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Effect of selected ions from lyotropic series on lipid oxidation rate

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Abstract

Organic or inorganic salts, commonly present in foods as natural components or ingredients, can affect the hydrophobic/hydrophilic interactions among food components. In particular, modifying the physicochemical equilibrium in the media, the ionic species forming salts could affect the kinetics of chemical reactions occurring in foods. The aim of the present research was to study the influence of different ionic species from lyotropic series on the kinetics of lipid oxidation. For this purpose, salts containing antichaotropic (carbonate and acetate), neutral (Na^+, K^+) and chaotropic ions (Cl^-) were added to soybean oil. Results indicate that potassium carbonate and potassium acetate present a strong antioxidant capacity, whereas no effect was detected for NaCl and KCl. The salt antioxidant activity was prevalently attributed to the antichaotropic anionic species present in the media, which could interact with hydroperoxides by virtue of their ability to form hydrogen bonds. These results appear to be of considerable interest for controlling the development of rancidity in foods.
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1. Introduction

Organic or inorganic salts are commonly present in foods as natural components, ingredients or additives. The latter are added to foods for a huge number of functional purposes. For instance, some of these act as flavouring, antimicrobial or pH control agents, and others as antioxidants and emulsifiers (Lindsay, 1996).

As is well known, in multi-component heterogeneous systems, such as food, salts can interact with other components, modifying the hydrophobic/hydrophilic interactions among molecules (Walstra, 2003). The specific effect of salt ionic species on the environment is often arranged in the so called lyotropic or Hofmeister series (Hofmeister, 1888). Previously, this series was established as solute series affecting the protein salting-in

and salting-out. Later, the same series was extended to the effect of ions in driving conformational transition of other biomolecules, namely lipids and DNA (Cacace, Landau, & Ramsden, 1997). The lyotropic series for some cations and anions of importance in food science are shown in Table 1.

According to Hofmeister's theory, the antichaotropic ions, by virtue of their ability to bind water, allow the formation of a "hydrophilic" structure around them which reduces their polar properties. Consequently, they do not favour the solubility of substances with low polarity and enhance hydrophobic bonding. On the contrary, the ions belonging to the chaotropic series are less hydrated, showing similar effects on water to low polar substances. By virtue of their ability to interact with apolar substances, chaotropic ions make these molecules more soluble in aqueous systems. It must be noted that the effect of anions and cations are roughly additive, although the anions seem to be dominant. In this context, sodium chloride (NaCl), the commonly used salt

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Table 1
Examples of chaotropic, antichaotropic and neutral ions (Hanstein, 1979; Franks, 1983)

Antichaotropic	Chaotropic	Neutral
SO_4^{2-}	Cl^-	K^+
HPO_4^{2-}	Br^-	Na^+
Acetate	I^-	Ba^{2+}
CO_3^{2-}	NO_3^-	Ca^{2+}
Citrate	NH_4^+	

in food production, can be considered neutral (Walstra, 2003).

Since chaotropic and antichaotropic ions could modify the physicochemical equilibrium in the media where they are dissolved, it is likely that they could also influence the development of chemical reactions occurring in foods. In particular, we would like to draw attention to the effect of ionic species on lipid–lipid interactions and, consequently, on the development of lipid oxidation, the most important deteriorative event occurring in lipid matrices.

The hypothesis that ionic species could affect the stability of lipids is supported by the fact that chaotropic ions are able to destabilize the lipid bilayer structure of cell membranes by reducing the energy required to expose the non-polar groups within the membrane to the environment (Cacace et al., 1997). The opposite effect is expected for antichaotropic ions. Therefore, one may speculate that ions could interact with lipids undergoing oxidation. Since the hydroperoxides are more polar than the lipids from which they originated (Nuchi, Hernandez, McClements, & Decker, 2002), ionic species may change hydroperoxide conformation, modifying oxidation kinetics.

Despite the importance of lipid oxidation affecting the shelf-life of foods, little is known about the effect of the presence of different ions on lipid oxidation rate. As expected, most studies deal with the effect of NaCl. However, literature data are very contradictory. In fact, while some authors have highlighted the pro-oxidant effect of NaCl (Matlock, Terrell, Savell, Rhee, & Dutson, 1984; King & Earl, 1988; Kanner, Harel, & Jaffe, 1991; Osinchak, Hultin, Zaijcek, Kellerher, & Huang, 1992), others evidenced its anti-oxidant capability (Lonyuan, McClements, & Decker, 1998). Finally, Okiy and Oke (1984) found that NaCl, added to palm oil as frying medium, does not affect the development of lipid oxidation.

On the basis of these observations, this study evaluates the effect of different ionic species on the kinetics of lipid oxidation. For this purpose, according to lyotropic series, antichaotropic ions (carbonate and acetate), neutral (Na^+ and K^+) and chaotropic ions (Cl^-) were selected. Experiments were carried out using soybean oil.

2. Materials and methods

2.1. Materials

Soybean oil was purchased at a local market. Sodium chloride, potassium carbonate, potassium acetate, potassium chloride, sodium acetate and acetic acid were from Carlo Erba (Milan, Italy).

2.2. Sample preparation

Aliquots of 10 g of oil, added at increasing percentages of different salts, were introduced into 100 ml screw-capped bottles and heated in a water bath (Dubnoff, mod. BE-SO, Bicasa, Milano) at 60 °C with stirring for up to 40 days. Salts showed low solubility in the oil. In fact, a precipitate was detected in the samples. Oxidation was periodically evaluated by analysing samples for peroxide value (PV) and hexanal by headspace GC.

2.3. Analytical determinations

2.3.1. Rancimat test

The Rancimat test was carried out according to the method described by Hasenhuettl and Wan (1992), using a model 679 Methrom Rancimat (Metrom, Herisau, Switzerland). Aliquots of 10 g of oil, treated with 10% (w/w) of salt, were put into reaction tubes and heated at 120 °C in a 20 l h^{-1} air flow. The air flow through the samples caused turbulence so that an intimate contact between oil and salt was achieved. An oil sample was tested as a reference. The oxidation curves obtained from the Rancimat test describe the resistance of oil to oxidation. Results are expressed as induction time to oxidation.

2.3.2. Peroxide value

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

2.3.3. Hexanal

Hexanal concentration was measured by static headspace GC, following the methodology described by Elizalde, Dalla Rosa, and Lerici (1991). A HGRC Mega 2 Series gas chromatograph (Fisons Instruments, Milan, Italy), equipped with a headspace sampler (Carlo Erba HS 250, Carlo Erba Strumentazioni, Milan, Italy), and a thermal conductivity detector (Fisons HWD Control, Fison Instruments, Milan, Italy) was used. Hexanal was separated isothermally at 80 °C on a glass column (2 m × 2 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 l min^{-1}. 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}) formation were calculated by linear regression of at least six points from the initial part of the curves, excluding the lag phase when present.

2.5. Data analysis

The results reported here are the averages 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 below 7 for peroxide value and 8 for hexanal formation. Oxidation kinetics were performed in duplicate and the difference between two determinations carried out on the sample did not exceed 5%.

One-way analysis of variance was carried out using the Tukey–Kramer test (JMP ver. 3.2.5, 1999, SAS Institute Inc., Cary, USA). Means were considered significantly different at $P < 0.05$.

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

3. Results and discussion

Fig. 1 shows the changes in PV of soybean oil treated with 10% (w/w) of potassium acetate and potassium car-

bonate during storage at 60 °C. Bulk oil was taken as control. It can be noted that the presence of the selected salts modified the evolution of the PV curve. In particular, both potassium acetate and potassium carbonate induced a significant decrease in the maximum of the the curve. As is well known, the PV changes result from a balance between the hydroperoxides produced and those decomposed during propagation and termination steps of oxidation reactions (Labuza, Tsuyuki, & Karel, 1969; Frankel, 1980; Frankel, 1991). Thus, both antioxidants and pro-oxidants could affect the shape of the peroxide curve (Frankel, 1993). While pro-oxidants can lower the PV curve by enhancing the rate of both hydroperoxide formation and decomposition, antioxidants can slow down the rate of hydroperoxide formation as well as inhibit their decomposition. Therefore, by only combining PV results with those of the formation of secondary oxidation products, it is possible to understand the main mechanism involved. Results obtained by analyzing the head space hexanal concentration clearly indicate that the considered salts had an antioxidant activity (Fig. 2). In fact, besides a reduction in the hexanal peak area at the end of storage, the addition of both salts caused an increase of the induction time of hexanal formation. It is interesting to note that the antioxidant capacity of potassium carbonate was also postulated by Xi, Yamaguchi, Sato, and Takeuchi (1998). These authors found that potassium carbonate may participate in the antioxidant activity of Stevia rebaudiana extracts against linoleic acid oxidation.

On the basis of these observations, the presence of potassium acetate and potassium carbonate significantly increased the oil stability, by reducing the development of both propagation and oxidation termination steps.
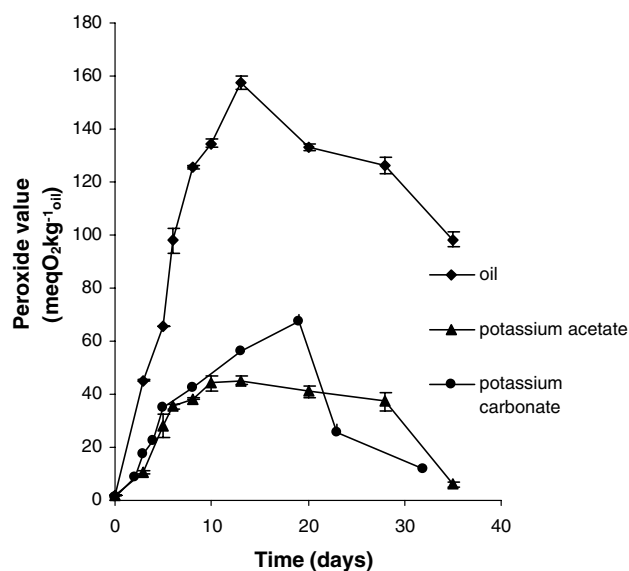

Fig. 1. Changes in peroxide value during storage at 60 °C of soybean oil treated with 10% (w/w) of potassium acetate or carbonate. Bulk oil was taken as control.
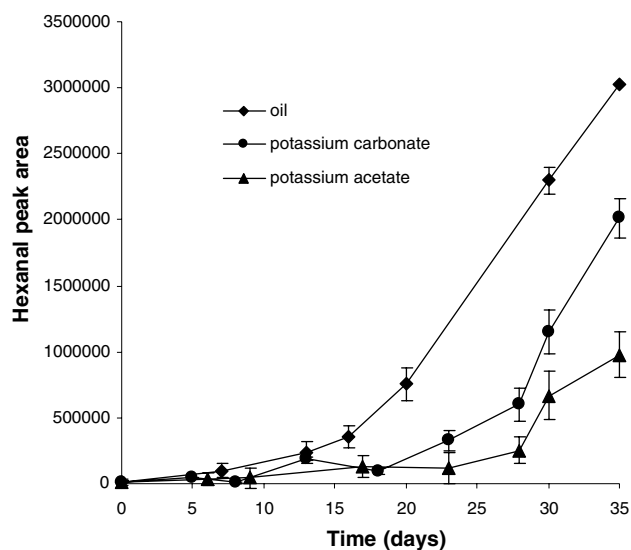

Fig. 2. Changes in hexanal peak area during storage at 60 °C of soybean oil treated with 10% (w/w) of potassium acetate or potassium carbonate. Bulk oil was taken as control.

However, from these results it is not clear whether the salt antioxidant activity could be attributed exclusively to the action of the single ions or to a complex interplay between the anion and the cation. To better understand the role of the single ions, soybean oil treated with 10% (w/w) of acetic acid, sodium acetate, potassium chloride or sodium chloride were considered. Table 2 shows the apparent zero order rate constants of peroxide formation (k_{PV}) and the induction time to hexanal formation (t_{hex}) of samples stored at 60 °C. These indices were calculated also for bulk oil and oil treated with potassium acetate or carbonate from data reported in Figs. 1 and 2. In addition, to verify the protective action of these salts against lipid oxidation, an accelerated oxidation test was performed by means of a Rancimat apparatus. The induction time to oxidation are also shown in Table 2. Due to the high volatility of acetic acid, a Rancimat test of oil added with this compound was not performed.

From Table 2, it is evident that the presence of sodium chloride or potassium chloride does not affect the development of oxidative reactions. In fact, the relevant indices of oxidation are of the same magnitude as that measured for the control sample. A further experiment carried out with oil treated with increasing percentages of NaCl (from 0% to 20% (w/w)) confirmed the above results (data not shown). Thus, it is likely that neither the neutral cations (Na^+ and K^+) nor the chaotropic anion Cl^- directly affect the antioxidant capacity.

On the other hand, all the other salts reduced the rate of peroxide formation. In particular, potassium acetate, potassium carbonate and acetic acid influenced the propagation step of oxidation in the same way, while sodium acetate seemed to be less active. The ability of acetic acid to inhibit the formation of hydroperoxides was also previously postulated by Hendry and Russel (1964). In particular, these authors found that the rate of peroxide formation during cyclohexene and cumene oxidation was slowed by the presence of acetic acid.

Different considerations could be drawn regarding the formation of secondary oxidation products. In fact, while potassium carbonate and acetate significantly increased the stability of oil, acetic acid and sodium acetate did not show any antioxidant activity. In other words, hydroperoxide decomposition seems to be favoured by the presence of acetic acid and sodium acetate, leading to a rancidity development comparable to that of bulk oil. These results seems to indicate that acetate ions are able to prevent oxidation reactions only in association with potassium ions. In particular, they could stabilize the hydroperoxides formed during the propagation step of oxidation, retarding their decomposition to acid. The modality of the action of K^+ and acetate is not easily understandable. It can be hypothesised that acetate, being an antichaotropic ion able to modulate the strength of hydrophobic/hydrophilic interactions between bio-molecules, may form weak bonds, such as hydrogen bonds, with oxidation products. The stabilising effect of compounds able to form hydrogen bonds with hydroperoxides was also previously assumed by other authors. In particular, Labuza et al. (1969) found that the presence of a low content of water in contact with the lipid matrices could inhibit oxidation by the formation of hydrogen bonds with hydroperoxides. Similar considerations were drawn by Cillard, Cillard, and Cormier (1980), who showed that the use of a polar solvent, such as ethanol, could reduce the rate of linoleic acid oxidation.

Since carbonate ions could also form hydrogen bonds with hydroperoxides, it can be hypothesised that potassium carbonate acts as antioxidant in the same way as potassium acetate.

Results obtained in this study clearly show that potassium carbonate and potassium acetate have strong antioxidant capacities. The latter could be prevalently attributed to the anion species present in the media. In fact, both anions could interact with hydroperoxides, by virtue of their ability to form hydrogen bonds, having a stabilizing effect on hydroperoxides and preventing their decomposition. Nevertheless, the molecular species associated with the anion played a critical role in enhancing or reducing the antioxidant capacity of the salt. In particular, potassium ions seems to be the more active cation species. These results appear to be of considerable interest as regards the control of the development

Table 2
Apparent zero order rate constants of peroxide formation (k_{PV}), induction time to hexanal formation (t_{hex}) and induction time in Rancimat test (t_{ranc}) of soybean oil treated with 10% (w/w) of potassium acetate, potassium carbonate, acetic acid, sodium acetate, potassium chloride or sodium chloride. Bulk oil was taken as control

Salt type	k_{PV}[A] (meq $O_{2\ att}$ kg^{-1}_{oil} day^{-1})	t_{hex} (days)	t_{ranc} (h)
Control	14.1 ± 1.15^a	14.5 ± 1.0^a	3.25 ± 0.42^a
Potassium acetate	4.52 ± 0.41^b	23.3 ± 1.5^b	11.4 ± 0.06^b
Potassium carbonate	3.51 ± 0.95^b	18.3 ± 0.9^c	7.67 ± 0.11^c
Acetic acid	3.40 ± 1.01^b	11.5 ± 1.1^a	–
Sodium acetate	7.12 ± 2.38^c	12.9 ± 1.2^a	3.32 ± 0.09^a
Sodium chloride	12.1 ± 1.00^a	13.5 ± 1.0^a	3.09 ± 0.11^a
Potassium chloride	11.5 ± 0.92^a	14.1 ± 1.5^a	3.40 ± 0.06^a

[a–c] Means with common letter are not significantly different ($p < 0.05$).
[A] $R^2 > 0.93$; $P < 0.05$.

of rancidity in foods. In fact, the selected salts are commonly present in foods as constituent ingredients or additives. Although further investigations are needed to highlight their mechanism of action, the use of these salts may be considered to be an interesting and unconventional antioxidant tool.

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