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Influence of Temperature and Water and Fat Contents on the Thermophysical Properties of Milk

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Heat capacity, thermal conductivity, and density of whole milk, skimmed milk, and partially skimmed milk were determined at concentrations varying from (72.0 to 92.0) mass % water content and from (0.1 to 7.8) mass % fat content, at temperatures ranging from (275.15 to 344.15) K. Heat capacity and thermal conductivity varied from (3.4 to 4.1) $J \cdot g^{-1} \cdot K^{-1}$ and from (0.5 to 0.6) $W \cdot m^{-1} \cdot K^{-1}$, respectively. Density varied from (1011.8 to 1049.5) $kg \cdot m^{-3}$. Polynomial functions were used to model the dependence of the properties upon the studied variables. A linear relationship was obtained for all the properties. In the tested range, water content exhibited a greater influence on the properties, while fat content showed a smaller influence.

Introduction

Milk is one of the main sources of nutrients worldwide, providing macro- and micronutrients necessary for human growth. It is composed basically of water (87.0 mass %), proteins (3.5 mass %), lipids (3.0 mass %), and lactose (4.5 mass %). Due to its chemical composition, it is an excellent medium for the development of microorganisms, desirable or not. Under refrigerated conditions, the development of psycrotrophics is possible, which can deteriorate milk, even after pasteurization.[1] In Brazil, contamination of pasteurized milk maintained under refrigeration is related to psycrotrophic acidifying bacteria. These bacteria are resistant to thermal treatment (HTST—high temperature, short time), resulting in sensory and chemical modifications and health and cost problems.[1] Thermal treatment is considered to be an efficient method for milk conservation, maintaining its initial sensory and chemical properties when properly controlled. An excessive treatment may affect its taste, producing off-flavors and color changes. On the other hand, if the thermal treatment is not sufficient, microorganisms will deteriorate milk.

Modeling the thermal processing has been utilized for design, control, and optimization purposes. The design and control of equipment are difficult due to the lack of information on the behavior of the thermophysical properties with composition and temperature. Simulation fails since the models derived from the concepts of material conservation need such information. Equipment size is usually overestimated to compensate for this lack of information, leading to a nonideal design with cost implications as well as inferior quality of the product.

Heat capacity (c_P), thermal conductivity (k), and density (ρ) are important parameters to determine the rate of heat transfer, to design equipment or its parts, and, in computer simulation, to analyze, optimize, and control several food processing operations such as pumping, heating, cooling/freezing, drying, and evaporation. A generalized correlation to predict the thermal characteristics of a food system has not been described in the literature, probably due to the physical complexity of food matrixes. Since the prediction of thermal properties based on a theoretical foundation is difficult, experimental measurements have been made.[2]

Thermophysical properties for a number of liquid foods such as tomato juice,[3] apple juice,[4] orange juice,[5] and coffee extract[6] have been reported in the literature. Reddy and Datta[7] determined heat capacity, thermal conductivity, and apparent viscosity of reconstituted milk between (40 to 70) mass % total solids and temperatures of (35 to 65) °C. Kessler[8] reported values of different properties of whole milk and skimmed milk, including viscosity, heat capacity, thermal conductivity, density, and interfacial tension, in the range of (0 to 100) °C.

Different measurement techniques of c_P, k, and ρ of foods have been reported in the literature.[9,10] Heat capacity measurements are often conducted using calorimeters.[7,11] The differential scanning calorimeter is often used.[4,12] Thermal conductivity can be determined by a simple method, according to Bellet *et al.*[13] The great advantage of this technique is that it is possible to determine c_P employing the same device and modeling the unsteady state heat transfer in the system.

This work addresses the measurements of c_P, k, and ρ of milk as a function of temperature and water and fat contents and develops empirical correlations for predicting these properties under different conditions.

Experimental Section

Materials. Bovine milk was initially concentrated in a rotoevaporator. Samples of whole milk, skimmed milk, and partially skimmed milk were prepared by diluting the concentrated milk with distilled water to obtain a range of concentration. An analytical balance was used with a give uncertainty of ±0.0001 g. Statistical analyses were made using the SAS statistical package.[14] The suitability

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Table 1. Values for the Thermophysical Properties of Milk for Different Temperatures and w_f Values ($w_w = 0.72$)

	$w_f = 0.0044$			$w_f = 0.0481$			$w_f = 0.0771$		
T/K	c_P/J·g^{-1}·K^{-1}	k/W·m^{-1}·K^{-1}	ρ/kg·m^{-3}	c_P/J·g^{-1}·K^{-1}	k/W·m^{-1}·K^{-1}	ρ/kg·m^{-3}	c_P/J·g^{-1}·K^{-1}	k/W·m^{-1}·K^{-1}	ρ/kg·m^{-3}
275.15	3.527	0.477	1049.5	3.472	0.475	1048.4	3.369	0.462	1046.3
281.15	3.476	0.477	1048.5	3.422	0.475	1045.3	3.391	0.471	1044.2
288.15	3.499	0.488	1045.1	3.448	0.486	1042.8	3.434	0.485	1041.9
293.15	3.518	0.495	1044.4	3.530	0.496	1040.1	3.464	0.493	1039.1
303.15	3.572	0.508	1040.0	3.555	0.505	1036.7	3.457	0.511	1035.7
314.15	3.622	0.524	1036.1	3.537	0.518	1032.9	3.495	0.523	1033.1
323.15	3.684	0.529	1032.0	3.623	0.531	1031.1	3.544	0.524	1031.1
333.15	3.709	0.539	1028.7	3.652	0.541	1028.7	3.590	0.541	1026.7
344.15	3.690	0.550	1024.9	3.694	0.554	1023.9	3.658	0.548	1022.9

of the fitted models was evaluated by the coefficient of determination (R^2), the level of significance (p), and residual analysis.

Apparatus and Methods. (a) Thermal Conductivity. Thermal conductivity at different milk compositions and temperatures was measured according to the method described by Bellet *et al.*[13] This technique uses a cylindrical cell[5,13] composed of two coaxial cylinders whose annular space is filled with the liquid whose properties are to be determined.

To keep the external temperature constant, the cell was immersed in a constant temperature water bath controlled within ±0.05 K. The power input to the heater resistance inserted inside the inner cylinder was conducted using a microprocessed, stabilized source which allowed the adjustment of the current with a stability of 0.05%. Temperature was monitored using a data logger with an accuracy of 0.6 K. Calibration of the cell was performed with distilled water and glycerin according to Romero *et al.*[5]

Under steady-state conditions, conduction inside the cell was 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.

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

$$T|_{R_1} = T_1 \tag{2}$$

$$T|_{R_2} = T_2 \tag{3}$$

where $\dot{q}$ is the heat flux, S is the area across which heat is transferred, r is a radial position, R_1 is the inner cylinder external radius, R_2 is the outer cylinder internal radius, and T_1 and T_2 are the inner cylinder and bath temperatures, respectively.

Integration of eq 1 with the boundary conditions in eqs 2 and 3 gives

$$k = \dot{q}\frac{\log\left(\frac{R_2}{R_1}\right)}{2\pi L(T_1 - T_2)} \tag{4}$$

where L is the length of the cell.

(b) Heat Capacity. The apparatus described above was also used to measure heat capacity, according to the method proposed by Dickerson.[15] Considering unsteady heat conduction through an isotropic, homogeneous medium, the equation of energy conservation can be written as

$$\frac{\partial T}{\partial t} = \frac{k}{\rho c_P}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) \tag{5}$$

with the initial and boundary conditions

$$T|_{r,0} = T_2 \tag{6}$$

$$T|_{R_2,t} = T_2 \tag{7}$$

$$\left(\frac{\partial T}{\partial r}\right)_{R_0,t} = -\frac{\dot{q}}{2\pi R_0 L k'} \tag{8}$$

$$k'\left(\frac{\partial \bar{T}}{\partial r}\right)_{R_1,t} = k\left(\frac{\partial T}{\partial r}\right)_{R_1,t} \tag{9}$$

where t is the time, $\bar{T}$ is the temperature of the cell, R_0 is the inner cylinder internal radius, and k' is the conductivity of the cell material (copper).

Equations 6−9 assume that the system is under thermal equilibrium, the surrounding temperature is constant, the heat flux at the heater is constant and uniform, and the heat flux is continuous at the sample/cell interface. Solution of eq 5 gives the time and space temperature distribution in the annular space between two infinite length coaxial cylinders. Details of the model solution and experimental procedure were presented elsewhere.[5,13]

(c) Density. Gravimetric determination of milk density at different temperatures and compositions was conducted, using an analytical balance with a give uncertainty of ±0.0001 g and a standard volumetric pycnometer. The pycnometer of 25.0 mL was previously calibrated with distilled water, at each temperature.

Results and Discussion

A series of experiments were designed to examine the influence of temperature and water and fat contents on thermal conductivity, heat capacity, and density of whole milk, partial skimmed milk, and skimmed milk. The temperature and fat content varied from (275.15 to 344.15) K and from (0.1 to 7.6) mass %, respectively, with water contents of (72.0, 84.0, and 92.0) mass %. Thus, a total of 81 experimental values were determined for each physical property.

Tables 1−3 include experimental values for specific heat, thermal conductivity, and density for the systen studied as related to temperature and fat and water contents of milk.

Polynomial models were fitted to the data, dependent upon both temperature and water and fat contents. Initially, the complete quadratic model was evaluated and the nonsignificant coefficients were discarded, on the basis of a t (student) test and $p > 0.05$. All fitted functions, described as a linear equation (eq 10) had $R^2 \geq 0.96$ and $p < 0.0001$. Table 4 shows the coefficients of eq10 for ρ, c_P, and k

$$\psi = a + bT + cw_w + dw_f \tag{10}$$

Table 2. Values for the Thermophysical Properties of Milk for Different Temperatures and w_f Values (w_w = 0.84)

	$w_f = 0.0044$			$w_f = 0.0481$			$w_f = 0.0771$		
T/K	c_P/J·g^{-1}·K^{-1}	k/W·m^{-1}·K^{-1}	ρ/kg·m^{-3}	c_P/J·g^{-1}·K^{-1}	k/W·m^{-1}·K^{-1}	ρ/kg·m^{-3}	c_P/J·g^{-1}·K^{-1}	k/W·m^{-1}·K^{-1}	ρ/kg·m^{-3}
275.15	3.840	0.514	1044.4	3.750	0.507	1041.1	3.776	0.511	1040.2
281.15	3.886	0.532	1041.3	3.821	0.529	1038.0	3.780	0.523	1039.2
288.15	3.891	0.545	1038.8	3.762	0.533	1035.7	3.736	0.530	1035.8
293.15	3.842	0.546	1036.1	3.775	0.543	1034.0	3.805	0.548	1034.1
303.15	3.923	0.572	1032.8	3.816	0.563	1031.8	3.820	0.564	1029.8
314.15	3.869	0.577	1029.0	3.809	0.574	1029.1	3.836	0.579	1026.0
323.15	3.889	0.588	1027.1	3.829	0.585	1025.0	3.825	0.585	1022.9
333.15	3.932	0.600	1024.8	3.870	0.597	1022.7	3.863	0.596	1020.7
344.15	3.968	0.609	1020.1	3.906	0.606	1018.0	3.852	0.598	1018.0

Table 3. Values for the Thermophysical Properties of Milk for Different Temperatures and w_f Values (w_w = 0.92)

	$w_f = 0.0044$			$w_f = 0.0481$			$w_f = 0.0771$		
T/K	c_P/J·g^{-1}·K^{-1}	k/W·m^{-1}·K^{-1}	ρ/kg·m^{-3}	c_P/J·g^{-1}·K^{-1}	k/W·m^{-1}·K^{-1}	ρ/kg·m^{-3}	c_P/J·g^{-1}·K^{-1}	k/W·m^{-1}·K^{-1}	ρ/kg·m^{-3}
275.15	4.098	0.544	1039.2	3.962	0.532	1037.0	3.923	0.531	1036.1
281.15	4.042	0.552	1038.2	3.971	0.548	1036.1	3.932	0.547	1035.1
288.15	4.114	0.578	1034.8	4.002	0.568	1032.7	3.962	0.559	1031.7
293.15	4.123	0.590	1033.1	3.978	0.575	1032.0	3.982	0.571	1031.1
303.15	4.124	0.608	1030.8	3.991	0.595	1027.7	4.027	0.593	1026.7
314.15	4.073	0.616	1026.1	4.025	0.616	1025.0	4.029	0.606	1022.9
323.15	4.069	0.637	1023.0	4.050	0.629	1020.9	3.978	0.617	1018.9
333.15	4.082	0.641	1020.7	4.095	0.644	1018.6	4.051	0.630	1015.5
344.15	4.117	0.641	1016.0	4.097	0.648	1013.9	3.984	0.638	1011.8

Table 4. Coefficients of Eq 10

	a	b	c	d	R^2
ρ/kg·m^{-3}	1185.64 ± 2.08	−0.341 ± 0.005	−58.239 ± 1.616	−58.107 ± 5.517	0.986
c_P/J·g^{-1}·K^{-1}	1.4017 ± 0.0906	0.0021 ± 0.0002	2.1816 ± 0.0704	−1.7430 ± 0.24	0.962
k/W·m^{-1}·K^{-1}	−0.2154 ± 0.0163	0.0014 ± 0.0001	0.4171 ± 0.0127	−0.0942 ± 0.0433	0.9740

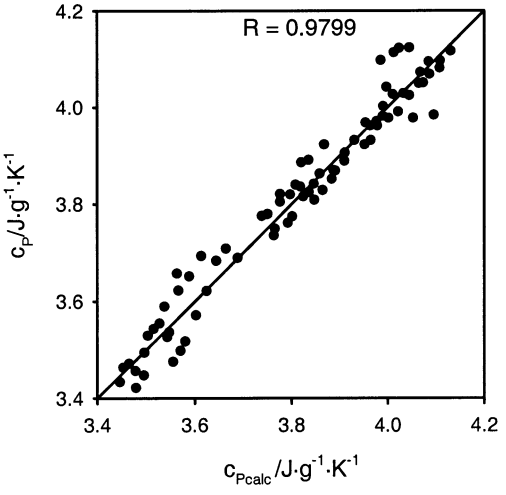

Figure 1. Plot of observed versus calculated values for heat capacity.

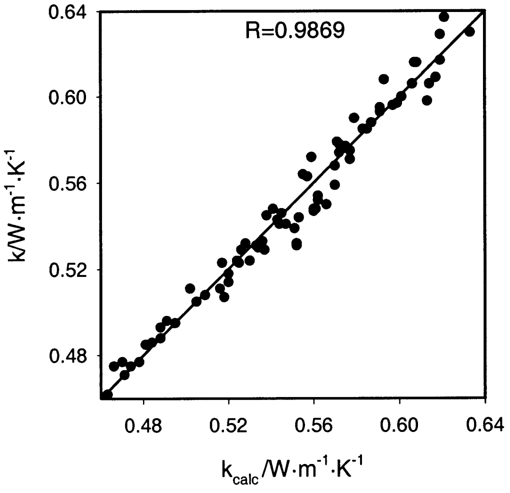

Figure 2. Plot of observed versus calculated values for thermal conductivity.

where ψ is the property, w_w is the water content, and w_f is the fat content.

Figures 1−3 show the residual analysis for the properties studied, indicating a good adjustment of the models. The correlation coefficient is depicted in the figures, and it is noted that they had values around 0.98, indicating the quality of the adjustment.

Density varied from (1011.8 to 1049.5) kg·m^{-3}. Heat capacity and conductivity varied from (3.4 to 4.1) J·g^{-1}·K^{-1} and from (0.5 to 0.6) W·m^{-1}·K^{-1}, respectively. Kessler[8] reports values for the same properties in the range of (0 to 80) °C. For whole milk and skimmed milk they found values for density of (1000 to 1034) kg·m^{-3} and (1010 to 1040) kg·m^{-3}, respectively. For whole milk they found values for heat capacity and thermal conductivity of (3.85 to 4.0) J·g^{-1}·K^{-1} and (0.53 to 0.64) W·m^{-1}·K^{-1}.

It was observed that k and c_P increased linearly with increase in both temperature and water content. Telis-Romero *et al.*[5,6] found a similar dependence of these properties, working with orange juice and coffee extract.

In all cases, w_w exhibited a stronger influence on the analyzed properties, while changes of T and w_f affected them slightly. Several works dealing with physical properties of foods reported the same behavior.[3−7] Despite the lower effect of w_f on the properties, this variable was maintained in the model because a few outlier points appeared when it was not included.

Conclusion

Simple linear polynomial functions relating the thermophysical properties of milk (k, ρ, and c_P) to temperature, water content, and fat content were fitted with good

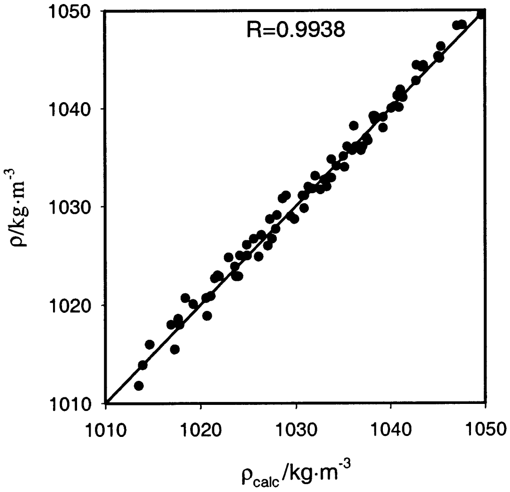

Figure 3. Plot of observed versus calculated values for density.

accuracy to the data. Water content had a large influence on the properties while fat content was the least significant. On the basis of these results, the proposed equations can be used for the calculation of the properties of milk.

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