

# Modelling the temperature dependence of oxidation rate in water-in-oil emulsions stored at sub-zero temperatures

Sonia Calligaris <sup>\*</sup>, Lara Manzocco, Maria Cristina Nicoli

*Dipartimento di Scienze degli Alimenti, University of Udine, via Marangoni 97, 33100 Udine, Italy*

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## Abstract

The aim of the present research was to model the temperature dependence of lipid oxidation rate in water-in-oil emulsions stored at sub-zero temperatures. In fact, the application of the well-known Arrhenius equation resulted precluded in such conditions. To this purpose, the physical state and the oxidation rate of sunflower oil–water emulsions were evaluated from  $-30$  to  $60$  °C. Results indicate that the rate of oxidation could be considered as a resultant of a complex interplay between the physicochemical changes occurring in the hydrophilic and hydrophobic phases as a consequence of phase transitions. By taking into account the changes in oil viscosity and in the reactant concentration in both lipid and water phase it was possible to set up a mathematical model able to describe the temperature dependence of oxidation rate in multiphase systems in the entire range of temperatures considered.

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## 1. Introduction

A number of literature studies show that the kinetics of oxidative reactions in bulk and in emulsified lipids greatly differ. In multiphase systems, oxidative reactions are an interfacial phenomenon, which are affected by a wide number of different factors, such as the chemical composition and the physicochemical properties of the oil and water phases, the types of surfactants and the surface area of the oil phase (Coupland & McClements, 1996; Frankel, 1998; Frankel, Huang, Kanner, & German, 1994; Mancuso, McClements, & Decker, 1999; Mei, McClements, Wu, & Decker, 1998; Nuchi, Hernandez, McClements, & Decker, 2002; Silvestre, Chaiyasit, Brannan, McClements, & Decker, 2000).

“Interfacial” oxidation is of a great concern to the food industry because it affects the stability of a large number of foods which exist as emulsions (mayonnaise, margarine,

butter, cream, sauce, cheese, ice cream, baby foods, etc.). In these foods, depending on their composition and storage temperature, lipid can exist, in the liquid phase, the solid phase, or in different solid/liquid ratios. In addition, at storage temperatures below zero, the crystallisation of water can occur besides that of lipids. Thus, the matrix could simultaneously contain ice, unfrozen water, lipid crystals and liquid oil.

Oxidative reactions proceed in food emulsions stored at sub-zero temperatures and are the primary cause of quality loss in frozen foods (Fu & Labuza, 1997). Although kinetic data of lipid oxidation below zero are essential for predicting the stability of frozen foods, at the moment they are lacking and/or are hard to decode. As shown by Eriksson (1997), the development of lipid oxidation at sub-zero temperatures is faster than one would expect due to temperature alone. Similar results were described by Singh and Wang (1977) regarding the oxidation of ascorbic acid. The reasons for this could be found in the chemical and physicochemical changes occurring in food, as a consequence of phase transitions.

<sup>\*</sup> Corresponding author. Tel.: +39 0432 590711; fax: +39 0432 590719.  
E-mail address: [sonia.calligaris@uniud.it](mailto:sonia.calligaris@uniud.it) (S. Calligaris).

Regarding water crystallisation, the latter is expected to cause a cascade of temperature-dependent events, such as change in solute concentration, changes in physicochemical properties (i.e., reactant solubility, pH, ionic strength, water activity, residual volume of concentrated phase, viscosity) and protein denaturation, affecting the kinetics of chemical reactions (Champion, Blond, & Simatos, 1997; Fennema, 1996; Parker & Ring, 1995). Moreover, the phase transitions of lipids, and the eventual transition from one crystal to another, may modify the oxidation kinetics (Calligaris, Manzocco, Conte, & Nicoli, 2004; Cervato, Viani, Masserini, Di Iorio, & Cestaio, 1988; Kristott, 2000; McLean & Hagaman, 1992). In particular, Calligaris et al. (2004) found that the occurrence of oil crystallisation causes a positive deviation from the Arrhenius equation. The changes in viscosity and unsaturated triacylglycerols (TAGs) concentration in the oil liquid phase surrounding fat crystals were indicated as the most critical parameters able to affect the kinetics of lipid oxidation in the partially crystallised lipid matrix. This hypothesis was supported by the development of a modified Arrhenius equation able to describe the kinetics of hexanal formation from  $-30$  to  $60$  °C. The mathematical model proposed considers viscosity and the reactant concentration in the liquid phase as additional variables beside temperature (Calligaris et al., 2004).

On the basis of these observations, it can be hypothesised that in emulsified systems stored below  $0$  °C the phase transitions of both water and lipid phase affect the development of oxidative reactions. Thus, the aim of this work was to evaluate the development of lipid oxidation in water-in-oil emulsions containing 80% (w/w) of oil during storage at different temperatures. The temperatures were selected in order to have samples in which both oil and water were present in different physical states. To this purpose, emulsions were stored at increasing temperature from  $-30$  to  $60$  °C. To evaluate the role and the importance of the presence of water, results were compared to those previously published on sunflower oil (Calligaris et al., 2004).

## 2. Materials and methods

### 2.1. Materials

Sunflower oil, purchased in a local market, was used. Amounts of 80 (w/w) and 0.5% w/w Tween 20 (Carlo Erba, Milano, Italy) were emulsified with distilled water by using a Polytron homogeniser (Polytron PT 3000, Kinematica, Littau, Germany). Speed setting was at 3000 rpm for 5 min. Emulsification did not induce oxidation in freshly prepared emulsions.

### 2.2. Oxidative stability

Aliquots of 3 g of sample were inserted in 10 ml capacity vials, sealed with butyl septa and metallic caps. Samples were then stored in darkness in a freezer (Freezer MF

120, Electrolux, Pordenone, Italy) at  $-30$ ,  $-18$ ,  $-7$  °C ( $\pm 1$  °C), in a refrigerator (MF1500/2EF, Perani, Milan, Italy) at  $5$  °C ( $\pm 1$  °C) and in an oven (Salvis Thermocenter, Oakton, Vernon Hills, IL, USA) at  $25$  and  $60$  °C ( $\pm 1$  °C) for up to 15 months. Oxidation was periodically evaluated by analysing samples for peroxide value (PV) and hexanal by headspace GC.

The addition of Tween 20 (0.5% w/w) alone to oil was found not to influence the oxidation kinetics.

### 2.3. Analytical determination

#### 2.3.1. Calorimetric analysis

Calorimetric analysis were made using a TA4000 differential scanning calorimeter (DSC) (Mettler-Toledo, Greifensee, Switzerland) connected to a GraphWare software TAT72.2/5 (Mettler-Toledo, Greifensee, Switzerland). Heat flow calibration was achieved using indium (heat of fusion 28.45 J/g). Temperature calibration was carried out using hexane (m.p.  $-93.5$  °C), water (m.p.  $0.0$  °C) and indium (m.p.  $156.6$  °C). Samples were prepared by carefully weighing 10–15  $\mu$ g of the material in 20  $\mu$ L aluminium DSC pans, closed without hermetic sealing. An empty pan was used as a reference. Samples were heated under nitrogen flow (10 ml/min) at  $40$  °C for 15 min, cooled to  $-80$  °C and then heated from  $-80$  to  $20$  °C after annealing at  $-30$  °C for 30 min. The start and the end of melting transition were taken as on-set ( $T_{on}$ ) and off-set ( $T_{off}$ ) points of transition, which are the points at which the extrapolated baseline intersects the extrapolated slope in the transition state. Total peak enthalpy were obtained by integration. DSC thermograms were converted into ASCII format for trace deconvolution, according to the methodology described by Riva and Schiraldi (1993).

By integration of the melting curve it was possible to calculate the liquid fraction (LF), defined as the liquid mass (g) per 100 g of oil. The LF calculation is based on the assumption that at  $-80$  °C the lipid mass, after annealing, is totally crystallised (LF = 0).

#### 2.3.2. Peroxide value

The peroxide values of oil samples were determined according to AOAC (1993).

#### 2.3.3. Measurement of hexanal by static headspace GC

Hexanal concentration was measured by static headspace GC, following the methodology described by Elizalde, Dalla Rosa, and Lericci (1991). A Mega 2 Series gas chromatograph (Fisons Instruments, Milan, Italy) equipped with a headspace sampler (Carlo Erba HS 250, Carlo Erba 17 Strumentazioni, Milan, Italy) and a thermal conductivity detector (Fisons HWD Control, Fisons Instruments, Milan, Italy) was used. Hexanal was separated isothermally at  $80$  °C on a glass column ( $2\text{ m} \times 2\text{ mm}$ ) packed with 6.6% Carbowax 20 M on Carbopack B 60–80 mesh. The GC conditions were as follows: sample temperature,  $35$  °C; injector and detector temperature,  $180$  °C;

nitrogen flow rate, 35 ml/min. Before analysis, samples were stored at 35 °C for 10 min in a temperature control bath to reach equilibrium conditions. The chromatograms were integrated using Chromcard (ver. 1.18, 1996, CE Instrument, Milan, Italy) chromatography data system software.

#### 2.4. Kinetic data analysis

Apparent zero order rate constants of peroxide ( $k_{PV}$ ) and hexanal ( $k_{hexanal}$ ) formation were calculated by linear regression of at least six points from the initial part of the curves, excluding the lag phase when present. The effect of temperature on the rate of lipid oxidation was evaluated by means of the Arrhenius equation:

$$\ln k = -\frac{E_a}{RT} + \ln k_0, \quad (1)$$

where  $k$  is the reaction rate constant;  $R$  is the molar gas constant (8.31 J/K/mol),  $T$  is the absolute temperature (K);  $E_a$  is the activation energy (J/mol) and  $k_0$  is the pre-exponential factor of frequency. Apparent activation energy and frequency factor were determined, respectively, from the slope and intercept of the line generated by regression of  $\ln k$  vs.  $T^{-1}$ .

#### 2.5. Oxygen solubility data

Due to the lack of literature data on oxygen concentration at frozen temperatures, oxygen solubility in water below zero was calculated by using the following equation:

$$\ln X = A + \frac{B}{T^*} + C \ln T^*, \quad (2)$$

where  $X$  is the molar fraction of oxygen in water,  $T^*$  is the temperature in Kelvin multiplied by  $10^{-2}$ ;  $A$ ,  $B$ ,  $C$  are equation constants which are  $-66.7354$ ,  $87.4755$  and  $24.4526$ , respectively (from International Union of Pure and Applied Chemistry “Solubility Data Series”, Gevantman, 2002).

#### 2.6. Data analysis

The results reported here are the average of at least three measurements and the relative standard deviation (RSD%), expressed as the percentage ratio between the standard deviations (SD) and the mean values, were lower than 6 for the enthalpy data, 7 for the peroxide values, 8 for hexanal formation, 5 for viscosity. Oxidation kinetics were performed in duplicate and the difference between two determinations carried out on the sample did not exceed 5%.

Least squares linear regression analysis were performed by using Statistica for Windows (ver. 4.5, 1993, Stat Soft Inc., Tulsa, USA).

### 3. Results and discussion

The crystallisation and melting curves of the water-in-oil emulsion containing 80% (w/w) of sunflower oil are shown

in Fig. 1. Data for sample melting were collected after annealing at  $-30$  °C to reach equilibrium conditions and the formation of the most stable polymorphic form of TAG crystals of sunflower oil (Calligaris et al., 2004). Both cooling and heating curves showed the presence of two distinct peaks, which can be associated with the phase transition of oil (peak 1) and water (peak 2). In fact, comparing peak 1 melting data with those of Calligaris et al. (2004) on bulk sunflower oil, the peaks can be overlaid as the on-set temperatures were similar ( $-30 \pm 1$  °C). The presence of water did not seem to influence the melting behaviour of sunflower oil. It can be inferred that, at a particular temperature, the physical state of oil is the same, whether it is contained in an emulsion or not. In addition, it is interesting to note that the water contained in the emulsion could not completely crystallise, as indicated by the peak 2 melting enthalpy, which was  $60.7 \pm 0.6$  J/g. Thus, about 8.9% of water remained as unfreezable water.

From melting data shown in Fig. 1, the liquid fraction ( $LF_{oil}$ ) of oil and the unfreezable water ( $LF_{water}$ ) present into the emulsion at equilibrium conditions were calculated (Table 1). Sunflower oil was liquid above 0 °C, a solid below  $-30$  °C and a semisolid matrix between these temperatures.

To evaluate the role of the food matrix's physical state on the oxidation kinetics, samples were stored at temperatures ranging from  $-30$  to 60 °C. Fig. 2 shows the changes

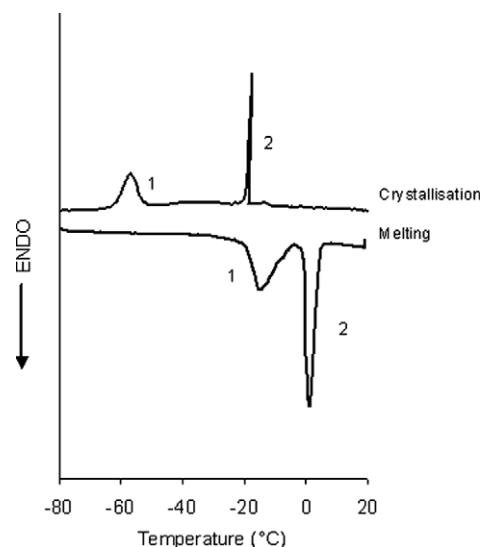


Fig. 1. Cooling and melting thermograms of water-in-sunflower oil emulsion.

Table 1

Oil liquid fraction ( $LF_{oil}$ ) and the unfreezable water ( $LF_{water}$ ) present in a sunflower oil water emulsion, as a function of temperature

Temperature (°C)	$LF_{oil}$	$LF_{water}$
-30	0.001	0.089
-18	0.050	0.089
-7	0.725	0.089
-5	0.990	0.089
0	1.000	1.000

in peroxide value (PV) of the emulsions as a function of storage time at  $-30$ ,  $-18$ ,  $-7$ ,  $5$ ,  $25$  and  $60$  °C. Although of different magnitude, the typical bell-shaped curves of PV changes were observed at the different temperatures. This indicates that oxidative reactions also proceed at low temperatures, where phase transition of both sunflower oil and water occurs. Apparent zero order rate constants of peroxide formation ( $k_{PV}$ ) were calculated from the increasing part of the curves by linear regression analysis ( $R^2 > 0.95$ ,  $P < 0.05$ ). In Fig. 3 the rate constants are presented in an Arrhenius plot. It can be observed that data referring to  $-30$  °C seems to be an outlier. In fact, the regression analysis performed between  $-18$  and  $60$  °C allows the description of experimental data with a higher precision than that obtained by fitting the data across the entire temperature range (Table 2).

Although the phase transition of both water and oil takes place at sub-zero temperatures, results clearly indicate that, from  $0$  to  $-18$  °C, the influence of the physical state of the food components on peroxide formation rate seems to be negligible. It is likely that oxygen, by virtue of its small molecular weight, can freely diffuse and react even in a partially crystallized matrix. It is interesting to note that, in this temperature range, the Arrhenius equation obtained was not significant by different from that of bulk sunflower oil (Calligaris et al., 2004).

On the other hand, the deviation observed at  $-30$  °C suggests that under such conditions factors other than temperature affect PV. Since PV changes result from a balance between the hydroperoxides produced and those that decomposed during propagation and termination steps of oxidation reactions (Frankel, 1980, 1991; Labuza, Tsuyuki, & Karel, 1969), secondary oxidation product formation was evaluated to better understand the deviation from the Arrhenius equation observed.

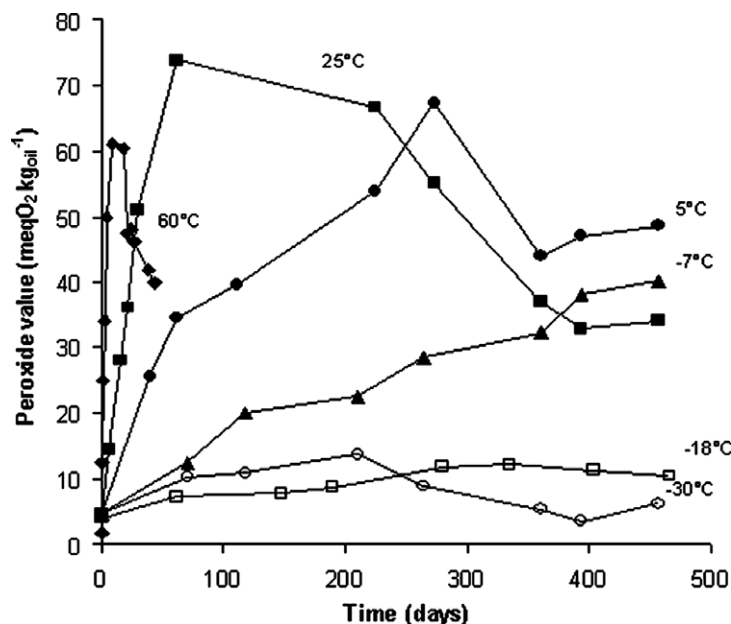


Fig. 2. Peroxide value of water-in-sunflower oil emulsion during storage at different temperatures.

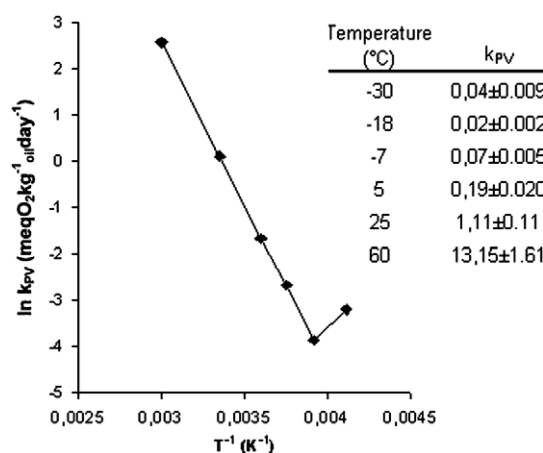


Fig. 3. Apparent zero order rate constants of peroxide formation as a function of temperature $^{-1}$ . Inset:  $k_{PV}$  data as a function of temperature.

Table 2  
Regression analysis of  $k_{PV}$  data, according to the Arrhenius equation

Temperature range (°C)	Slope	SD	$R^2$	$P$	SS <sup>a</sup> of residuals
-30/60	-5781.0	813.0	0.92	0.002	2.43
-18/60	-6990.4	78.0	0.99	$< 10^{-4}$	0.33

<sup>a</sup> SS = sum of square.

The zero order rate constants obtained by linear regression analysis of hexanal formation ( $k_{\text{hexanal}}$ ,  $r^2 > 0.90$ ,  $P < 0.05$ ), excluding the lag phase if present, are presented in Fig. 4 in an Arrhenius plot. Results of the linear regression analysis are also shown. Although the latter appear statistically significant, a deviation from the Arrhenius equation seems to occur below with. Similar results were  $0$  °C obtained for bulk oil (Calligaris et al., 2004). As shown in the introduction, in such case a modified Arrhe-

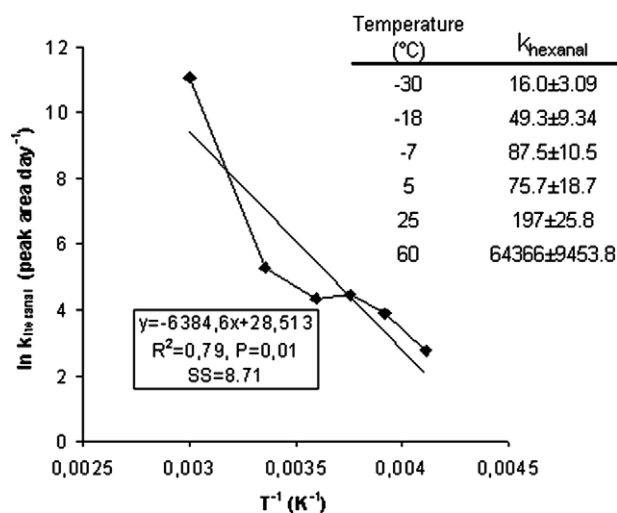


Fig. 4. Apparent zero order rate constants of hexanal formation as a function of temperature<sup>-1</sup>. Inset:  $k_{\text{hexanal}}$  data as a function of temperature.

nus equation, accounting for both temperature and physical state changes, was proposed to describe the kinetics of oxidation of bulk oil:

$$\ln(k_{\text{hexanal}}) = -\frac{E_a}{RT} + \ln k_0 + \Delta k, \quad (3)$$

where  $k_{\text{hexanal}}$  is the rate of hexanal formation,  $R$  is the molar gas constant (8.31 J/K/mol),  $T$  is the absolute temperature (K),  $E_a$  is the activation energy (J/mol),  $k_0$  is the pre-exponential factor and  $\Delta k$  is a correction factor which takes into account factors, other than temperature, which affect the reaction rate below zero. In the case of bulk oil,  $\Delta k$  was defined as the reciprocal of the product between  $LF_{\text{oil}}$  and viscosity of oil, which were indicated as the main factors involved in the Arrhenius deviation.

In order to evaluate the main factors involved in the Arrhenius deviations observed for  $k_{\text{PV}}$  in the emulsified system, data referring to emulsions were analysed according to Eq. (3). The application of this model appears to be feasible due to the fact that the physical state of the oil in the emulsion was comparable to that of the bulk oil (Fig. 1). The statistical parameters obtained from the regression analysis are shown in Table 3. The regression analysis of the new dependent variable ( $k_{\text{PV}} \cdot FL_{\text{oil}} \cdot \eta$ ), as a function of the reciprocal of temperature, presents a less precise estimation than the Arrhenius equation (Table 2). It was confirmed that the oil physical state does not influence the kinetics of primary oxidation product formation. Since the main driving force involved in peroxide formation is the oxygen availability, the presence of water could influence the oxidation, by favouring the access of oxygen to

Table 3  
Regression analysis of  $k_{\text{PV}}$  using Eqs. (3) and (4)

Dependent variable	Slope	SD	$R^2$	$P$	SS <sup>a</sup> of residuals
$k_{\text{PV}} \cdot FL_{\text{oil}} \cdot \eta$	-9077.8	1175.5	0.94	0.001	4.42
$k_{\text{PV}} \cdot O_2$	-7480.2	716.6	0.96	<10 <sup>-4</sup>	1.65

<sup>a</sup> SS = sum of square.

the lipid surface. For this reason, the correction factor,  $\Delta k$ , in Eq. (3) was considered to be related to the increase in oxygen concentration as temperature decreases. In particular, it was defined as the ratio between the concentration of oxygen at the selected temperature and at 60 °C ( $O_2$ ). Data referring to the oxygen concentration (M) in pure water calculated by using Eq. (2) at the temperature of interest were reported in Table 4. Since oxygen solubility data below zero were estimated from those measured at higher temperature, the results presented are open to some uncertainties but suggest the role of oxygen on the  $k_{\text{PV}}$  deviation from the Arrhenius equation. On the basis of these considerations, Eq. (3) was modified as follows:

$$\ln(k_{\text{PV}}) = -\frac{E_a}{RT} + \ln k_0 + \ln O_2. \quad (4)$$

The regression results generated considering the oxygen concentration are presented in Table 3. It is evident that the new model allows a reduction in the difference between the experimental and predicted value more than Eq. (3) and the Arrhenius equation itself. This suggests that, as temperature decreases, the role of oxygen concentration becomes critical.

Results obtained by using Eq. (3) on hexanal data allow a better description of the temperature dependence of secondary oxidation products formation compared to the standard Arrhenius equation (Table 5). Thus, the physical state of oil seems to influence the reaction kinetics. Nevertheless, it is likely that water also affects the reaction rate. Hexanal is formed from the decomposition of hydroperoxides. The latter, by virtue of their polarity being higher than the lipids from which they are formed, would be able to migrate to the surface of the emulsion droplets (Nuchi et al., 2002; Silvestre et al., 2000). In these conditions, as indicated by Silvestre et al. (2000), they could interact with the aqueous phase oxidation catalysts, such as transition metals, increasing the oxidation rate. In fact, even if at low concentrations, metal contaminants are always present in water (Dunford, 1987). Below 0 °C, the concentration of

Table 4  
Concentration of oxygen in pure water at different temperatures, obtained by using Eq. (2)

Temperature (°C)	Oxygen concentration (M)
-30	0.0062
-18	0.0038
-7	0.0026
5	0.0019
25	0.0015
60	0.0009

Table 5  
Regression analysis of  $k_{\text{hexanal}}$  using Eqs. (3) and (6)

Dependent variable	Slope	SD	$R^2$	$P$	SS <sup>a</sup> of residuals
$k_{\text{hexanal}} \cdot FL \cdot \eta$	-9697.1	1499.3	0.91	0.002	7.23
$k_{\text{hexanal}} \cdot FL_{\text{oil}} \cdot \eta \cdot FL_{\text{water}}$	-12460.4	1167.3	0.97	<10 <sup>-4</sup>	4.38

<sup>a</sup> SS = sum of square.

hydroperoxides as well as of other oxidants is likely to increase, as a consequence of ice separation. Thus, the increase in reactant concentration could accelerate chemical reactions occurring in the aqueous phase or at the interface between the two phases. For this reason, the concentration of reactants in the aqueous phase was considered as an additional driving force to hexanal formation.

Since the local concentration of reactants can be readily related to the reciprocal of the percentage of unfreezable water ( $LF_{\text{water}}$ ), which was previously calculated by calorimetric analysis (Table 1), the  $\Delta k$  proposed for hexanal was

$$\Delta k = \frac{1}{LF_{\text{oil}} \cdot \eta \cdot LF_{\text{water}}} \quad (5)$$

and consequently Eq. (3) became

$$\ln(k_{\text{hexanal}}) = \frac{E_a}{RT} + \ln k_0 - \ln LF_{\text{oil}} - \ln \eta - \ln LF_{\text{water}}. \quad (6)$$

The regression results for the new dependent variable ( $\ln k_{\text{hex}} \cdot LF_{\text{oil}} \cdot \eta \cdot LF_{\text{water}}$ ), generated to take into account the effect of temperature, reactant concentration in the hydrophilic and hydrophobic phase and the oil viscosity, are reported in Table 5. The good quality of the statistical parameters confirms that the physical state of both water and lipid phase greatly affect the formation of secondary oxidation products at sub-zero temperature. In other words, the overall reaction rate in the water-in-oil emulsions can be considered as the resultant of the direct effect of temperature and some other physicochemical changes occurring in the system, as a consequence of phase transitions.

#### 4. Conclusions

Results obtained in this study emphasised that the physical state of the constituents of a frozen food could play an important role in determining its stability. In particular, the rate of oxidation could be considered as the resultant of a complex interplay between the physicochemical changes occurring in the different food phases as a consequence of phase transitions. In such conditions, the application of the well-known predictive Arrhenius model was insufficient. Only by taking into account the changes in oil viscosity and in the reactant concentration in both lipid and water phase was it possible to describe the temperature dependence of oxidation rate in multiphase systems. The developed equations appear promising in meeting the challenge to find out mathematical models able to predict the stability and, hence, the shelf-life of frozen foods, which is still a time-consuming and costly process.

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