Mass transfer coefficients during osmotic dehydration of apple in single and combined aqueous solutions of sugar and salt

A.M. Sereno *, R. Moreira, E. Martinez

Faculty of Engineering, Department of Chemical Engineering, University of Porto, Rua dos Bragas, 4050-123 Porto, Portugal

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Abstract

Apple cylinder samples were dehydrated by immersion in binary aqueous solutions of sucrose and sodium chloride with different concentrations and temperatures, as well as in ternary solutions of both solutes. Experimental data on sample moisture content and solids gain against time were fitted to a simplified diffusion model valid for short operation times. A net flow of solids towards the solution was observed during the initial contact with salt solutions, which changed later to an actual solids gain as with sugar solutions. Mass transfer coefficients calculated for binary solutions of a single solute were successfully used to estimate the coefficients for ternary solutions of both solutes, for the range of concentration and temperature studied, by means of a ‘parallel flow’ model. The ratio of water loss to solids gain (WL/SG) for each osmotic treatment was particularly high in the case of salt solutions, due to a low solids gain. In the case of ternary mixed solutions, intermediate values for WL/SG were obtained. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Osmotic treatment of fruits and vegetables has been the object of steady research attention during recent years as a convenient method to improve the economics of dehydration processes (Jayaraman & Das Gupta, 1992), the nutritional and organoleptic characteristics of the products which usually undergo further drying by conventional methods (Raoult-Wack, 1994; Karathanos, Kostaropoulos, & Saravacos, 1995; Lazarides & Mavroudis, 1995) or still to produce intermediate moisture foods of improved shelf life stability with the help of combined preservation methods (Maltini & Torregiani, 1981; Monsalve-González, Barbosa-Cánovas, & Cavali, 1993; Alzamora, Tapia, Argaz, & Welti, 1993). These osmotic treatments involve product immersion in a hypertonic aqueous solution leading to a loss of water through cell membranes of the product which flowing along inter-cellular space diffuses into the solution. Usually other material flows occur simultaneously as the loss of natural fruit solutes and product impregnation by the solute (or solutes) in the solution (Ponting, 1973).

The rate of water loss depends on several factors such as solution concentration, its temperature, contact time, level of agitation, sample size and geometry, solution to solid volume ratio and operating pressure, particularly the use of vacuum (Rastogi, Raghavarao, & Miranjan, 1997).

Solute choice and concentration depend on several factors, namely the effect on organoleptic quality properties, solute solubility, cell membrane permeability, its stabilising effect and cost (Qi, LeMaguer, & Sharma, 1998). The two most common solute types used for osmotic treatments are sugars (mainly with fruits) and salts (with vegetables, fish, meat and cheese), with relevance for sucrose and sodium chloride which show advantages already described by several authors (Ponting, 1973; Curry, Burns, & Heidelbangh, 1976; Lenart & Flink, 1984a).

Previous works have also pointed out the effectiveness in combining both solutes to obtain a maximum water loss with low solids gain by the product without significantly affecting product taste (Lenart & Flink, 1984b). Qi et al. (1998) found optimum operating conditions for carrot dehydration with 44% sucrose/7% sodium chloride solutions (w/w), Lerici, Pinnavaia, Dalla Rosa, and Bartolucci (1985) found that the addition of a small amount of sodium chloride (2% max. w/w) to different
sugar solutions in apple dehydration led to a higher dehydration rate without increasing solids gain.

In this work, mass transfer coefficients for water elimination and solute impregnation during apple dehydration by sucrose and sodium chloride in single solute solutions and static systems were measured at several solute concentrations and temperatures. These results were then used to estimate similar mass transfer coefficients for ternary systems sucrose/salt/water. Solute concentrations studied are typical of food products both from the viewpoint of process kinetics and organoleptic characteristics (Lewicki, Lenart, & Turska, 1984). In general, low salt concentration is used in fruit processing to avoid a significant decrease of perceived organoleptic properties.

2. Theory

It is common practice to base on a diffusional analysis the description of mass flows involved in osmotic dehydration of material samples of different geometries (Beristain, Azuara, Cortés, & García, 1990; Rastogi et al., 1997). Typically, water loss rate from a food material by an osmotic solution decreases after a relatively short period of time; this fact has suggested the use of simplified versions of non-steady state form of Fick’s second law, considering short processing time, constant solution concentration and negligible external resistance to mass transfer (Crank, 1975; Hawkes & Flink, 1978) and leading to a linear dependence of water loss and solids gain on the square root of residence time

\[
NMC = 1 - k_w \theta^{0.5},
\]

\[
NSC = 1 + k_s \theta^{0.5},
\]

where, \(k_w\) and \(k_s\) represent overall mass transfer coefficients for water and solute, respectively, \(\theta\) is the dehydration time and normalised moisture content (NMC) and normalised solids content (NSC) are defined as

\[
NMC = X/X_0,
\]

\[
NSC = S/S_0,
\]

where \(X, X_0\) represent moisture content, \(S, S_0\) solids content in the sample at time \(\theta\) and 0, respectively.

Mass transfer coefficients for single solute binary solutions were modelled, as suggested by Magee, Hassaballah, and Murphy (1983), as depending on the concentration (\(C\), mass fraction) and temperature (\(T\), °C) as follows:

\[
k_i = AC^aT^b,
\]

where \(k_i\) is the mass transfer coefficient for water or for the solute (\(k_w\) or \(k_s\)). Owing to existing experimental conditions with high solute concentrations and increased solution viscosity, these coefficients should be viewed as overall transfer coefficients, taking into account both internal and external resistances to mass transfer (Lazarides, Katsanidis, & Nickolaidis, 1995).

For the estimation of overall transfer coefficients in the case of ternary solutions, a ‘mixing rule’ based on the model of simultaneous independent diffusions of each solute expressed in terms of a parallel association of resistance to mass transfer is proposed

\[
k_{12} = M_m \left( \frac{k_1}{M_1} + \frac{k_2}{M_2} \right),
\]

where \(M_i\) (\(i = 1, 2\)) is the molar mass of each solute, \(k_1\) and \(k_2\) the corresponding transfer coefficients for single binary solutions and \(M_m\) the average molar mass evaluated as

\[
M_m = \sum_{i=1}^{n} x_i M_i,
\]

where \(x_i\) is the mass fraction of each solute in the solution on a water-free basis.

3. Material and methods

Golden delicious apples were used as the product to be dehydrated. Samples were cut as cylinders of 8 mm diameter and 24 mm length (\(L/D = 3\)). Cylindrical

\(NMC\): normalised moisture content
\(NSC\): normalised solids content
\(X\): moisture content
\(S\): solids content
\(C\): solution concentration
\(k\): mass transfer coefficient
\(M\): molecular weight
\(a\), \(b\): exponents
\(m\): average
\(0\): initial
shape was preferred to slices as its higher specific surface leads to higher dehydration rates (Monsalve-González et al., 1993). The cylinders were cut from the parenchymatic apple tissue with a metallic cork borer and oriented parallel to the natural apple axis.

Binary osmotic solutions of sucrose (40%, 50%, 60% w/w) and sodium chloride (15%, 22%, 26.5% w/w) were used along with ternary solutions of 30/10, 40/10, 50/10 and 20/15, 30/15, 40/15 wt.% of sucrose and sodium chloride, respectively. In all experiments, a weight ratio of solution to apple samples of 40:1 was used, considered high enough to neglect concentration changes during the process. The samples were processed for 4 h, enough to reach essentially stable conditions (Lerici, Mastracola, & Nicola, 1988; Simal, Deyá, Frau, & Roselló, 1997). The experiments were conducted under static conditions at 5°C, 20°C, 40°C, 60°C. At given intervals, three sample cylinders were taken from each solution and analysed for weight reduction (WR), water loss (WL), solids gain (SG) using the following relations:

\[
WR = \frac{(w - w_0)}{s_0}, \quad \text{(8)}
\]

\[
SG = \frac{(s - s_0)}{s_0}, \quad \text{(9)}
\]

\[
WL = SG - WR, \quad \text{(10)}
\]

where \(w, w_0\) are the present and initial sample masses, and \(s, s_0\) are the present and initial masses of solids in the sample, respectively.

Moisture content of each sample was measured by an oven drying at 70°C under a pressure of less than 10 kPa, during 24 h.

4. Results

4.1. Sucrose solutions

Typical temperature effect on dehydration kinetics is presented in Fig. 1 for a 40% solution. Experimental data up to 2 h are shown together with diffusional model proposed (Eq. (1)) valid for this period. It was observed that temperature has an important effect on the apple dehydration rate; after 1 h of contact, normalised moisture content falls to 0.94, 0.89, 0.85 and 0.78 with increasing processing temperatures of 5°C, 20°C, 40°C, 65°C, respectively. This strong temperature influence has been clearly shown before in previous work (Lenart & Flink, 1984b; Lazarides et al., 1995) using other products and geometry.

Concentration effect is similar to all temperatures and presented in Fig. 2 for 25°C. Owing to an increase of osmotic pressure difference with an increase in solution concentration, a corresponding increase in dehydration rate was observed; to reduce 10% sample moisture content with 40%, 50%, 60% solutions, processing time decreases from 65 to 50 and 35 min.

By fitting all the experimental data obtained to the model expressed by Eq. (5), the following expression was obtained (Fig. 3). A good agreement between experimental and predicted data was obtained (deviations less than 3%).

![Fig. 1. Kinetics of the simultaneous apple dehydration/sucrose impregnation at several temperatures. Example for 40% sucrose solution.](image1)

![Fig. 2. Kinetics of the simultaneous apple dehydration/sucrose impregnation at different solution concentrations. Example for treatment at 25°C.](image2)

![Fig. 3. Overall mass transfer coefficients during the osmotic treatment of apple with sucrose solution.](image3)
with $k_w$ expressed in s$^{-0.5}$, C in mass percent and $T$ in °C.

With respect to solids gain, Figs. 1 and 2 also show the effect of temperature and concentration, respectively. Similarly, solids gain clearly increased with temperature and solute concentration during the first part of the experiment, reaching soon a stage of near-kinetic equilibrium. For this reason the model proposed was used to represent only the first phase of the process, typically for a maximum of 1.5–2 h.

By fitting again the available experimental data on transfer coefficient as a function of solution temperature and concentration, the following expression was obtained:

$$(k_w)_{\text{sucrose}} = 0.00172 \ C^{0.36} T^{0.371},$$

(11)

with $k_w$ expressed in s$^{-0.5}$, C in mass percent and $T$ in °C.

Analysing WL/SG ratio in Table 1 after 2 h of osmotic treatment, it is observed that this ratio increases with the use of high concentration solutions, due to the fact already mentioned that for longer processing time, WL continues to increase while SG essentially stops after a short processing time. In general, the higher the WL/SG ratio the better the dehydrated product obtained.

4.2. Sodium chloride solutions

Experiments with sodium chloride solutions were conducted in a similar way as described with sucrose solutions. The effect of solution temperature is typically presented in Fig. 4 for 22% w/w solution. It was observed that in this case the effect was not as strong as with sucrose, probably due to a smaller effect on solution viscosity.

In addition, at a high temperature (65°C) dehydration was observed only during the first 30 min, increasing the moisture content after that. This phenomenon was also observed at a lower temperature after a longer processing time (4 h) and was also reported by Biswal, Bozorgmehr, Tompkins, and Liu (1991) when working with green beans at temperatures over 40°C. It is supposed that impregnation with sodium chloride combined with temperature may change permeability properties of cell membranes leading to changes in diffusional flow. In the temperature range of 5–40°C, the samples reach nearly constant moisture content after 1 h, which will be the period for which the proposed model is valid. As a typical example, using 22% solution for 1 h, NMC is slightly reduced from 0.89 to 0.88 and 0.87 when temperature increases from 5°C to 25°C and 40°C, demonstrating clearly a very low effect of temperature on NMC unlike the results obtained with sucrose.

Solution concentration has a more noticeable effect on dehydration rate, similar to all temperatures tested (Fig. 5). To reduce by 10% NMC at 25°C with 17%, 22%, 26.5% solutions, processing time decreased from 50 to 35 and 20 min.

By fitting again all experimental data obtained to the model expressed by Eq. 5 the following expression was obtained (Fig. 8). A good agreement between experimental and predicted data was obtained (deviations less than 4%)

$$(k_w)_{\text{NaCl}} = 0.00863 \ C^{0.21} T^{0.121}$$

(13)
with \( k_w \) expressed in \( s^{-0.5} \), \( C \) in mass percent and \( T \) in °C.

With respect to solids gained by apple samples, Figs. 4 and 5 also show the effect of temperature and concentration, respectively. The behaviour of this variable was found to be more complex in this case than with sucrose. At 5°C and 25°C NSC decreased very quickly for about 10 min, starting then to increase steadily for about 30 min, reaching after 1 h an essentially constant solids content. At 40°C NSC increased to a level higher than the initial value, while at 65°C the curve of NSC against time goes through a maximum, stabilising at a level which is lower than the initial solid content. This complex behaviour is certainly related to structural changes in the cell membrane with a reflex on its physical properties and the existence of a competitive flow of soluble solids, mostly sugars, towards the solution and of NaCl which probably due to its smaller molecular size penetrates further into the product structure than sucrose (Lenart and Flink, 1984b). The shape of the curves suggest in fact that following an initial net flow of solutes to the solution, the solids content in the sample increases due to a continued contact with the salt solution. This, however, deserves further investigations. This complex behaviour could not be described satisfactorily by the Magee model (Eq. (5)). WL/SG ratio relations obtained with sodium chloride are presented in Table 2 after 2 h of solution contact. Results are significantly higher than obtained with sucrose, mainly due to a lower solids gain, and show that such a ratio increases with the concentration of the solution at a higher temperature, where dehydration effect seems to dominate. Minimum values of WL/SG ratio were obtained at 25°C corresponding to a higher solids content as shown in Fig. 4.

4.3. Mixed sucrose/sodium chloride solutions

To measure the combined effects of ternary solutions of sucrose and sodium chloride, experiments were conducted with solutions of different relative concentrations as described before. Fig. 6 exemplifies the behaviour of apple dehydration kinetics for changing the sucrose concentration at two levels of sodium chloride, respectively of 10% and 15% w/w. In both cases it is observed that dehydration rate increases with the osmotic solution pressure. The same type of dependence was verified at different temperatures. In this way, after one contact hour, at 25°C, NMC obtained with solutions of (30–40–50%) sucrose/10% NaCl and (20–30–40%) sucrose/15% NaCl was 0.86, 0.82, 0.79 and 0.83, 0.79, 0.76, respectively.

The increase in salt concentration led to a faster reduction in apple moisture content within the range of temperature covered. In fact after the same one hour of contact with solutions of 40% sucrose/10% NaCl and 40% sucrose/15% NaCl, normalised moisture content observed was 0.85, 0.82, 0.75, 0.70 and 0.81, 0.76, 0.71, 0.65 for 5°C, 25°C, 40°C, 65°C, respectively. Fig. 6 is an example of temperature effect obtained with one of the systems studied.

The analysis of the experimental data obtained was made using a model which considers the elimination of water as the result of two parallel flows as due to an independent effect of each of the solutes, sucrose and sodium chloride, present in the solution.

### Table 2

<table>
<thead>
<tr>
<th>Concentration (% w/w)</th>
<th>Temperature (°C)</th>
<th>5</th>
<th>25</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.0</td>
<td></td>
<td>4.65</td>
<td>1.90</td>
<td>3.72</td>
</tr>
<tr>
<td>22.0</td>
<td></td>
<td>3.67</td>
<td>2.49</td>
<td>4.25</td>
</tr>
<tr>
<td>26.5</td>
<td></td>
<td>3.16</td>
<td>4.12</td>
<td>6.22</td>
</tr>
</tbody>
</table>

![Fig. 6. Effect of sucrose concentration on the kinetics of apple dehydration by mixed sugar/salt solutions (for 10% and 15% sodium chloride and 5°C). (Curves (a) and (b) are coincident.)](image)

![Fig. 7. Kinetics of the simultaneous apple dehydration/sucrose + salt impregnation at several temperatures. Example for 30% sucrose/15% NaCl solution.](image)
Fig. 7 also shows the effect of solution temperature on normalised solids content of apple samples during osmotic treatment (same behaviour varying sucrose concentration, but not showed). In both cases solids content increased during the operation (as with a single sugar solution) but the effect of these variables was less important.

Table 3 and Fig. 8 shows experimental overall transfer coefficients measured and values calculated according to the proposed model (Eq. (6)). A fairly good agreement between the two set of coefficients was found; the average percent deviations calculated for solutions of 10% and 15% sodium chloride were 5.5% and 9.3% in the range of temperature and sucrose concentration considered. To determine transfer coefficients for each of the solutes, a detailed analysis of each treated sample is required and will be considered for further work.

Concerning WL/SG ratio, the results found (Table 4) were intermediate between the ones corresponding to each individual solute. Such ratios are considerably higher than when apple is dehydrated with sucrose alone, supposedly due to structural changes in the cell membrane produced by sodium chloride.

Table 3
Experimental and calculated values of overall water transfer coefficients for mixed osmotic solutions

<table>
<thead>
<tr>
<th>NaCl/sucrose (% w/w)</th>
<th>Temperature (°C)</th>
<th>5</th>
<th>25</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td>Measured</td>
<td>Calculated</td>
</tr>
<tr>
<td>10/30</td>
<td>0.0019</td>
<td>0.0019</td>
<td>0.0024</td>
<td>0.0025</td>
</tr>
<tr>
<td>10/40</td>
<td>0.0024</td>
<td>0.0023</td>
<td>0.0030</td>
<td>0.0031</td>
</tr>
<tr>
<td>10/50</td>
<td>0.0027</td>
<td>0.0027</td>
<td>0.0033</td>
<td>0.0037</td>
</tr>
<tr>
<td>15/20</td>
<td>0.0020</td>
<td>0.0023</td>
<td>0.0034</td>
<td>0.0030</td>
</tr>
<tr>
<td>15/30</td>
<td>0.0024</td>
<td>0.0028</td>
<td>0.0039</td>
<td>0.0037</td>
</tr>
<tr>
<td>15/40</td>
<td>0.0036</td>
<td>0.0034</td>
<td>0.0047</td>
<td>0.0044</td>
</tr>
</tbody>
</table>

5. Conclusions

The treatment of apple samples with aqueous sucrose solutions produced a dehydration effect of the solid tissue. The dehydration rate increased with the osmotic pressure and temperature of the solution. Simultaneously an increase in solids content of the sample by sucrose impregnation was observed. Both transfer processes were described by means of a simplified model, previously proposed by Magee et al. (1983), and valid during the early stages of operation when such changes were more important and thus relevant for industrial osmotic treatment processes. Such a model allows overall mass transfer coefficients to be expressed in terms of process variables, solution concentration and temperature.

In the case of sodium chloride solutions, the same model was able to describe dehydration transfer coefficients but not the transfer of solute to the material. This may be due to a more extensive penetration of such small molecules into the apple tissue with possible changes induced in its cell membrane, particularly at high temperatures. This effect coupled with the leaching of naturally occurring solutes in the apple may lead to a decrease in the total solids content of the sample. Further research is required to describe this complex behaviour.
In the case of dehydration by combined solutions of both solutes, a mixing rule to predict overall water transfer coefficients based on a model considering the independent effect of each solute acting in parallel is proposed. The model was validated for a range of solution temperatures/concentrations and a processing time, which includes typical industrial processing conditions for these materials. Average percent deviations between experimental and calculated transfer coefficients were in all cases less than 10%.

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References


