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Influence of Fluid Concentration on Freezing Point Depression and Thermal Conductivity of Frozen Orange Juice

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ABSTRACT

The freezing point depression (FPD) of orange juice at different concentrations was measured by using a simple apparatus. Results showed that the initial freezing point decreased approximately 90% with the increase of juice concentration between 46° and 66°Brix (water content respectively between 52.8 and 32.8% w/w). The thermal conductivity of orange juice as a function of fluid concentration was also investigated by using a coaxial dual-cylinder apparatus. Below the freezing point, the thermal conductivity was strongly affected by both the orange juice concentration and temperature. Simple equations in terms of water content and temperature could be adjusted to experimental data of FPD and thermal conductivity.

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INTRODUCTION

For many years, orange juice has been produced in numerous forms, such as frozen concentrated, pasteurized juice, and more recently as fresh squeezed orange juice. Brazil is the largest orange producer and the 1998/1999-crop production was about 30% of total world production. Brazil is also the major producer and exporter of concentrated orange juice. The total export of concentrated orange juice in 2001/2002 was around 827,094 tons, mainly to European Union, Asia, and Mercosul.[1] These figures show the great importance of orange juice industry for Brazilian economy and justify research aiming to optimize the design and operation of the concentration processes.

Most unit operations involved in orange juice processing comprise heat transfer. Modeling and optimization of these operations are difficult, since juice physical properties change considerably with concentration and temperature.

The effect of temperature and water content on rheological and thermophysical properties—specific heat, thermal conductivity, thermal diffusivity and density—of orange juice above the initial freezing point has been studied in previous work.[2,3] Knowledge of thermal properties of frozen orange juice, however, is essential to calculate the temperature distribution during freezing and frozen storage, and to estimate the freezing time. Food engineers are interested in predicting freezing times in order to estimate the refrigeration requirements for freezing systems and to design the necessary equipment for effective processing. Minimization of the energy requirement, reliability, safety, and quality of the product must also be considered.[4]

According to Miyawaki and Pongsawatmanit[5] that investigated the effective thermal conductivity of aqueous solutions of glucose, sucrose, potato starch, gelatin and egg albumin in the frozen state, the best model to predict the effective thermal conductivity of frozen food was the Maxwell-Eucken model, with ice as the dispersed phase. These authors stated that thermal conductivity is also helpful in the analysis of the ice structure formed during freezing, which will be important to design and control of related operations, such as freeze-drying and freeze concentration.

Freeze-drying is a two-step dehydration process where the product is initially frozen and water is then removed by sublimation. Freeze dried foods present high-quality attributes, such as low bulk density, high porosity, superior taste, aroma retention, and rehydration properties than products obtained by alternative drying processes, including air, vacuum, microwave, and osmotic drying.[6] The freeze concentration is based on the separation of ice crystals formed during freezing of an aqueous solution, which results in the concentration of the remained fluid. This operation can be applied to heat sensitive liquid solutions, since it is carried out at low temperature, as well as to products containing aroma components, as it may be conducted in the absence of a gas phase. Fruit juices (especially citrus juice), beer, vinegar, coffee, and tea extracts have been commercially concentrated by freeze concentration. The major disadvantages of the process are the high capital costs and a limit in the maximum concentration degree of up to 55% due to increased product viscosity.[7–9]

The freezing point temperature relative to 0°C, also called "freezing point depression" (FPD), which increases with increasing solute concentration, is an important thermophysical property in freezing processes. In general, a food consists of product solids and water. As sensible heat is removed, the temperature of the mixture containing solids and water decreases. Just below the initial freezing point, the water begins to convert into ice.

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As more heat is removed, more of the water converts into ice, and the remaining solution becomes more concentrated in terms of product solids. Because of the higher solids concentration, the temperature at which freezing is depressed.[10]

Chen and Chen[11] determined the FPD of NaCl solutions at different concentrations and obtained results in the range of −10°C–0°C. They found that the solution concentration, sample size, supercooling, and location of the measuring point could all affect this property. Freezing point data are also available for some other aqueous solutions, milk and coffee extract.[12–14]

The aim of this work was to measure the FPD of orange juice at different concentrations by using a simple experimental apparatus, as well as measuring the thermal conductivity of frozen orange juice as affected by fluid concentration and temperature.

MATERIAL AND METHODS

Sample Preparation

All the experimental measurements were made with samples prepared from the same batch of concentrated orange juice (66.2°Brix and 0.345% w/w pectin), produced with orange cv. Pera-Rio in a 7-stage TASTE® evaporator and stored at −18°C. In order to obtain different water contents, the concentrated juice was diluted with distilled water.

Experimental Apparatus and Measurement Procedure

Freezing Point Depression

A schematic diagram of the apparatus used for experimental measurement of the FPD, similar to that described by Chen and Chen,[11] is shown in Fig. 1. It consists of two major sections: a freezing vessel and a data acquisition system. The freezing vessel is a Dewar flask containing liquid nitrogen, closed with an inverted aluminum cone supported by a polystyrene cap. The aluminum cone has an angle of 90°, wall thickness of 1 mm, and largest diameter of 4 cm. Each experiment was carried out by supplying the orange juice to the bottom of the cone, which was then cooled by the evaporating nitrogen inside the Dewar flask. The temperature of the sample contained in the cone was measured by a thermocouple fixed on a lab stand. The thermocouple was placed at a distance of 5 mm from the cone bottom and was connected to a temperature transmitter (Model TT302, SMAR, Sertãozinho, SP, Brazil).

Effective Thermal Conductivity

The system used to measure thermal conductivity is a coaxial dual-cylinder apparatus and is schematically shown in Fig. 2. This method was originally presented by Bellet et al.[15] and was already used by Telis-Romero et al.[2,16] for measuring thermal conductivity of orange juice above the freezing point. The heater is a uniformly distributed electric resistance inserted along the axis of the inner cylinder (220 mm long and 20 mm in diameter) to provide a radial heat flux. Samples were loaded into the annular space

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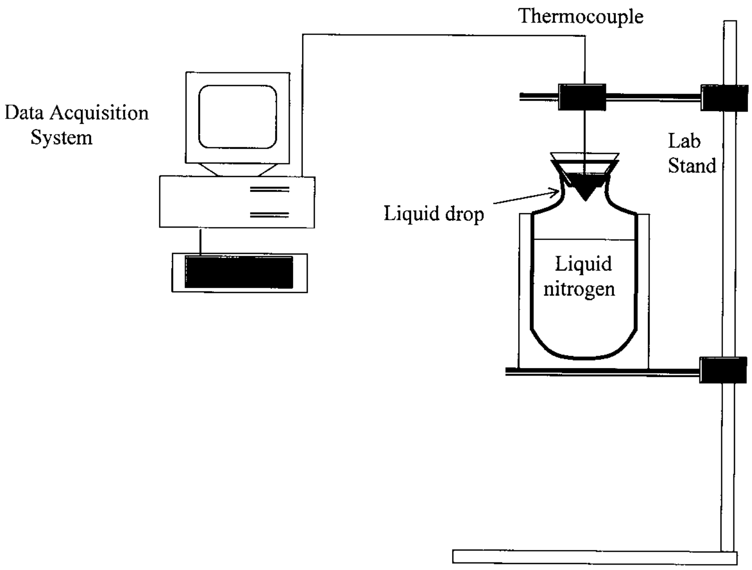

Figure 1. Schematic diagram of the apparatus used for measuring freezing point depression.

between the inner and outer cylinders (inner diameter of 42 mm and length of 220 mm), with both ends being fitted with nylon stoppers to prevent axial heat transfer. Before being loaded, samples were degassed under vacuum for 20 min to remove air bubbles. Only 95% of the available volume was filled with sample in order to allow for expansion during freezing. The apparatus was then immersed in a thermostatic bath (Model MA-184, Marconi, São Paulo, Brazil) containing ethyl alcohol. The power input to the heater resistance was made by means of a laboratory DC power supply (Model MPS-3006D, Minipa, São Paulo, Brazil), which permitted to adjust the current with a stability of 0.05%. Temperatures were monitored with an accuracy of 0.6°C by a HP data logger model 75.000-B, an interface HP-IB and a HP-PC running a data acquisition program written in IBASIC. In order to measure temperature, respectively one and three copper-constantan thermocouples were embedded at the surfaces of the inner and outer cylinders.

In the steady state, conduction inside the cell is described by the Fourier equation in cylindrical coordinates, with boundary conditions corresponding to heat transfer between two concentric cylindrical surfaces kept at constant temperatures, as given by Eqs. (1)–(3).

$$\frac{\partial \dot{q}}{\partial S} = -\lambda(T)\frac{\partial T}{\partial r} \quad (1)$$

$$T(r = R_1) = T_1 \quad (2)$$

$$T(r = R_2) = T_2 \quad (3)$$

were $\dot{q}$ is the heat flux in the thermal resistance (W), r the radius (m), R_1 and R_2 respectively the external and internal radius of the cylinder (m), S the surface area of a cylinder of radius r (m^2), T the temperature (°C), T_1 the steady state temperature at the internal cylinder (°C), T_2 the steady state temperature in the thermostatic bath where cell

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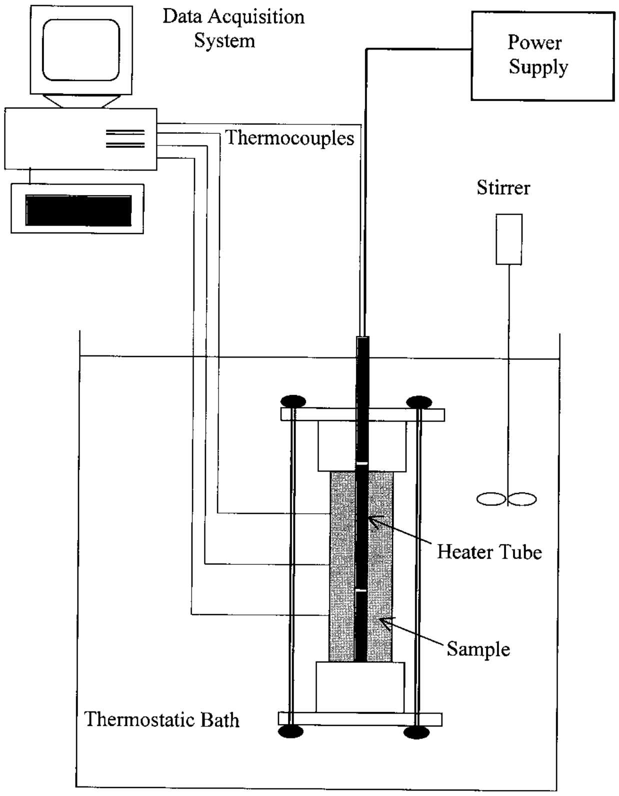

Figure 2. Schematic diagram of the apparatus used for measuring effective thermal conductivity.

was immersed (°C), and λ the thermal conductivity of the sample at the average temperature $(T_1 + T_2)/2$ (W/m °C).

According to Bellet et al.,[15] Eq. (1) can be integrated as

$$\lambda = \dot{q}\frac{\log(R_2/R_1)}{2\pi(T_1 - T_2)} \quad (4)$$

permitting to calculate the sample thermal conductivity, λ, from experimental measurements of T_1 and T_2 under steady state conditions.

RESULTS AND DISCUSSION

Freezing Point Depression

The apparatus used for measuring FPD was calibrated by using ethylene glycol, which has a well-known FPD. Twenty-six replicated experiments were carried out and the average result is presented in Table 1, as well as a reference value reported by Perry and Chilton.[17]

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Table 1. Data obtained during calibration of the experimental apparatus for freezing point depression (FPD) and thermal conductivity.

Property	Experimental value	Standard deviation	Standard error	Reference value
FPD of pure ethylene glycol	−15.0°C	0.74°C	0.14°C	−15.6°C[a]
Thermal conductivity of water (−20°C)	2.280 W/m K	0.175 W/m K	0.034 W/m K	2.220 W/m K[b]

[a]Perry and Chilton.[17]
[b]Valentas et al.[20]

A very good agreement was observed between the experimental and reference values. The reproducibility of results was also satisfactory, as shown in the histogram of data distribution (Fig. 3) that presents a normal distribution of measurements around the average value. Values of the standard deviation (SD) and standard error (SE) were also included in Table 1.

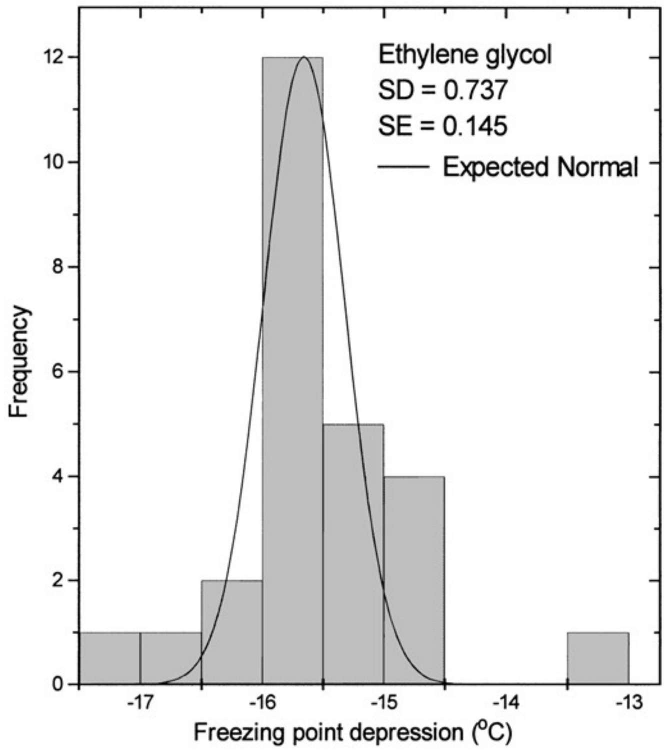

Figure 3. Distribution histogram of freezing point depression obtained for ethylene glycol and used for checking apparatus performance.

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Generally, it was expected that the larger the sample size, the slower the cooling process. This effect could interfere with the measurement of the initial freezing point and, in order to detect this source of experimental errors, samples of approximately 0.2, 0.3, 0.4, and 0.5 mL of orange juice at different concentrations (46°–66°Brix) were tested in separated runs. In these experiments the thermocouple position was fixed at about 5 mm from the bottom of the cone. The freezing curves were recorded and the set of curves corresponding to juice with 63.1°Brix is shown in Fig. 4. Once the liquid sample became solid (very fast in the case of a small sample), the temperature decreased. It was observed that the sample size did not have a large effect on the plateau temperature of the freezing curves and the initial freezing point was similar for all sample sizes. For the 63.1°Brix juice, values of the FPD obtained with different sample volumes varied in the small range of −16.21 to −16.42°C. Similar behavior was observed for the other tested concentrations.

The effect of thermocouple position on the measurement of FPD was also investigated. Figure 5 shows the freezing curves obtained with the thermocouple placed at distances varying from 2 to 5 mm from the cone bottom. The freezing curves were not affected by the different positions of the temperature measuring point. Nevertheless, Chen and Chen[11] observed some different plateau temperatures in the freezing curves measured at different positions within NaCl solutions. The authors have explained this result by considering that the solvent near the measuring point was frozen very quickly to permit detection of the initial freezing point.

Taking into account that the freezing curves were not affected by thermocouple position and sample volume, FPD of the orange juice at different concentrations was measured with a fixed sample volume of 0.5 mL and thermocouple placed at 5 mm from the cone bottom. As expected, the initial freezing point decreased with increasing juice

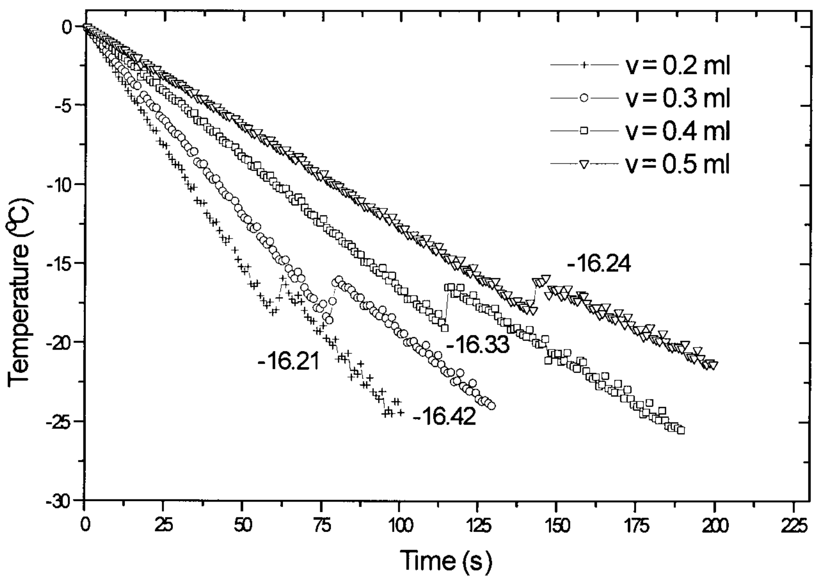

Figure 4. Freezing curves of orange juice (63.1°Brix) determined with different sample volumes. Thermocouple placed at 5 mm from cone bottom.

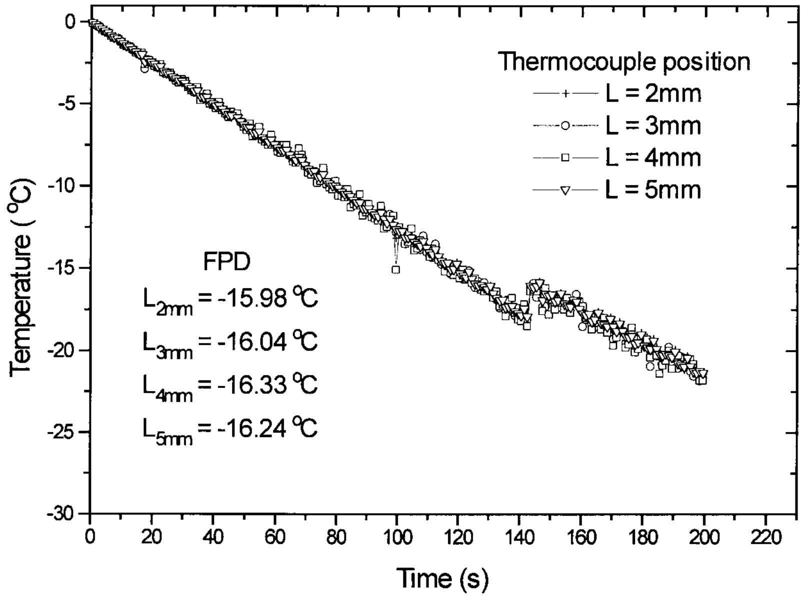

Figure 5. Freezing curves of orange juice (63.1°Brix) determined with different thermocouple positions. Sample volume of 0.5 mL.

concentration between 46° and 66°Brix (Table 2). The results showed that the FPD increased about 90% with a 43% increase in juice concentration. Chen and Chen[11] studied the FPD in solutions of different NaCl concentrations and observed a decrease of about 60% in the initial freezing point when the NaCl concentration increased from 5.93% to 13.86%.

The model presented by Miles et al.,[18] which express the initial freezing point as a function of sample moisture content, could have been satisfactorily fitted to experimental values. This adjustment resulted in Eq. (5), with a determination coefficient (r^2) of 0.996:

$$T_f = \frac{13.498(1 - X_W)}{0.792(1 - X_W) - 1} \tag{5}$$

Table 2. Freezing point depression at different orange juice concentrations.

Water content (% w/w)	°Brix	Freezing point depression (°C)	Standard deviation (°C)	Standard error (°C)
32.8	66.0	−18.83	0.77	0.29
35.7	63.1	−16.83	0.57	0.22
40.6	58.2	−14.43	0.57	0.21
43.1	55.7	−13.73	0.49	0.18
49.2	49.6	−10.86	0.85	0.32
52.8	46.0	−9.89	0.29	0.11

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Thermal Conductivity

The performance of the coaxial dual-cylinder apparatus was checked for accuracy according to the procedure indicated by Pongsawatmanit et al.[19] that used pure water containing 0.5% agar to prevent the convection effect during experiments in the range of 0° to −30°C. An analysis of the influence of temperature difference across the sample on the measured thermal conductivity was conducted by varying the heat flux applied to the heater and the temperature of the water bath. Current values of 0.33, 0.96, 1.52, 2.08, 2.56, 3.14, and 3.84 ampere were applied, whereas bath temperatures of −20 and −10°C were tested to determine the optimum temperature difference. Figure 6 shows the observed temperature difference across the water sample and the measured thermal conductivity of ice as a function of the heat flux. A temperature difference between 0.8 and 3.2°C did not have a significant effect on the observed thermal conductivity for all range of heat flux (0.33–3.84 ampere). As expected, the increase of heat flux produced an increasing of temperature difference, but this behavior was independent of the bath temperature. The measured thermal conductivity of water is presented in Table 1, as well as a reference value reported by Valentas et al.[20] Values of the standard deviation and standard error are also included. The experimental error found in the water thermal conductivity was less than 2%. Tables 3 and 4 and Fig. 7 present the thermal conductivity of orange juice at different temperatures (0° to −26°C) and sample concentrations (46°–66°Brix).

It is observed that above the freezing point, the thermal conductivity had a low decrease with increasing concentration and was almost independent of temperature (Table 3). The concentration effect may be due to the lower intrinsic thermal conductivity of the solute compared with that of water. Equation (6), which was obtained by

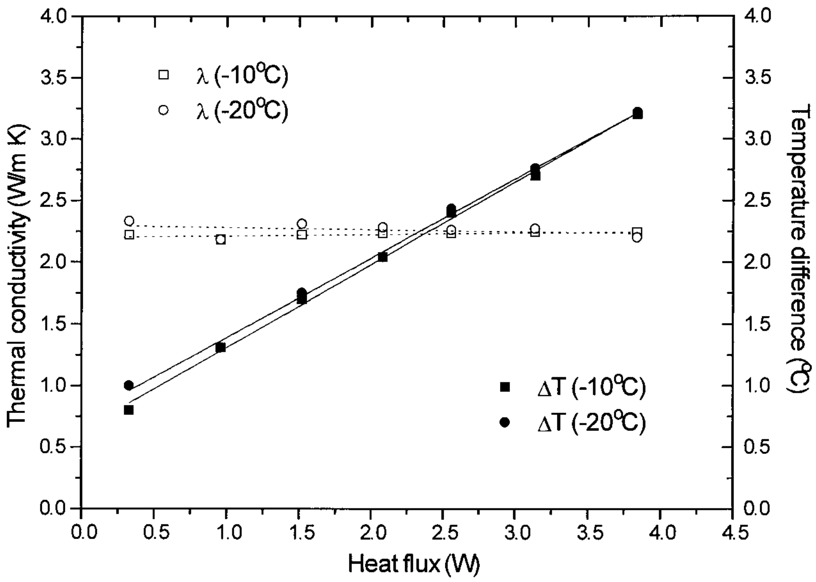

Figure 6. Effect of heat flux on thermal conductivity of ice and on temperature difference across the sample.

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Table 3. Thermal conductivity at different orange juice concentrations and temperatures above freezing point.

Water content		Temperature (°C)									
(% w/w)	°Brix	−18	−16	−14	−12	−10	−8	−6	−4	−2	0
		Thermal conductivity (W/m K)									
32.8	66.0	0.252	0.249	0.253	0.248	0.255	0.254	0.251	0.255	0.257	0.257
35.7	63.1	—	0.263	0.270	0.261	0.274	0.269	0.263	0.271	0.272	0.271
40.6	58.2	—	—	0.289	0.286	0.300	0.295	0.287	0.290	0.304	0.297
43.1	55.7	—	—	—	0.305	0.306	0.308	0.301	0.315	0.312	0.305
49.2	49.6	—	—	—	—	0.335	0.341	0.328	0.351	0.345	0.333
52.8	46.0	—	—	—	—	0.348	0.360	0.364	0.350	0.357	0.368

Table 4. Thermal conductivity at different orange juice concentrations and temperatures below freezing point.

Water content (% w/w)	°Brix	Temperature (°C)							
		−26	−24	−22	−20	−18	−16	−14	−12
		Thermal conductivity (W/m K)							
32.8	66.0	0.405	0.372	0.325	0.280	—	—	—	—
35.7	63.1	0.455	0.426	0.370	0.334	0.278	—	—	—
40.6	58.2	0.538	0.528	0.476	0.414	0.365	0.291	—	—
43.1	55.7	0.601	0.567	0.524	0.472	0.430	0.349	0.285	—
49.2	49.6	0.759	0.709	0.648	0.606	0.570	0.505	0.403	0.348
52.8	46.0	0.787	0.805	0.739	0.704	0.676	0.606	0.513	0.423
		Frozen water fraction[a]							
32.8	66.0	0.091	0.071	0.048	0.019	—	—	—	—
35.7	63.1	0.127	0.108	0.085	0.057	0.023	—	—	—
40.6	58.2	0.181	0.162	0.140	0.113	0.081	0.040	—	—
43.1	55.7	0.205	0.186	0.164	0.136	0.103	0.062	0.008	—
49.2	49.6	0.289	0.272	0.251	0.227	0.197	0.159	0.111	0.047
52.8	46.0	0.330	0.313	0.293	0.269	0.240	0.203	0.156	0.094

[a]Estimated by Eq. (7).

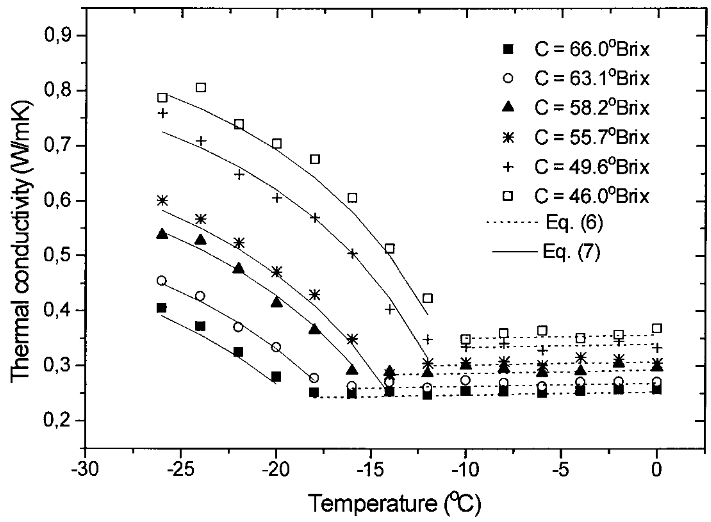

Figure 7. Thermal conductivity of orange juice at different temperatures and concentrations.

Telis-Romero et al.[2] and depends on water fraction (X_W) and temperature, was adjusted to experimental data above freezing point.

$$\lambda = 0.0797 + 0.5238(X_W) + 5.8 \times 10^{-4}(T) \tag{6}$$

In the frozen state, however, the thermal conductivity was strongly affected by both juice concentration and temperature (Table 4). Thermal conductivity increased with decreasing concentration and temperature. This behavior is a consequence of the higher fraction of ice present in the more diluted samples exposed to temperatures well below their initial freezing point. Schwartzberg[21] presented a mathematical study of the food freezing process and reported that the thermal conductivity of ice is roughly 3.7 times as large as that of water, what explains the marked increase in thermal conductivity of foods during freezing.

In order to allow for analysis of the quantitative effect of frozen water fraction on thermal conductivity below the initial freezing point, the Van Beek equation [Eq. (7)], presented by Miles et al.,[18] was used to estimate the corresponding values, which were included in Table 4.

$$X_{\text{ice}} = X_W\left(1 - \frac{T_f}{T}\right) \tag{7}$$

In the above equation, T and T_f are respectively the sample temperature and the initial freezing temperature (°C). The experimental results of thermal conductivity below freezing point could be described by the Fikiin equation,[18] which was fitted to the experimental data by a multiple regression procedure and resulted in a determination coefficient of 0.986. Comparison of Eqs. (7) and (8) reveals that, except for the constants, they exhibit the same dependence of temperature and water fraction, reinforcing the conclusion that the

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frozen water fraction is the main factor affecting thermal conductivity in the frozen domain.

$$\lambda = 1.717 X_W \left(1 - \frac{T_f}{T}\right) + 0.234 \tag{8}$$

CONCLUSIONS

A simple apparatus could have been used in the accurate measurement of FPD of orange juice. It was shown that the freezing curves were not affected by thermocouple position and sample volume. The average value of FPD varied between -9.89 and -18.83°C for orange juice concentrations in the range of 46°–66°Brix. As expected, the initial freezing point decreased with increasing orange juice concentration. The coaxial dual-cylinder method was applied with good accuracy to measuring the effective thermal conductivity of frozen orange juice at different concentrations. In the frozen state, the thermal conductivity decreased with increasing concentration and temperature. The mass fraction of ice in the orange juice increased during freezing, causing an increase in the thermal conductivity of the aqueous mixture due to the higher thermal conductivity of ice compared to that of pure water.

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