the electroactive species of milk which may be the result of the re-oxidation of electroreduced species of milk. The decline of DO during treatment is due to electroreduction of oxygen at the cathode. The decrease of the DO for all milk samples during storage shows the consumption of the dissolved oxygen concentration in the samples which can be a result of the oxidation of polyunsaturated fatty acids in milk and/or re-oxidation of electroreduced.

During storage, the storage factors of headspace and temperature showed an important impact on the ORP value as well as on the DO value of all samples whether electroreduced or not. The factor of headspace in the electroreduced samples at 4 V showed that when the amount of oxygen present is higher (headspace of 50%), the ORP

value reaches higher values more quickly than when the amount of oxygen present is lower (headspace of 10% and 0%). The dual effect of storage temperature and headspace had an important effect on the decrease in the DO value as well.

One reason that can cause the decrease of DO value of emulsion samples involves the autoxidation of unsaturated fatty acid which may consume the dissolved oxygen present in the sample jars. Autoxidation reactions which take place via free radical reactions may be initiated by hydroperoxide decomposition, metal catalysis such as iron or copper, and exposure to light and oxygen. Even though the concentration of lipids in skim milk is very low, the main fat molecules present in skim milk are phospholipids, which are very sensitive to the presence of oxygen. Also, in the emulsion prepared, canola oil was used, which approximately contains 32% poly unsaturated fats and approximately 61% monounsaturated fats which are unstable in reacting with oxygen and light. Another possible reason which causes the decrease of DO value may be due to the presence of the intrinsic microflora enzyme. Although sodium azide was used to eliminate bacteria in this study, the enzymes released during the destruction of microflora may have remained active, and they could have had a role in the consumption of remaining oxygen.

5 Conclusion

These results indicate that when electroreduced samples are kept in optimal storage conditions in regards to storage temperature and the absence of oxygen (or when oxygen is limited), the low values of ORP may be maintained for a longer period, up to 14 days. This matter may be helpful for preventing or controlling many of the unwanted oxidation–reduction reactions that take place in milk especially lipid oxidation reactions. The results of this study can be used in order to improve the quality of dairy products as well as the enhancement of the shelf-life of the dairy products, such as omega-3-enriched milks.

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