Estimation of the diffusivities of sodium chloride, potassium sorbate and sodium bisulphite in mango slices processed by hurdle technology

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1. Introduction

Mango (Mangifera indica L.) is one of the most important tropical fruits. This fruit is relished for its succulence, exotic flavor and delicious taste; moreover, mango is a rich source of carotenoids and provides high vitamin A content (Pott et al., 2003). According to FAO (2007), more than 26.5 millions of metric tons of mango were produced worldwide, with México as the fourth most important producer after India, China and Thailand, but being the major exporter country in the world, providing about 29.7% of the exportation volume. Most mangoes are consumed fresh, but some non fibrous pulpy mango varieties are used for processing. However, substantial quantities of mangoes are wasted because of poor post-harvest management and lack of appropriate facilities in developing countries. Therefore, development and application of inexpensive preservation techniques to produce high quality and acceptable products of mango could be valuable, allowing a better use of the fruit (Ulloa et al., 2008). Hurdle technology, characterized by an intelligent combination of some soft treatments, or hurdles (Leistner, 1995; Leistner and Gorris, 1995), has confirmed to be an economic and useful method in production of processed fruit. If the process conditions are appropriately selected, microbial quality and good appearance of the products during storage may surely be guaranteed (Alzamora et al., 1995; Tapia de Daza et al., 1996).

Solute diffusion phenomena through inside or outside of the processed material, plays an important role in a variety of unit operations of the food industry, such as dehydration (Daudin, 1983), osmotic treatments (Karel, 1976) and leaching processes (Schwartzberg and Chao, 1982). Due to its effects on quality characteristics, texture, flavor, color and microbial stability, the diffusion mechanism of certain additives has been researched for some foods (Rosselló et al., 1993; Lombardi and Zaritzky, 1997; Han and Floros, 2000; Souza-Filho et al., 2000; Sacchetti et al., 2001; Sereno et al., 2001; Franssen et al., 2004; Choi et al., 2005; Haros et al., 2005). The classical method of processing fruits by hurdle technology consists in taking the blanched fruit to a stage of water activity depression in a vessel containing syrup. This syrup is generally prepared using sucrose, citric acid (pH 3.0–4.1), potassium sorbate or sodium benzoate, and sodium bisulphite; the container with the fruit and syrup is then kept at room temperature for a period of 3–5 days. When concentration reaches a pseudo-equilibrium stage, fruit slices are drained and packed in glass jars, or high density polyethylene bags, with enough syrup to cover them up (Alzamora et al., 1993, 1995; Tapia de Daza et al., 1996). This minimum process is important not only because of its simplicity and energy efficiency, but also because it generates products with...
similar characteristics to the fresh ones, adding longer shelf life and high sensorial quality, and a particular texture which very often is difficult to achieve in canned fruits (Leistner, 1995). Unfortunately, the described process is expensive and high in time consumption, justifying research on canned fruit stabilization or auto-stabilization.

Until now most of the studies about hurdle technology have been focused on showing the effects of the impact of combine barriers on microbial control, as well as on some other physicochemical parameters related to the quality of fruits and vegetables (López-Malo et al., 1994; Jayaraman et al., 1999; Vijayanand et al., 2001) and other nutritional systems (Lombard et al., 2000; Karthikeyan et al., 2000; Guyon et al., 2005).

In order to characterize the fruit auto-stabilization process, it is essential to know the syrup components diffusivities in the fruit. Until now there are not many trustable results on diffusivity parameters of chemical barriers used in auto-stabilized processes of fruits by hurdle technology. There are studies on sucrose and salt diffusivities in fruits for osmotic dehydration throughout high concentration solutions (Panagiotou et al., 1998; Qi et al., 1999; Souza-Filho et al., 2000; Sacchetti et al., 2001; Sereno et al., 2001), but these high concentration system conditions are quite different from the ones used in the proposed technology. Similarly, citric acid, as well as sulfites, has been extensively studied in relation to their effect on controlling darkness and microbial inhibition in food systems (Rodríguez and Zaritzky, 1986; Castañer et al., 1996; Gunes and Lee, 1997; Weller et al., 1997; Haros et al., 2005); however, still there is not enough information about their diffusivities which allows reasonable explanation about their behavior in food processing, specially when the chemical barriers in syrups solutions diffuse through the fruit segments (Lombardi and Zaritzky, 1997). With respect to the potassium sorbate diffusivity, there are many studies to demonstrate the convenience of using eatable films as carriers of that antimicrobial (Redl et al., 1996; Han and Floros, 1998a, 2000; Ozdemir and Floros, 2001; Franssen et al., 2004; Choi et al., 2005), but still there is not information about potassium sorbate diffusivity in fruit processing, particularly in mango fruit segments.

The purpose of this investigation is to study a particular system commercially used, and obtaining the effective diffusivities of sodium chloride, potassium sorbate and sodium bisulphite, through modeling their diffusion kinetics, and learn about the syrup temperature influence in the auto-stabilization process of sliced mango by hurdle technology.

**2. Materials and methods**

**2.1. Mango slices preparation**

For this research, mango Kent variety samples from ‘Empacadora Libra’, located in Navarrete community of San Blas County, Nayarit, México, were used. The fruit penetration force was of 7.9 ± 1 N, using a Texture Analyzer (Model TA-XT2 from Texture Technologies, Corp., Scarsdale, NY, USA) as is recommended by Soliva-Fortuny et al. (2002), and they were immersed in a water bath (four parts of water by one of mango) at 90 °C for 10 min (this variety of mango resists the treatment without been seriously affected; fruit penetration force was reduced to 5.2 N after blanching). A group of 30 sterilized glass jars, each containing two slices of mango, was filled with 500 ml of syrup containing the chemical barriers. Each jar was sealed with a metallic lid, with a hole in the center, to allow sampling and monitoring concentration changes. The mango slices were totally immersed into the syrup by using an ‘M-shaped’ glass pipe and the system was stirred by using a Stirrer Hotplate (Diagger®) at 800 rpm; with a magnetic bar of 2.7 cm long and 0.8 cm in diameter. Fig. 1 shows a diagram of the experiment. Three different temperatures (25 °C, 50 °C and 70 °C) were used to study effective diffusivity. Syrup formulation was prepared according to procedure reported in Ulloa et al. (2004): 250 g sucrose, 1.5 g sodium chloride, 0.5 g potassium sorbate and 0.25 g sodium bisulphite, filling with sterilized water – adjusting pH at 3.6 using citric acid to complete a kilogram of syrup.

**2.2. Analysis of the chemical barriers**

Sodium bisulphite and potassium sorbate concentrations in syrup samples were obtained by high-performance liquid chromatography (HPLC, Perkin Elmer, Wellesley, Mass, USA). Operation of chromatographic system was isocratic and samples of 10 μl were used and processed before injection with 0.45 μm pore size filters (A. Daigger and Company, Vernon Hills, IL, USA). Sodium bisulphite analysis was done by using 100 × 87 mm column Phenomenex
Rezet fast Fruit 8% H (Phenomenex, Terrance, Ca, USA), according to the method described in McFeeters and Barish (2003). To analyze potassium sorbate, the method suggested by Pylpyw and Grether (2000) was readily followed: a Supelcosil silica-based HPLC column LC-18, 250 × 4.6 mm (Supelco, Bellefonte, PA, USA), at temperature of 60°C with a mobile phase flow rate of 1.8 ml/min, was used. Collection samples were obtained at every 20 min (UV/Vis Perkin Elmer detector Model 785–255 nm), and potassium sorbate concentration was calculated by an equation generated by nine points of standard concentrations samples from 0.02% to 0.6%. Sodium chloride concentration in syrup samples was obtained by using a flame photometer Sherwood (Model 410, Cambridge, UK), following the method described in AOAC (1990). Before doing the analysis, samples were diluted with de-ionized distilled water (1:100), and sodium chloride concentration was calculated by an equation generated by five points of standard concentrations samples from 5 to 50 mg/l. All analytical standards solutions for sodium bisulphite, potassium sorbate and sodium chloride were prepared by using Sigma–Aldrich reagents (St. Louis, MO. USA). The calibration lines are highly linear with coefficients of determination 0.99.

2.3. Theoretical considerations to obtain effective diffusivity

To estimate effective diffusivities of different solutes into the mango slices, an analytical solution of ‘Second Fick’s Law’ for diffusion from a stirred solution of limited volume is considered. In the experimental procedure, mango slice is immersed in a syrup solution of limited volume so the solute concentration decreases as well solute penetrates in to the slice. If syrup solution is well-stirred, the concentration depends only on time and is determined by the condition that the total amount of the solute in syrup and in the mango slice remains constant as diffusion proceeds. Since the rate of uptake of solute by the slice of mango can be estimated from observations of the uniform concentration in the syrup, then a limited amount of time becomes helpful. The problem can then be mathematically modeled as one-dimensional effective diffusion through an infinite slab of uniform material, having thickness 2L, in contact with a well-stirred solution of limited volume. The mango slice occupies the space −L < x < L, while the syrup occupies the spaces −L − a ≤ x ≤ −L, L ≤ x ≤ L + a. Moreover, the concentration of the solute in syrup is always uniform and is initially C0, while initially the slice is free from solute (Crank, 1956).

Under these conditions, the diffusion equation becomes:

\[ \frac{\partial C}{\partial t} = D_{eff} \frac{\partial^2 C}{\partial x^2} \]  

(1)

The initial condition is C(x, 0) = 0, and the boundary conditions are

\[ \left. \frac{\partial C}{\partial x} \right|_{x = \pm L} = \pm D_{eff} \frac{\partial C}{\partial x} \]  

(2)

These boundary conditions express the fact that the rate at which solute leaves the solution is always equal to that at which it enters the sheet over the surfaces x = ±L. Assuming that the concentration of solute just within the surface of the sheet is the same as that in the solution, the differential Eq. (1) can be solved using Laplace’s transforms. The solution is

\[ M_t = 1 - \sum_{n=1}^{\infty} \frac{2x(1 + x)}{1 + x^2 + x^2 \cdot q_n^2} \cdot \exp(-D_{eff} q_n^2 L^2 / t) \]  

(3)

where \( M_t \) is the total amount of solute in the sheet at time \( t \), and \( M_\infty \) represents the corresponding quantity after infinite time. The \( q_n \)'s, are the non-zero positive roots of \( \tan q_n = -3q_n \), and \( x = q/c \cdot \sigma \), the ratio of volumes of syrup and sample. For high values of \( x (x > T) \), there is practically no change in roots values (Table 4.1, Crank, 1956). Finally, effective diffusivities are estimated by fitting the curve model to experimental data. Once the effective diffusivity behavior is defined as a function of temperature for each chemical barrier, prediction of the system’s behavior at different temperatures becomes possible with the aid of equation (3).

3. Results and discussion

The ratio of volumes of syrup and mango slices, \( \alpha \), was experimentally determined by knowing the syrup volume, \( V = 70 \) cm³, used to cover the mango slices volume, \( V = 70 \) cm³, obtaining \( \alpha = 7.14 \). The values of the six non-zero positive roots used to estimate the diffusion coefficients were taken from Table 4.1, Crank, 1956. These values are: \( q_1 = 1.6385, q_2 = 4.7359, q_3 = 7.8681, q_4 = 11.0057, q_5 = 14.1451 \) and \( q_6 = 17.2852 \). With this information, Eq. (3) was used to estimate effective diffusivity values, \( D_{eff} \), with the aid of Gauss–Newton method (Chapra and Canale, 1999).

Diffusion kinetics of sodium chloride, potassium sorbate and sodium bisulphite into mango slices at experimented temperatures (25, 50 and 70 °C), are shown in Figs. 2–4, respectively. Diffusion kinetics, obtained by Eq. [3], fit data with a good determination coefficient: for sodium chloride \( R^2 = 0.988 \), for potassium sorbate \( R^2 = 0.99 \), and for sodium bisulphite \( R^2 = 0.983 \). For sodium chloride, an increase in temperature has a little benefit on its diffusion into the mango slices. This behavior has been observed in previous studies of diffusion in other foods and systems like desalting of pickles (Pflug et al., 1967; Bomben et al., 1974). On the other hand, the influence of temperature on the diffusivities of potassium sorbate and sodium bisulphite was significantly higher (Figs. 3 and 4). Sodium bisulphite had the shortest observed time to reach equilibrium between syrup and mango slices, roughly 250 s at 70 °C. Numerical values for the effective diffusivity coefficients obtained for the three chemical barriers at different temperatures are presented in Table 1.

Results presented in this paper fall in the order of magnitude of previous studies on effective diffusivities for salt and sorbate in others food systems and processing methods. Baroni and Hubinger (1999) reported diffusivities from 0.38 to 1.42 × 10⁻⁹ m²/s for salt in dehydrated onions by immersion of them in salt solutions at temperatures from 22 to 40 °C, using Fickian diffusion model and profiles of salt penetration. Mujaffar and Sankat (2006) analyzing salt uptake in shark meat slices, obtained effective diffusivity coefficients values of salt between 1.5 and 2.51 × 10⁻⁹ m²/s, during osmotic dehydration in the temperature range of 20–50 °C. Han

![Fig. 2. Absorption kinetics for sodium chloride in mango slices. Solid lines indicate data adjustment to the mathematical model of Eq. (3).](image-url)
Sodium chloride (2.63 x 10^-6) and potassium sorbate (8.30 x 10^-9) were experimented at temperatures of 25, 50, and 70°C. The diffusivity of potassium sorbate through American processed cheese was 1.31 x 10^-10 m²/s for Mozzarella cheese was 10 x 10^-10 m²/s.

The penetration of surface-applied potassium sorbate into cheese was examined by using diffusion models and computer programming for examining the residual surface concentration and the diffusivity of potassium sorbate in cheese. Jaya and Das (2005) reported the effective diffusivity of potassium sorbate in model food gels, 10 x 10^-10 m²/s, and for Mozzarella cheese was 10 x 10^-10 m²/s. Diffusivity of sorbic acid in model food gels, with mono and tridimensional diffusion methods and three methods of calculation (eye fitting, eye fitting graphical method or computerized fitting method) were studied by Giannakopoulos and Guilbert (1986a,b), reporting values from 0.45 to 8.9 x 10^-10 m²/s at 25°C, depending on gelling agent concentration in gel containing water and glycerol.

Even though a lot of research has been done in osmotic dehydration of mango (Alakali et al., 2006; Welti et al., 1995; Giraldo et al., 2003), or in its stability (Montero et al., 2005), and shelf life (Jaya and Das, 2005), there is not available information on effective diffusivity coefficients in mango of the components of the chemical barrier presented in this work. Information about sulphite effective diffusivities in food is scarce (Rodríguez and Zaritzky, 1986; Haros et al., 2005). A significant contribution of this work is that provides information about effective diffusivities of sodium sulphite in mango which is not usually available.

Fig. 5 shows the temperature dependency of the three chemical barriers at the tested conditions. This dependency could be well represented by an Arrhenius model:

\[ D_{\text{eff}} = D_0 \exp \left(-\frac{E_a}{RT}\right) \]  

where \( D_0 \) is the pre-exponential factor of Arrhenius (m²/s), \( E_a \) is the activation energy (kJ/mol), \( R \) is the ideal gas constant (J/mol K) and \( T \) is the absolute temperature (K). Table 2 shows the activation energy and obtained correlations. The magnitude of the activation energy is an indication of the temperature influence of each of the barriers on the process. For instance, value of \( E_a \) for sodium chloride, indicates very low diffusivity dependence on temperature.

Numerous studies, including this, have successfully showed that the effective diffusivity is temperature dependent following an Arrhenius equation (Díaz et al., 1994; Redl et al., 1996; Han and Floros, 1998b; Maldonado and Zuritz, 2003; Teerakarn et al., 2002; Alakali et al., 2006). However, it is important to realize that deviations from the Arrhenius model may occur since it is possible that higher temperature promote major penetration of small solutes in the vegetal tissues, due to the induced structural changes in cellular membranes (Sereno et al., 2001). Moreover, diffusion of small solutes in foods is controlled by complex mechanisms which depend on solute characteristics (size, forms, and concentration), structure and viscoelasticity of food, physical state of the polymeric matrix, solvent concentration and all kind of intermolecular interactions of components (Le Mestle, 1995).

![Fig. 3. Absorption kinetics for potassium sorbate in mango slices. Solid lines indicate data adjustment to the mathematical model of Eq. (3).](image)

![Fig. 4. Absorption kinetics for sodium bisulphite in mango slices. Solid lines indicate data adjustment to the mathematical model of Eq. (3).](image)

**Table 1**

<table>
<thead>
<tr>
<th>Chemical barrier</th>
<th>Effective diffusivities (m²/s) at 25°C</th>
<th>Effective diffusivities (m²/s) at 50°C</th>
<th>Effective diffusivities (m²/s) at 70°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride SD⁴</td>
<td>2.63 x 10^-9 (±1.07 x 10^-10)</td>
<td>3.05 x 10^-9 (±1.34 x 10^-10)</td>
<td>3.54 x 10^-9 (±1.09 x 10^-10)</td>
</tr>
<tr>
<td>Potassium sorbate SD⁴</td>
<td>8.30 x 10^-10 (±2.65 x 10^-11)</td>
<td>1.90 x 10^-9 (±7.22 x 10^-11)</td>
<td>3.88 x 10^-9 (±1.67 x 10^-10)</td>
</tr>
<tr>
<td>Sodium bisulphite SD⁴</td>
<td>5.98 x 10^-8 (±2.09 x 10^-9)</td>
<td>1.05 x 10^-7 (±3.31 x 10^-9)</td>
<td>1.83 x 10^-7 (±7.04 x 10^-9)</td>
</tr>
</tbody>
</table>

* Standard deviation.
4. Conclusions

Modeling experiments with an analytical solution of Fick's second law for the case of one dimension effective diffusion through a flat plate from a stirred solution of limited volume, presents a good agreement with experimental data; therefore, diffusion kinetics obtained by Eq. (3) fit data for sodium chloride with a mean square error of 98.8%, for potassium sorbate of 99.5%, and for sodium bisulphite of 98.33%.

Behavior of the three barriers with temperature is different: in comparing effective diffusivity with temperature for potassium sorbate and sodium bisulphite against sodium chloride, it is possible to observe that the last one has a flat slope indicating the almost null influence of temperature. Consequently, effective diffusion coefficients for potassium sorbate and sodium bisulphite were sensitive to temperature as expected. They behavior were well adjusted by an Arrhenius equation. Among the three barriers, potassium sorbate was the most sensitive, explaining its substantial reduction in equilibrium times and the increase in its diffusivity with temperature.

Combining solutions of Fick's second law with Arrhenius model for each chemical barrier, could allow us to simulate diffusion kinetics at other temperatures different from the experimental ones.

Among the three experimented chemical barriers, sodium bisulphite was the one having the highest effective diffusivity coefficients and, consequently, reaching equilibrium in shortest time, followed by sodium chloride and potassium sorbate. Consequently, stabilization stage of mango slices is defined in terms of potassium sorbate. There are limitations of this model to estimate sodium bisulphite diffusivity. This system is more complex due to its high reactivity, either as HSO₃ or as SO₂ gas, which explains its antioxidant power and characteristic as food preserver. Experimental value for obtained effective diffusivity may be higher than the right one due to the following:

(a) The analytical method detects both, sodium bisulphite and SO₂; therefore, sorption kinetics is a weighted value of both solutes.

(b) Once the bisulphite forms SO₂, diffusion may occur either from the solution to the sample or from the solution to the space above the system. However, this situation may be partially overcome since concentration data, at the beginning of kinetics, was taken right from a syrup sample in direct contact with the fruit segment.

It is necessary a better understanding of all factors influencing diffusion and chemical activity of sodium bisulphite, in order to precisely evaluate the diffusion coefficient of this compound.

Acknowledgments

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References


Table 2

<table>
<thead>
<tr>
<th>Component</th>
<th>( D_{eff} ) (m²/s)</th>
<th>( E_0 ) (kJ/mol)</th>
<th>( n^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>2 \times 10^{-8} exp \left( \frac{-669.7}{T^*} \right)</td>
<td>5.45</td>
<td>0.9890</td>
</tr>
<tr>
<td>Potassium sorbate</td>
<td>8 \times 10^{-9} exp \left( \frac{-669.7}{T^*} \right)</td>
<td>28.0</td>
<td>0.9973</td>
</tr>
<tr>
<td>Sodium bisulphite</td>
<td>3 \times 10^{-9} exp \left( \frac{-669.7}{T^*} \right)</td>
<td>20.45</td>
<td>0.9833</td>
</tr>
</tbody>
</table>

**Absolute temperature (°C)**


