Evaluation of water, sucrose and minerals effective diffusivities during osmotic treatment of pork in sugar beet molasses

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Abstract
Effective diffusivities of water, sucrose and minerals in osmotic treatment of pork cubes (M. *triceps brachii*) were calculated using Response Surface Methodology (RSM), with respect to temperature (20, 35 and 50 °C) and concentration of sugar beet molasses, (60, 70 and 80 mass%). The numerical solution of Fick's law for unsteady-state mass transfer in a perfect cube configuration was used to calculate the effective diffusivities of water, sucrose and minerals (Na, K, Ca and Mg). Zugarramurdi and Lupin's model was used to predict the equilibrium condition, which has shown to be appropriate for water loss and solute uptake during osmotic treatment. Effective diffusivity of water was found to be in the range of 6.95×10^{-10}–8.03×10^{-10} m^2 s^{-1}, the sucrose effective diffusivity was between 6.39×10^{-10} and 8.25×10^{-10} m^2 s^{-1}, while diffusivities for minerals (m^2 s^{-1}) were in the range: 6.34×10^{-10}–8.82×10^{-10} for Na, 6.27×10^{-10}–7.43×10^{-10} for K, 6.44×10^{-10}–8.94×10^{-10} for Ca and 3.47×10^{-10}–5.66×10^{-10} for Mg.

Keywords: pork, sugar beet molasses, osmotic treatment, diffusion, mass transfer.

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Physicochemical, sensory and technological properties of fresh meat are related with water content. Water is held in myofibrils, functional organelles of meat, but also it may exist in the intracellular space between myofibrils and sarcoplasm. The water content in meat depends on many factors, including the tissue itself and how the product is handled (time, temperature, treatments) [1–3].

Various meat preservation techniques usually include the introduction of high salt content, but nowadays consumers demand lower content of salt incurporated in the final product [4]. The interest of consumers in processed products with lower salt content is due to changes in the sensory preferences, but the main reason is the public concern as regards the high intake of sodium in the diet, which is known to increase the threat of cardiovascular damage [5]. The decrease of sodium content by partial substitution of sodium chloride with some other salts (like potassium chloride) is one of the most commonly used methods [6–8]. Nevertheless, there is little knowledge regarding the influence of the salts formulation on the kinetics and its influence on the salting step [6], as in the post-salting stage [9–12]. Recently, the mineral uptakes in pork brined with NaCl and K-lactate for obtaining low sodium meat products have been studied [13].

One of the preservation techniques for producing food with low water content and improved nutritional, sensorial and functional properties is osmotic treatment (OT). Osmotic treatment of foods presents some advantages compared with common drying techniques, such as minimizing heat damage to the color and flavor, inhibiting enzymatic browning and reducing energy costs. The use of OT as a complementary treatment in food processing, particularly prior to drying and freezing operations, reduces energy requirements of these processes. The technique aims to dehydrate food products by immersing them in hypertonic solution.The diffusion of water is accompanied by the simultaneous counter-diffusion of solute(s) from the osmotic solution into the meat tissue. Since the membrane responsible for osmotic transport is not perfectly selective, other solutes can also be leached into the osmotic solution [2,14]. Osmotic treatment of meat with salt solutions leads to complex phenomena, due to the dynamics of the actin–myosin–salt interactions which modify continuously the relative importance of mass transfer mechanisms.

The use of NaCl solutions during osmotic treatment provokes an increase of the muscles water holding capacity [3]. This is due to existing Cl$^-$ bonds with actin and myosin filaments, which increase negative charges, amplifying the repelling forces among the filaments, leading to muscle swelling. The direction of liquid flow

in the intercellular spaces cannot be predicted only from the solution osmotic pressure because capillary forces play a major role on liquid flow. Osmotic treatment of raw meat with salt solutions leads to salt and water transfers, in the same directions or in counter-current, depending on the osmotic solution concentration.

Different approaches have been proposed to explain the rates of mass transfer during osmotic treatment. The first is based on the tissue cellular structure, and the water transport is modeled according to the thermodynamics of irreversible processes [3,15]. Alternatively, the analytical solutions of Fick's second law of diffusion in non-stationary solids of different geometries can be used, allowing estimation of effective diffusion coefficients for water and solutes [16–24]. Rastogi *et al*. [14] reported Fickian unsteady-state diffusion as the most appropriate mechanism for the estimation of diffusion coefficients during osmo-concentration. However, the major drawback in the application of this law is the long experimental time required to attain equilibrium water loss.

Much work has been done in developing models to predict the mass-transfer kinetics of osmotic treatment, and some empirical and semi-empirical models have been proposed, [22–24]. These models correlate processing variables with water loss or solid gain without taking into account the underlying phenomena, and include multivariable regressions, response surface analysis, models derived from mass balances and others. Although mechanistic models give a description of the mass-transfer mechanism, the diffusion approach has a number of assumptions which are difficult to fulfill [1,25], and the effective diffusivity becomes an adjustable kinetic parameter that strongly depends on the experimental conditions and the physical properties of the meat [26]. Also, a cellular physiology approach depends on the knowledge of a large number of biophysical properties, such as membrane permeability and material properties, elastic modulus, void fraction and tortuosity, which are not always available [2,15,25]. On the other hand, even though the empirical and semi-empirical models that have been proposed in the literature give a reasonable fit to experimental data, their use is limited because they are only capable of representing data in conditions similar to those on which such models were developed, and they cannot take into account the process complexity [26, 27]. Andrade *et al.* [28] determined the effective diffusivity of sucrose and water during osmotic treatment of jenipapo based on analytical solution of Fick's second law. Schmidt *et al*. [26], studied the osmotic treatment kinetics of chicken breast cuts over a range of salt concentrations.

The use of a ternary system (water/sugar/salt) in the osmotic treatment of fruits has been studied by some researchers [29], and results have shown that higher rates of water loss are achieved when salt is added, even with solutions with low concentrations of solutes [30]. Most of the works published using the ternary solution provide only diffusion of solids, through determination of total solids by a gravimetric method, without analyzing separately the diffusion of the two solutes used in the solution, [29–31]. According to Bohuon *et al*. [32], the use of ternary solutions presents some advantages in the osmotic treatment process, without excessive over-sweetness or over-salting the product and without reaching the limits of saturation.

No studies relating to the osmotic treatment of pork cubes using sugar beet molasses were found in the current literature. Sugar beet molasses is an excellent medium for osmotic treatment, primarily due to the high dry matter (more than 80%) and specific nutrient content. According to Sauvant *et al*. [33] and Grbeša [34] the concentrations of cations in sugar beet molasses are as follows: 3920 mg K/100 g, 680–1300 mg Na/100 g, 100 mg Ca/100 g, 50–320 mg Mg/100 g and 11.7 mg Fe/100 g. The specific chemical composition (approximately 51% sucrose, 1% raffinose, 0,25% glucose and fructose, 5% proteins, 6% betaine, 1,5% nucleosides, purine and pyramidine bases, organic acids and bases) and high content of solids (around 80%) provide high osmotic pressure in the solution, so molasses appear to be an excellent osmotic medium [35,36].

The current study intends to investigate the effects of sugar beet molasses concentration and immersion duration on the effective diffusivities of water and solutes during the osmotic treatment of pork. Sugar beet molasses as hypertonic solution is presented in this article because of high dry matter content and the enrichment of the food material in minerals and vitamins, which penetrate from molasses to the meat tissue. This investigation is also focused on finding the appropriate mathematical model for water loss, solid gain, sugars and minerals content, during OT of pork in sugar beet molasses. Simple regression models were proposed for calculation of the effective diffusivities of water, sucrose and minerals (Na, K, Ca and Mg) as function of the independent variables. The presented Na, K, Ca and Mg diffusivities during osmotic treatment of pork are presented for the first time, with no data to be compared in the literature.

MATERIALS AND METHODS

Osmotic treatment

Pork (*M. triceps brachii*, 24 h *post mortem*) was purchased just before use. Initial moisture content of

the fresh meat was 72.83%. Before the osmotic treatment, fresh meat was cut into cubes, dimension of nearly $1\times1\times1$ cm^3. Sugar beet molasses solution, with initial dry matter content of 85.04%, was obtained from the sugar factory Pećinci, Serbia. Distilled water was used for dilution of solutions. Sugar beet molasses, was diluted to concentration of 60, 70 and 80 mass%. The sample to solution mass ratio was 1:5. The process was performed in laboratory jars at processing temperature of 20, 35 and 50 °C, with agitation on every 15 min under atmospheric pressure. The jars were kept in water bath, in order to retain samples at constant temperature. The osmotic treatment process was performed in a period of 0–5 h. Samples were withdrawn from the osmotic solution at determined intervals of time (1, 3 and 5 h), drained and dried with filter paper to remove adhering solution.

Analytical determinations

Dry matter content of the fresh and treated samples was determined by drying the material at 105 °C for 24 h in a heat chamber until constant weight was achieved (Instrumentaria Sutjeska, Croatia). All weight measurements were carried out in accordance to AOAC method [37]. Soluble solids content of the molasses solutions was measured using Abbe refractometer, (Carl Zeis Jenna, Germany) at 20 °C.

Mineral content of the raw pork and osmotic treated pork in the solution of sugar beet molasses was investigated. The combination of thermal treatment at 350 °C, and wet acidic treatment at 160 °C, was used for preparation of the samples. The dry samples were processed for minerals determination by wet digestion, where approx. 5 g each were weighed exactly to four decimal places, and transferred to vessels into which 4.5 ml 65% HNO$_3$ and 10.5 ml 35% HCl were added. The treatments were repeated to obtain the white sediments that were dissolved in 0.07 M HNO$_3$.

The content of minerals present in the corresponding solutions was determined by inductively coupled plasma optic emission spectrometry (ICP-OES). ICP-OES measurement was performed using Thermo Scientific ICAP 6500 Duo ICP (Thermo Fisher Scientific, Cambridge, United Kingdom) spectrometer equipped with RACID86 Charge Injector Device (CID) detector, standard glass concentric nebulizer, quartz torch, and alumina injector. Multi-elemental plasma standard solution (Multi-Element Plasma Standard Solution 4, Specpure®, 1000 μg/ml) certified by Alfa Aesar GmH & Co KG, Germany, was used to prepare calibration solutions for ICP-OES measurement. Measurements were performed on emission-lines NaI (818.326 nm), KI (766.490 nm), CaI (431.865 nm) and MgI (285.213 nm). Value of radio frequency power of generator (RF) was 950 W, and radial plasma view was used. Samples were analyzed in triplicate.

Sucrose and invert sugar content have been determined according to Luff-Schoorl method, based on Cu^{2+} reduction. By using this method, values of the total invert sugar (%) and natural invert sugar (%) content, could be determined. Based on this result, sucrose content (%) in the fresh and dehydrated pork could be calculated. All experiments were repeated three times.

Kinetic model

The developed model, based on Fick's unsteady-state law of diffusion, determines the amount of water leaving the meat cube and the solutes diffusing into the meat as a function of time. According to Crank (1975), [38], Fick's second law solution for diffusion, for perfect cubes, assuming the diffusion to be perpendicular to the surface of the cube, is given by Eq. (1):

$$X_r = \frac{x_t - x_0}{x_{eq} - x_0} = \frac{8}{\pi^2}\sum_{i=0}^{\infty}\exp\left(-i^2\pi^2 D_{eff}\frac{t}{L^2}\right) \tag{1}$$

where X_r denotes the dimensionless values of water loss, sucrose uptake or minerals uptake; x_t, x_0 and x_{eq} are the moisture or the solute contents of a sample at treatment time t, at the outset and at equilibrium, respectively; D_{eff} (m^2 s^{-1}) is the effective diffusivity, L (m) is the half thickness of the sample and t (s) is the immersion time.

For long drying periods, Eq. (1) can be simplified to the first term of the series, and moisture ratio can be expressed in the logarithmic form:

$$\ln X_r = \ln\frac{8}{\pi^2} - \left(\pi^2\frac{D_{eff}t}{L^2}\right) \tag{2}$$

$$D_{eff} = D_0\exp\left(-\frac{E_a}{TR}\right) \tag{3}$$

where the effect of temperature on effective diffusivity is expressed using Arrehnius type relationship. E_a is the activation energy of moisture diffusion (kJ mol^{-1}), D_0 is the diffusivity value for infinite moisture content, and R represent universal gas constant (kJ mol^{-1}). T is absolute process temperature (K).

Values of the effective diffusion coefficient (D_{eff}) were obtained by non-linear regression analysis from Eq. (1), taking into account the first two terms of the series, as shown in Eq. (2) [39].

The following assumptions were used in the development of the model: samples of pork cubes are perfect cubes (dimension $1\times1\times1$ cm^3); initial water and solute concentrations in the pork cubes are uniform; the process is isothermal; simultaneous counter-current flows; the diffusion of water from the pork cubes and the diffusion of sugar and salt into the pork cubes are only considered; other mass transfers do not occur;

shrinkage is neglected; external resistance to mass transfer is negligible.

The following mathematical model, with an exponential approach to the equilibrium value of moisture and solutes contents, was proposed by Zugarramurdi and Lupin [40]:

$$\frac{dX_i(t)}{dt} = k_i \left(X_i^*(t) - X_i(t) \right) \tag{4}$$

$$X_i(t) = \frac{m_i(t)}{m - \sum_{j=1, j \neq i}^{n} m_j} , \quad X_i^*(t) = \frac{m_i^*(t)}{m - \sum_{j=1, j \neq i}^{n} m_j} \tag{5}$$

where *i* represents the index of moisture, or mineral content, m_i is mass of *i*-th component at time *t*, m_i^* is mass of *i*-th component at equilibrium, *m* is total mass, k_i is specific rate constant for variation of *i*-th component.

Equilibrium (4) can be integrated with the following initial condition (*t* = 0):

$$X_i(0) = X_i^0 \tag{6}$$

The solution is:

$$X_i(t) = X_i^* + e^{-k_i t} \left(X_i^0 - X_i^* \right) \tag{7}$$

The assumption was made that the Zugarramurdi and Lupines' model Eq. (7) would predict the moisture and solutes content in the kinetics of pork cubes, including equilibrium solute content during the process.

Experimental design and data analysis

The experimental data were used for effective diffusivities calculation using Eq. (2). Effective diffusivities of moisture content, minerals (Na, K, Ca and Mg) and sucrose content were calculated considering the diffusive model expressed in Eq. (2), and the estimation of "equilibrium" conditions (x_{eq}), for certain temperature and sugar beet molasses concentration, using Zugarramurdi and Lupines' model, Eq. (7). After calculation of effective diffusivities values for certain temperature and sugar beet molasses concentration, 3^2 full factorial experimental design (3 level-2 parameter) with 9 runs (1 block) was accepted for moisture, minerals and sucrose effective diffusivities presentation (Table 2). It was used to design tests for osmotic treatment of pork cubes considering two factors: sugar beet molasses solution concentrated 60, 70 and 80 mass%, and temperature (20, 35 and 50 °C). The considered dependent variables were the effective diffusivity of water (D_w), the effective diffusivity of sucrose (D_{suc}) and effective diffusivity of minerals (D_{Na}, D_K, D_{Ca} and D_{Mg}).

The following second order polynomial (SOP) model was fitted to the data. Six models of the following form were developed to relate four responses (Y) and three process variables (X):

$$Y_k = \beta_{k0} + \sum_{i=1}^{2} \beta_{ki} X_i + \sum_{i=1}^{2} \beta_{kii} X_i^2 + \beta_{k12} X_1 X_2 , \, k = 1-6 \tag{8}$$

where: β_{kn} are constant regression coefficients; *Y*, either $D_w(Y_1)$, $D_{suc}(Y_2)$, $D_{Na}(Y_3)$, $D_K(Y_4)$, $D_{Ca}(Y_5)$ or $D_{Mg}(Y_6)$; X_1 osmotic temperature; X_2 solution concentration.

Descriptive statistical analyses for calculating the means and the standard error of the mean were performed using MicroSoft Excel 2007 software. All obtained results were expressed as the mean ± standard deviation (*SD*). Regression analysis and analysis of variance (ANOVA) tests for lack of fit, determination of the regression coefficients and generation of contour plots were performed, using StatSoft Statistica 10 software (Statsoft Inc., Tulsa, OK, USA) [41].

The response variables *Y* were calculated by multiple regressions, and response surface equations were calculated using a definitive model which considered only the influence of significant factors (*p* < 0.05). The response surfaces were drawn by plotting *Y* as a function of two factor variables, molasses concentration and immersion temperature.

RESULTS AND DISCUSSION

Obtained results are presented in Table 1.

Water loss and solute uptake

At the beginning of osmotic process there is an initially high rate of water loss and a quick incorporation of solutes, followed by a slower rate of water loss and solute uptake in the later stages of the process, Table 1. During osmotic treatment of pork cubes, the moisture content (x_w; g water per g of dry solids), sucrose content (x_{suc}; g per g of sample) and mineral content (x_{Na}, x_{Ca}, x_K, x_{Mg}, mg per g of sample) were experimentally determined in samples at different immersion times for all of the experiments. Moisture and solute contents at equilibrium conditions were determined using Zugarramurdi and Lupines' model, Eq. (7), and are given in Table 2. Zugarramurdi and Lupines' equation proved to be suitable for modeling water removal, sucrose and minerals uptake, as the determination coefficients were above 0.98 for all treatments (Table 2).

Effective diffusivities of water, sucrose and minerals

The effective diffusivities at any given set of conditions were calculated using non-linear regression analysis from Eq. (2). It is generally assumed that diffusion occurs at a constant rate under the influence of a uniform moisture gradient. However, this does not appear to be true in biological materials, especially

Table 1. Changes in water loss and solute uptake during osmotic treatment of pork cubes

Immersion time, h	Temp. °C	Solution concentration, %	Water loss %	Solid gain, mg/g				
				Na	K	Ca	Mg	Sucrose
1	20	80	0.22	174.01	502.71	45.28	19.23	4.80
3	20	80	0.40	284.68	822.41	74.08	31.46	7.85
5	20	80	0.47	348.19	1005.88	90.61	38.48	9.60
1	20	60	0.24	227.11	656.09	59.10	25.10	6.26
3	20	60	0.38	321.43	928.57	83.65	35.53	8.86
5	20	60	0.42	368.59	1064.81	95.92	40.74	10.16
1	20	70	0.23	172.43	498.14	44.87	19.06	4.75
3	20	70	0.39	274.93	794.23	71.55	30.39	7.58
5	20	70	0.45	330.26	954.08	85.94	36.50	9.11
1	35	80	0.29	247.34	714.55	64.37	27.34	6.82
3	35	80	0.46	350.01	1011.13	91.08	38.69	9.65
5	35	80	0.52	405.51	1171.49	105.53	44.82	11.18
1	35	60	0.28	247.67	715.48	64.45	27.37	6.83
3	35	60	0.41	333.98	964.84	86.91	36.91	9.21
5	35	60	0.44	373.14	1077.96	97.10	41.24	10.29
1	35	70	0.29	219.38	633.75	57.09	24.25	6.05
3	35	70	0.44	313.87	906.73	81.68	34.69	8.65
5	35	70	0.48	361.20	1043.46	94.00	39.92	9.96
1	50	80	0.38	352.84	1019.32	91.82	39.00	9.73
3	50	80	0.54	447.51	1292.80	116.46	49.46	12.34
5	50	80	0.59	495.01	1430.03	128.82	54.71	13.65
1	50	60	0.34	300.39	867.81	78.17	33.20	8.28
3	50	60	0.47	378.71	1094.05	98.55	41.86	10.44
5	50	60	0.49	409.86	1184.05	106.66	45.30	11.30
1	50	70	0.36	298.49	862.31	77.68	32.99	8.23
3	50	70	0.51	384.98	1112.16	100.18	42.55	10.62
5	50	70	0.54	424.31	1225.78	110.42	46.90	11.70

Table 2. Parameters of Zugarramurdi and Lupin's model fitted to experimental data

Temp., °C	Solution conc., %	WL		X_{Na}		X_K		X_{Ca}		X_{Mg}		$X_{Sucrose}$	
		x_∞^{WL}	r^2	x_∞^{Na}	r^2	x_∞^{K}	r^2	x_∞^{Ca}	r^2	x_∞^{Mg}	r^2	$x_\infty^{Suc.}$	r^2
20	80	0.65	0.998	479.03	0.998	1490.72	0.997	121.27	0.993	37.80	0.915	12.93	0.991
20	60	0.59	0.997	369.61	0.997	1067.75	0.995	96.18	0.993	40.85	0.940	10.19	0.996
20	70	0.51	0.994	413.60	0.999	1239.10	0.998	108.65	0.995	35.00	0.993	11.38	0.994
35	80	0.67	0.996	465.03	0.993	1348.58	0.998	124.10	0.994	43.21	0.953	12.93	0.991
35	60	0.58	0.992	386.08	0.999	1096.43	0.995	105.77	0.996	41.73	0.993	10.87	0.994
35	70	0.54	0.999	386.46	0.997	1116.45	0.994	100.57	0.991	42.71	0.908	10.66	0.998
50	80	0.68	0.997	524.29	0.994	1514.61	0.999	136.44	0.996	66.99	0.989	14.46	0.995
50	60	0.62	0.998	406.63	0.997	1174.71	0.996	111.46	0.993	180.11	0.998	11.33	0.993
50	70	0.54	0.999	401.91	0.996	1161.06	0.995	104.59	0.991	44.42	0.994	11.08	0.999

after the initial stages of the process, as the physical structure of the material begins to change as the osmotic treatment continues. A non-uniform moisture gradient is developed over the course of osmotic treatment and the effective diffusivity changes with geometrical position of specific point inside the material, and time duration of treatment [14]. In meat, D_w,

generally, shows a decreasing trend over time because of the shrinkage phenomenon [42]. Thus, it is assumed that in meat materials D_w does not show a pseudo linear correlation with time, as was also reported by Rastogi *et al.* [14].

Values of effective diffusivity of water, sucrose and minerals at different temperatures and concentrations

Table 3. Average effective diffusivities of water, sucrose and minerals (10^{10}/$m^2 \cdot s^{-1}$) during osmotic treatment of pork

Temp., °C	Solution conc., %.	D_w	D_{Na}	D_K	D_{Ca}	D_{Mg}	$D_{Suc.}$
20	80	6.92	5.08	4.89	5.35	2.72	5.22
20	60	7.15	5.21	5.08	5.52	2.89	5.38
20	70	7.39	5.50	5.28	5.64	3.29	5.54
35	80	7.28	5.47	5.24	5.54	3.27	5.44
35	60	7.46	5.52	5.43	5.78	3.55	5.65
35	70	7.64	5.73	5.64	5.96	4.07	5.86
50	80	7.80	6.14	5.83	5.83	4.74	5.80
50	60	7.93	6.11	6.03	6.14	5.14	6.06
50	70	8.06	6.24	6.25	6.39	5.77	6.32

of the osmotic solution are presented in Table 3. These results are in agreement with fundamental theories which state that mass diffusivity strongly depends on the temperature, pressure, and on the components involved. Many investigations require the effective diffusivity to be determined at a range of precise temperatures. Frequently, the relationship between effective diffusivity and temperature follows a first order rate process described by an Arrhenius relationship, Eq. (2).

Several authors have made important model studies on the diffusion coefficients of sodium chloride and other solutes in meat [13,23,24,43]. The diffusion coefficient is suggested to be affected by changes in Na concentration, swelling and degree of treatment [23].

Table 4 presents the analysis of perturbation caused by temperature and concentration.

The regression coefficients for the six diffusive models, obtained by the fitting of experimental data to Eqs. (1) and (2), using Eq. (3), are presented in Table 4. These models were obtained considering only the influence of significant factors ($p < 0.05$), thus some insignificant interaction parameters are absent in the regression equations.

The determination coefficients (r^2) for D_w, D_{Suc}, D_{Na}. D_K, D_{Ca} and D_{Mg}. models were 0.993, 0.998, 0.999, 0.992, 0.999 and 0.998, respectively. The average error between the predicted values and experimental values (calculated by Eq. (2)) were below 10%. According to Andrade *et al.* [28], values of average error below 10% indicate an adequate fit for practical purposes. To verify the significance of the models, analysis of variance (ANOVA) was conducted and the results indicate that all models were significant with minor lack of fit, suggesting they adequately represent the relationship between responses and factors.

For D_w calculation, only interactions between temperature and concentration, and quadratic term of concentration were not significant at $p < 0.05$ level. These two independent variables positively affect D_w. The linear effect of temperature mostly influenced D_w calculation, followed by the linear effect of molasses concentration. Similarly, it was verified in the literature

that D_w is dependent on the temperature, the osmotic solution concentration (using different sugars – sucrose, glucose, fructose, maltodextrin and sorbitol), and on the combination of both parameters for the osmotic treatment [25,27]. These researchers modeled D_w calculation, using non-linear regression and found an equation much alike to the equation determined in this study (Table 4).

Figure 1 presents response surfaces for D_w, valid for temperatures ranging from 20 to 50 °C, sugar beet concentrations between 60 and 80%. Figure 1 shows that the influence of temperature on D_w is stronger than the influence of molasses concentrations. It is also possible to observe the quadratic effect of these variables and the effect of the interaction between temperature and concentration on D_w calculation. Higher values of D_w were obtained at temperatures between 45 and 50 °C, and molasses concentrations from 75 to 80%. Experiment 9 was performed in these operating conditions, and it showed the highest values for the effective diffusivity of water (Table 3).

In this study, obtained results for effective diffusivity of water are in the range of 6.92×10^{-10}–8.06×10^{-10} $m^2 \cdot s^{-1}$. The effective diffusivities of water in shark filets during brining, found by Mujaffar & Sankat [18], were between 0.17×10^{-9} and 0.24×10^{-9} $m^2 \cdot s^{-1}$, at temperatures between 20–50 °C, in NaCl solution. The differences between the results of this study and the results found in the literature could be explained by the use of different types of materials. Another reason for this difference is the use of a sugar beet molasses solution during dehydration process. The presence of the different nutrients in the osmotic solution affects the mechanism involved in the simultaneous flows of water removal and solute penetration and, consequently, affects the diffusivity values.

Table 4 and Fig. 1 show that the influence of temperature on $D_{Suc.}$ is stronger than the influence of molasses concentrations. Higher values of $D_{Suc.}$ were obtained at higher temperatures and higher molasses concentrations. The effective diffusivity of sucrose in

*Table 4. Analysis of perturbation of response variables (D_w, D_{Na}, D_K, D_{Ca}, D_{Mg}, $D_{Suc.}$) $\times 10^{10}$ ($m^2 \cdot s^{-1}$) caused by changes in osmotic temperature and solution concentration; * – significant at p < 0.05 level, 95% confidence limit*

D	Source	Effect	t(3)	p	−95% Conf. lim.	+95% Conf. lim.	Reg. coeff.
D_w	Mean/Interc.*	2.995±0.014	207.702	<0.01	2.949	3.040	2.995±0.014
	Temp. lin.*	0.307±0.016	19.410	<0.01	0.256	0.357	0.153±0.008
	Temp. quad.	0.012±0.027	0.424	0.70	−0.075	0.099	0.006±0.014
	Conc. lin.*	0.137±0.016	8.666	<0.01	0.087	0.187	0.068±0.008
	Conc. quad.	0.006±0.027	0.236	0.83	−0.081	0.094	–
	Temp. x Conc.	−0.037±0.019	−1.907	0.15	−0.098	0.025	–
D_{Na}	Mean/Interc.*	2.214±0.010	228.994	<0.01	2.184	2.245	2.214±0.010
	Temp. lin.*	0.355±0.011	33.479	<0.01	0.321	0.388	0.177±0.005
	Temp. quad.*	0.109±0.018	5.955	0.01	0.051	0.168	0.055±0.009
	Conc. lin.*	0.114±0.011	10.794	<0.01	0.081	0.148	0.057±0.005
	Conc. quad.*	0.047±0.018	2.584	0.08	−0.011	0.106	0.024±0.009
	Temp. x Conc.*	−0.031±0.013	−2.374	0.09	−0.072	0.010	−0.015±0.006
D_K	Mean/Interc.*	2.157±0.004	534.840	<0.01	2.144	2.170	2.157±0.004
	Temp. lin.*	0.385±0.004	87.251	<0.01	0.371	0.400	0.193±0.002
	Temp. quad.*	0.106±0.008	13.796	<0.01	0.081	0.130	0.053±0.004
	Conc. lin.*	0.154±0.004	34.770	<0.01	0.140	0.168	0.077±0.002
	Conc. quad.*	0.019±0.008	2.457	0.09	−0.006	0.043	0.009±0.004
	Temp. x Conc.	0.002±0.005	0.365	0.74	−0.015	0.019	–
D_{Ca}	Mean/Interc.*	2.302±0.014	167.602	<0.01	2.258	2.346	2.302±0.014
	Temp. lin.*	0.249±0.015	16.544	<0.01	0.201	0.297	0.124±0.008
	Temp. quad.	0.033±0.026	1.259	0.30	−0.050	0.116	–
	Conc. lin.*	0.162±0.015	10.791	<0.01	0.114	0.210	0.081±0.008
	Conc. quad.*	−0.026±0.006	−5.207	0.05	−0.038	0.080	−0.013±0.003
	Temp. x Conc.	0.039±0.018	2.125	0.12	−0.019	0.098	–
D_{Mg}	Mean/Interc.*	1.420±0.005	274.093	<0.01	1.403	1.436	1.420±0.005
	Temp. lin.*	0.905±0.006	159.562	<0.01	0.887	0.923	0.453±0.003
	Temp. quad.*	0.380±0.010	38.700	<0.01	0.349	0.412	0.190±0.005
	Conc. lin.*	0.322±0.006	56.777	<0.01	0.304	0.340	0.161±0.003
	Conc. quad.*	0.098±0.010	9.969	<0.01	0.067	0.129	0.049±0.005
	Temp. x Conc.*	0.079±0.007	11.336	<0.01	0.057	0.101	0.039±0.003
$D_{Suc.}$	Mean/Interc.*	2.269±0.008	280.026	<0.01	2.243	2.295	2.269±0.008
	Temp. lin.*	0.272±0.009	30.671	<0.01	0.244	0.300	0.136±0.004
	Temp. quad.	0.010±0.015	0.673	0.55	−0.039	0.059	0.005±0.008
	Conc. lin.*	0.157±0.009	17.718	<0.01	0.129	0.186	0.079±0.004
	Conc. quad.	−0.001±0.015	−0.051	0.96	−0.050	0.048	–
	Temp. x Conc.*	0.031±0.011	2.841	0.07	−0.004	0.065	0.015±0.005

pork cubes was found to be in the range of 5.22×10^{-10}– -6.32×10^{-10} $m^2 \cdot s^{-1}$.

The effective diffusivity of Na in pork cubes, obtained in this study, was estimated and values between 5.08×10^{-10}–6.24×10^{-10} $m^2 \cdot s^{-1}$ were found (Table 3), and it was compared with other studies. Schmidt *et al.* [26] investigated osmotic treatment in chicken breast cuts, at 5 °C, under stirring conditions, in NaCl solutions, between 0 and 20%. Obtained effective diffusivities of Na were between 2.5×10^{-10} and 2.8×10^{-10} $m^2 \cdot s^{-1}$. Gravier *et al.* [24] used NaCl solutions between 30 and 200g/L for osmotic treatment of pork, and the

obtained effective diffusivities ranged between 0.6×10^{-10} and 5.0×10^{-10} $m^2 \cdot s^{-1}$. Figure 1 and Table 4 show that the influence of temperature on D_{Na} is stronger than the influence of molasses concentrations. Higher values of D_{Na} were obtained using higher temperatures and higher molasses concentrations.

The results shown in Fig.1 and Table 4 indicate that the influence of temperature is stronger than the impact of molasses concentration for D_K, D_{Ca} and D_{Mg} calculation. Higher effective diffusion values were obtained at higher temperatures and higher molasses concentrations. The effective diffusivities for K, Ca and
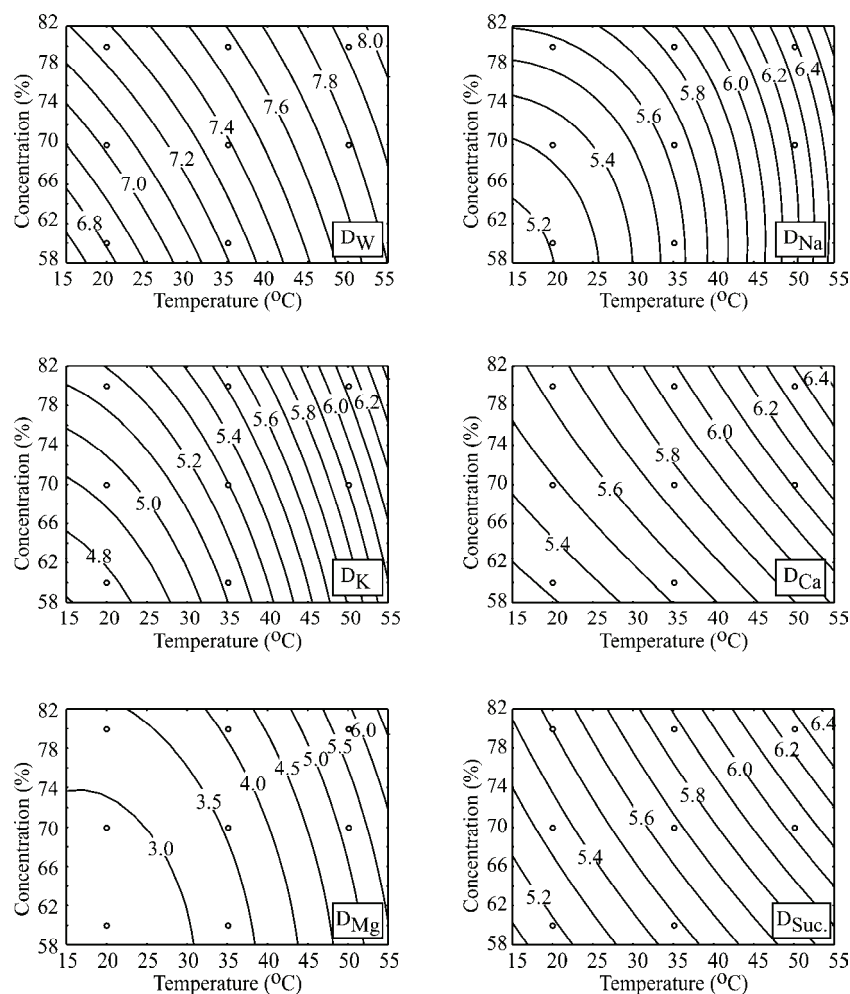
Figure 1. Response surface for effective diffusivity of water, Na, K, Ca Mg and sucrose as a function of temperature and molasses concentrations (×10^{-10} m^2·s^{-1}).

Mg in meat cubes were estimated, and values between 4.89×10^{-10} and 6.25×10^{-10}, 5.35×10^{-10} and 6.39×10^{-10} and 2.72×10^{-10} and 5.77×10^{-10} m^2·s^{-1} were obtained. Due to the lack of data in the literature, presented results could not be compared.

The differences between the results of this study and the results found in the literature can be explained by the use of different cultivars of pork cubes, and also with different degrees of maturation. Another reason for these differences is the use of sugar beet molasses solution. The presence of the different minerals in the osmotic solution affects the mechanism involved in the simultaneous flows of water removal and solute penetration, and, consequently, affects the diffusivities values.

CONCLUSIONS

During dehydration experiments of pork in sugar beet molasses solution, performed at different immersion times (1, 3 and 5 h), sugar beet molasses concentrations (60, 70 and 80%) and temperatures (20, 35 and

50 °C), equilibrium moisture content decreased with the temperature rise, while equilibrium content of observed minerals increased with the temperature enhancement. Zugarramurdi and Lupin's model was used for equilibrium values evaluation, and coefficients of determination showed good fitting capabilities.

Fick's unsteady-state diffusion equation has shown to be suitable for determining the mass effective diffusivity of water and solutes in pork cubes. The temperature and osmotic solution composition showed significant effects on all the responses studied. Increases in temperature, and/or molasses concentration led to higher effective diffusivity of water. Effective diffusivities of sucrose were higher at higher temperatures and molasses concentrations. For the above conditions of osmotic treatment, the effective diffusivity of water was found to be in the range of 6.92×10^{-10} and 8.06×10^{-10} m^2·s^{-1}. The sucrose effective diffusivity was between 6.39×10^{-10} and 8.25×10^{-10} m^2 s^{-1}, while diffusivities (m^2 s^{-1}) for minerals were in the range 6.34×10^{-10}–8.82×10^{-10} for Na, 6.27×10^{-10}–7.43×10^{-10} for K, 6.44×10^{-10}–8.94×10^{-10} for Ca and 3.47×10^{-10}–

−5.66×10^{-10} for Mg. Second order polynomial models fitted the effective diffusion data well.

Acknowledgements

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IZVOD

PRIVIDNI KOEFICIJENTI DIFUZIJE VODE, SAHAROZE I MINERALA PRI OSMOTSKOM TRETMANU SVINJSKOG MESA U MELASI ŠEĆERNE REPE

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(Naučni rad)

Metoda odzivne površine (Response Surface Methodology - RSM) je korišćena pri matematičkom modelovanju i izračunavanju vrednosti prividne (efektivne) difuzije vode, saharoze i minerala tokom osmotskog tretmana kockica svinjskog mesa (*M. triceps brachii*), na temperaturi 20, 35 i 50 °C i pri koncentracijama osmotskog rastvora (melasa šećerne repe) od 60, 70 i 80 mas.%. Numeričko rešavanje Fikovog (Fick) zakona o prenosu mase, pri nestacionarnim uslovima, za idealnu kocku je korišćeno za izračunavanje efektivnog koeficijenta difuzije vode, saharoze i minerala (Na, K, Ca and Mg). Sadržaj vlage i minerala je izmeren u tri ponavljanja. Korišćen je model Cuguramurdija (Zugarramurdi) i Lupina (Lupin) za predviđanje ravnotežnih uslova i ispostavilo se da je taj model pogodan za izračunavanje gubitka vlage i priraštaja suve materije tokom procesa osmotskog tretmana. Metoda odzivnih površina, koje se široko koristi za modelovanje i kontrolu procesa u prehrambenoj industriji, a u ovom radu je korišćena za predviđanje efektivnog koeficijenta difuzije vode, saharoze i minerala, pri određenoj temperaturi imerzije i koncentraciji melase šećerne repe. Matematički modeli koji su dobijeni na osnovu eksperimentalnih podataka obrađuju kompleksne nelinearne relacije sa interakcijama između procesnih promenjljivih. Dobijene vrednosti efektivne difuzivnosti ($m^2\ s^{-1}$) za vodu bili su u rasponu od $6{,}95\times10^{-10}$ do $8{,}03\times10^{-10}$, za efektivnu difuzivnost saharoze bili su između $6{,}39\times10^{-10}$ i $8{,}25\times10^{-10}$, dok su difuzivnosti za minerale bile u opsezima: $6{,}34\times10^{-10}$–$8{,}82\times10^{-10}$ (Na), $6{,}27\times10^{-10}$––$7{,}43\times10^{-10}$ (K), $6{,}44\times10^{-10}$–$8{,}94\times10^{-10}$ (Ca) i $3{,}47\times10^{-10}$–$5{,}66\times10^{-10}$ (Mg). Korišćenjem razvijenih matematičkih modela dobijene su vrednosti efektivnih koeficijenata difuzije, sa tačnošću izraženom preko koeficijenata determinacije (r^2) za D_w, D_{Suc}, D_{Na} . D_K, D_{Ca} i D_{Mg}, i to: 0,993; 0,998; 0,999; 0,992; 0,999 i 0,998, redom. Širok opseg procesnih promenljivih veličina razmatranih u formiranju ovih modela, kao i njihova laka implementacija u tabelarnim proračunima, čini ove modele veoma praktičnim za projektovanje i kontrolu procesa.

Ključne reči: Svinjsko meso • Melasa šećerne repe • Osmotski tretman • Difuzija • Prenos mase