EFFECT OF TEMPERATURE ON PHYSICAL PROPERTIES OF CANADIAN MAPLE (*Acer saccharum Marsh.*) SYRUP

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Abstract: The optimization of industrial operations require knowledge of thermodynamics related to process, which can be determined either experimentally or by prediction based on an appropriate model and a set of data. Although maple syrup is almost an unprocessed natural product, its industrial manufacture applies usual chemical-mechanical fluid operations, then appropriate equipment design are conditioned by sufficient information on mixing thermodynamics. In this paper, we analyze the temperature effect on the maple syrup and its aqueous dilution in terms of different properties, trying to explain their special physico-chemical behavior to explore the strength of the interactions among heavy covalent macromolecules and shorter chain polar solvent.

Keywords: Food engineering, Canadian maple syrup, Thermodynamic properties; Theoretical model

EFEITO DA TEMPERATURA NAS PROPRIEDADES FÍSICAS DE SAROPE DE BORDO (*Acer saccharum Marsh.*) CANADENSE

Resumo: A otimização de operações unitárias industriais necessita informação termodinâmica relativa aos processos, que pode ser adquirida experimentalmente ou de forma teórica usando um modelo matemático e um conjunto básico de dados. Mesmo sendo o xarope de bordo um produto natural considerado em termos nutricionais e de alto valor agregado, quase sem processamento industrial, a indústria de manufatura aplica igualmente operações e processos típicos de engenharia mecânica e química, sendo o desenho dos equipamentos condicionado ao conhecimento básico de propriedades termodinâmicas do produto. Neste trabalho, analisamos o efeito da temperatura no xarope de bordo canadense e a suas diluições em água em termos de volumetria e características acústicas, tentando explicar o seu comportamento físico-químico especial, analisando as interações entre as macromoléculas solúveis e solvente polar.

Palavras-chave: Engenharia de alimentos; Xarope de bordo canadense; Propriedades termodinâmicas; Modelo teórico

1. INTRODUCTION

Canada produces more than 78 per cent of the world's maple syrup. In 2016, Canadian producers exported 45 million kg of maple products, with a value of US$381 million. Canada's share of the world's maple production increased by over 225 per cent in the last decade, exporting to over 50 countries. The most important export market is the United States, to which Canadian producers send 65 per cent of total exports. Other principal markets are Germany (11%), Japan (7%), United Kingdom (4%), Australia (4%) and France (4%). The chemical complexity of taste of maple syrup is not completely known yet. Flavor compounds of maple syrup include volatile phenolic compounds, carbonyl compounds and alkylpyrazines [1], typical products of the advanced stages of the Maillard reaction, have been the subject of numerous studies because of the impact on flavour and color of different foods [2]. The most widely accepted mechanism for the formation of pyrazines in food systems is via the Strecker degradation of amino acids which in the presence of α-diketones result in the formation of α-aminoketones and Strecker aldehydes [3]. The formation of pyrazine compounds is considered to require sugar fragments. It was reported that alkaline conditions promote sugar fragmentation and resulted in an increased formation of pyrazines. These compounds, mostly found in heated foods, have organoleptic characteristics [4]. Different aminoacids [5] and sucrose, glucose or fructose [6-7] present in the maple sap, are the principle precursors of the pyrazines in maple syrup. Maple syrup is considered as a better alternative to traditional refined sugar among many other available natural sweeteners due to its oligoelements profile and high amount of bioactive compounds with well-known antioxidant potential action [8-10]. Despite its economical and nutritional importance of this natural product, only a few studies in the last years, have been developed closely related to chemical determination [11-12], the application of instrumentation techniques for quality control, adulteration and compounds identification [11, 12] or treatment procedures but most of them are related with narrow operational conditions and chemical constitution of maple sap or syrup but not with thermophysical characteristics, their temperature dependence and potential application on the industrial elaboration. In what is referred to the unit operation field, the optimization of industrial operations, require knowledge of the thermodynamics of compounds and mixtures related to process, which can be determined either experimentally or by prediction based on an appropriate model, and a set of data. Although maple syrup is almost an unprocessed natural product, its industrial manufacture applies usual chemical and mechanical fluid operations, then the optimization and adequate design of equipment are conditioned by a sufficient knowledge of mixing thermodynamics. Operations as pumping, evaporation or filtration are required for the sap treatment, a quality control during the process being applied, which is based on the evolution of physical properties of the sap throughout the process. In fact, refractive techniques are usual applied to determine the mature point of evaporation and the quality of the maple syrup, although no bibliographic data have been found in open literature.

In this paper we analyze the temperature effect (278.15-323.15 K) on the maple syrup and aqueous dilution of this product, in terms of density and isentropic compressibility, assuming that in the last steps of maple syrup concentration no significant chemical changes take place and only water is removed. We have attempted to explain the physico-chemical behaviour of the mixtures indicated above, to explore the strength and nature of the interactions among the complex evolved components. Due to the importance of theoretical on industrial design, the prediction of physical property values was realized applying different methods, for density a modified equation of Subbiah-Barber and an empirical equation for ultrasonic velocity, the obtained results being analyzed, and commented upon. Various parameters such as intermolecular free length (L_f), specific acoustic impedance (Z), van der Waals' constant (b), collision factor (S), and compressibility hydration number (n_h) were computed. The analysis of these volumetric and acoustic magnitudes pointed out the availability of intense effects among solute + solvent molecules at determined range of concentration and temperature. Attending to the deviation computed data, we arrive at the conclusion that the application of these models show close agreement with the experimental data reported in this paper. The present study of thermodynamics shows the strong dependence of these properties on temperature and the amazing trend of the isotherms, showing them as an accurate alternative procedure for determining the optimal point of syrup concentration by sap evaporation.

2. METHODOLOGY

Maine law requires maple syrup to be evaporated to a density greater than 66 percent Brix at 68 degrees F. Remember that syrup having a density reading below 66 percent Brix is illegal. Such syrup is more likely to ferment. With a density above 68 percent Brix it may crystallize, causing consumer complaint. Various instruments can be used to check the density: hydrometers, hydrotherms, refractometers, light transmittance meters or any others. While the particular grade of pure maple syrup is largely determined by color, it is essential that all grades of syrup meet minimum density standards. In most maple syrup producer countries the minimum allowable density of maple syrup is 66.0 percent by weight of soluble solids (66.0 degrees Brix at 68 degrees F). Although syrup density can be measured in three ways (1) weight, (2) use of an optical refractometer and (3) use of a hydrometer, only the refractometer and hydrometer methods are recommended for producer use. Weight of syrup may be used as an estimate of volume, but it is too imprecise to be used as an indicator of density. While the minimum syrup density of 66.0 degrees Brix is a legal requirement in most states, there are also several practical reasons for carefully controlling the finished density of maple syrup. Viscosity, a measure of a fluids resistance to flow is an important characteristic of maple syrup. Until the sugar concentration of maple sap exceeds 30 degrees Brix, an increase in sugar percentage has relatively little effect on viscosity. However, as the sugar concentration increases toward and through that of standard density syrup, the increase in viscosity is more pronounced. Maple syrup having a density only 0.5 degrees to 1 degrees Brix below standard density syrup feels and tastes thin. Conversely, an increase of only 1 degrees Brix above standard density causes the syrup to acquire a thick, pleasant feel to the tongue, and the perception of considerably increased sweetness. This explains why some producers finish their syrup slightly above standard syrup density; customers can tell the difference between 66 degrees and 67 degrees Brix and prefer the heavier syrup. Syrup density also affects how well quality is maintained when the syrup is stored. Light density syrup spoils faster. Syrup with a density of more than 67 degrees Brix may precipitate sugar crystals when stored at room temperature for extended periods. Finally, the higher the density at which syrup is finished, the less that can be made from a given amount of sap. Using a refractometer to determine the density of syrup by measuring its refractive index is a relative accurate, yet simple method. This possibility has been checked in earlier works for other kind of mixtures. A refractometer works by measuring the refractive index of a solution (syrup) which is directly related to the amount of dissolved solids (sugar) present in the solution. Refractometers are precise instruments and are particularly well suited for determining the density of syrup in Brix units at room temperatures. They are not well suited for measuring the density of hot syrup (180 degrees F and above) but are very convenient for larger operations which buy and sell syrup. They are also commonly used to determine the density of syrups entered in various competitions. But as far as we know, there is not exist open literature data of refraction for maple syrup, taking into account this magnitude is strong dependent on temperature. This fact potentially is the cause of wrong determination of optimal point of dehydration due to inaccurate data of refraction to translate experimental measurements and inaccuracy in controlling the temperature of samples to be measured. Moreover, the computation of density by means refraction leads to errors in the final density values. To avoid these problems, it is necessary the use of direct magnitude measurements and the disposable of its dependence with temperature.

2.1 Data treatment

The measured physical properties were correlated as a function of temperature using Eq. 1:

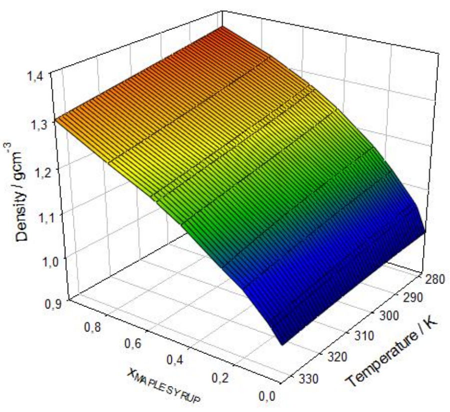
$$P = \sum_{i=0}^{N} A_i T^i \qquad (1)$$

where P is density (gcm^{-3}) or ultrasonic velocity (ms^{-1}), T is absolute temperature in Kelvin and A_i are fitting parameters. N stands for the extension of the mathematical serie, optimised by means of the Bevington test.

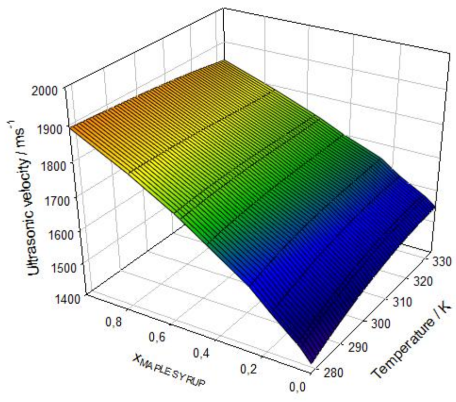
The fitting parameters were obtained by the unweighted least squared method applying a fitting Marquardt algorithm. The root mean square deviations were computed using Eq. 2, where z is the value of the property, and n_{DAT} is the number of experimental data.

$$\sigma = \left(\frac{\sum_{i=1}^{n_{\mathrm{DAT}}} \left(z_{\mathrm{exp}} - z_{\mathrm{pred}} \right)^2}{n_{\mathrm{DAT}}} \right)^{1/2} \qquad (2)$$

Figure 1. Effect of temperature for (a) density and (b) ultrasonic velocity of Canadian maple syrup + water



(a)



(b)

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In Figures 1a and 1b, the temperature trend of density and ultrasonic velocity are gathered.

3. RESULTS AND DISCUSSION

3.1 Derived properties

We have attempted to explain the physico-chemical behaviour of this mixture, in order to explore the strength and nature of the interactions between the components by deriving various thermodynamic parameters from the new collection of density and ultrasonic velocity. The parameters derived from the experimental measured data were intermolecular free length (L_f), specific acoustic impedance (Z), van der Waals' constant (b), and collision factor (S). As observed, intermolecular free length decreases from pure solvent (water) towards pure solute (maple syrup), showing the lowest values for low temperatures, as expected. While van der Waals constant gathers a linear performance in terms of composition or temperature effect, the specific acoustic impedance and collision factor show an inverse trend of the enclosed pure substances, mainly due to the nature of the complex collection of covalent molecules enclosed into the "maple syrup concept", showing how much resistance an ultrasound beam encounters as it passes though the liquid phase or, in other way, as the probability of collision among molecules rises for high concentration compositions and low temperatures.

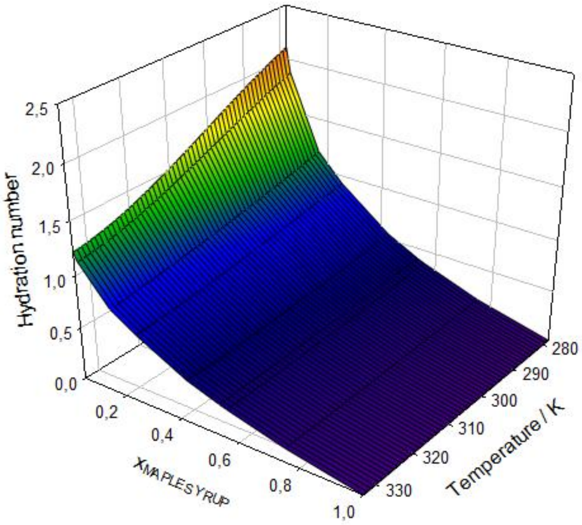
3.2 Compressibility hydration numbers

Despite solvation numbers of covalent molecules into aqueous solution are key parameters necessary when discussing intermolecular interactions or interfacial phenomena, these data are extremely scarce and dispersed into open literature. If the search for these data was related to other solvent than water, the situation is strongly still worse. Solvation numbers are based on isentropic compressibilities (computed by the Newton-Laplace equation from density and ultrasonic velocity), a parameter easily derived from acoustic measurements, as previously commented.
The compressibility solvation numbers or compressibility hydration numbers for aqueous environment, are calculated using the following equation, attending to usual expressions:

$$n_S = \left(\frac{n_{solvent}}{n_{solute}}\right)\cdot\left(1 - \frac{\kappa_S}{\kappa_{So}}\right) \tag{3}$$

where $n_{solvent}$ and n_{solute} are the mol number of solvent and solute into a binary mixture, respectively. The equation used for computing compressibility hydration number assumes that the solvation layer around the corresponding solute molecule is incompressible, which is not the case. Despite this, it provides an acceptable approximation of the extent of interaction of the solute or solutes with solvent. These parameters are derived from isentropic compressibility measurements and therefore, account for the first two layers of solvent around the solute. For example, Figure 2 shows the evolution of the compressibility hydration number for the mixture maple syrup + water as a function of temperature, gathering the strong diminution of disposable solvent molecules for establishment of layers around each theoretical solute molecule. As observed, only a slight effect is produced by variation of temperature at the studied range. When the temperature is increased, there is a corresponding decrease in the ultrasonic velocity for concentrated solutions and then, an increment of entropy of the system, the strongest values of solvation numbers being observed for low temperatures.

Figure 2. Effect of temperature for compressibility hydration number of Canadian maple syrup + water



3.3 Measured properties estimation

The physical property packages used in powerful chemical simulators typically rely on generalized equations for predicting properties as a function of temperature, pressure, etc. In the last few years, despite the success developing several procedures of density estimation for pure compounds or mixtures, really, only a few of them may be of practical application and high accuracy for fats and oils. The procedure proposed by Subbiah et al. for description of density of aqueous sucrose using a polynomic expansion has demonstrated to be accurate, only requiring a description of pure sucrose density dependence with temperature as suggested by Barber:

$$1/\rho = \sum_{i=1}^{N} \frac{w_i}{\rho_i} \quad (4)$$

$$\rho_{sucrose} = a + b \cdot w_{sucrose} + c \cdot w_{sucrose}^2$$

$$a = 1662.7 - 2.5025 \cdot T + 0.0306 \cdot T^2$$

$$b = -57.953 + 2.2511 \cdot T - 0.0417 \cdot T^2$$

$$c = -40$$

where ρ is the density of the mixture, w_i is the mass fraction of the mixture.

Ultrasonic velocity has been systematically measured in the last years but this kind of thermodynamic data is extremely scarce yet for biological solutions, specifically into food engineering. The experimental data were compared with the values obtained by the Junjie equation, which is dependent on the values of density and ultrasonic velocity of each component into mixture:

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$$u = \frac{\sum_{i=1}^{N} \left(x_i M_i / \rho_i \right)}{\left(\sum_{i=1}^{N} \left(x_i \cdot M_i \right) \right)^{1/2} \left(\sum_{i=1}^{N} \left(x_i M_i / \left(\rho_i^2 u_i^2 \right) \right) \right)^{1/2}} \quad (5)$$

where M_i is the molar mass of each component and x_i is the molar fraction composition. Table 2 shows the deviation of these estimation methods.

Table 2. Deviation of the estimation methods for density and ultrasonic velocity for the mixture Canadian maple syrup + water at 298.15 K

Mixture	Subbiah-Barber equation	Junjie equation
Maple Syrup + Water	0.18693 gcm^{-3}	33.81ms^{-1}

4. CONCLUSION

Maple syrup and sugars during refining are examples of complex solutions into high polar environment. The physical properties of such systems are necessary for an adequate design and optimization of processes and for a deeper understanding of the behavior of the final product. Literature shows limited disposable data and even less rigorous analysis of the physical properties of maple syrup. A fundamental thermodynamic approach provides an effective basis for the analysis and prediction of these properties. The main focus of this study was to increase volumetric and acoustic property data as a function of temperature for aqueous solutions of Canadian maple sugar graded as Canada Grade A Golden (delicate taste, ≥75.0 %T), (former Canada #1, Extra Light), compute derived thermodynamic properties and analyze the accuracy of theoretical empirical models for predicting data. From the experimental investigation and the above discussions, following conclusions have been drawn:

1. The tested methods Subbiah-Barber equation (SBE), and the Junjie equation (JE) showed accurate capability of prediction of the measured magnitudes at the range of application, specially for low compositions, despite of their empirical character and complexity of the studied solutions. These models have better predictive capacity at low temperatures for density, and high temperatures for ultrasonic velocity. The consideration of maple syrup as a concentrated solution of sucrose was a strong simplification but the applied models deviations were acceptable.
2. A review of volumetric and acoustic properties of Canadian maple syrup revealed an important gap into disposable open literature thermodynamic data, despite its economic importance and its strong influence as necessary tool for accurate establishment of optimal point of thermal operation, the gathered data being a new contribution of consistent technical information for industrial maple operators.

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