MODELLING TEMPERATURE AND CONCENTRATION DEPENDENCE OF SELECTED BRAZILIAN HONEYS RHEOLOGICAL PROPERTIES

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RESUMO – A viscosidade no cisalhamento constante (η) e viscosidade complexa (η*) são propriedades reológicas importantes no processamento e controle de qualidade de méis. Assim, o objetivo deste trabalho foi investigar o comportamento destas propriedades em função da temperatura (°C) e concentração (°BRIX) em 40 amostras de méis brasileiros. A reologia no cisalhamento estacionário foi investigada em taxas de cisalhamento entre 0,1-100 s⁻¹ e o teste oscilatório foi realizado em frequências entre 0,1-10 Hz, ambos de 10°C a 60°C. Todos os méis apresentaram comportamento como-líquido nas temperaturas e espectro mecânico avaliados. Modelos simplificados foram propostos na determinação da η e η* a partir do efeito combinado da temperatura e concentração, os quais apresentaram R² igual a 0,9540 e 0,9334, e RMSE igual a 8,00 e 10,44, para η e η*, respectivamente. Assim, os modelos obtidos neste estudo fornecem informações importantes para adequada industrialização de méis e produtos à base de mel.

ABSTRACT – The steady shear viscosity (η) and complex viscosity (η*) are important rheological properties in processing and quality control of honeys. Thus, the objective of this study was to investigate the behavior of these properties in function of temperature (°C) and concentration (°BRIX) in 40 samples of Brazilian honeys. Steady shear rheology was investigated in the shear rate range of 0.1-100 s⁻¹ and oscillatory tests were performed in a frequency range between 0.1-10 Hz, both at 10°C to 60°C. All honeys showed liquid-like behavior in the temperatures and mechanical spectra evaluated. Simplified models were proposed to determine the η and η* from the combined effect of temperature and concentration, which presented R² equal to 0.9540 and 0.9334, and RMSE equal to 8.00 and 10.44 for η and η*, respectively. Thus, all models obtained in this study provided important information for proper industrialization of honeys and honey-based products.

PALAVRAS-CHAVE: Viscosidade, viscosidade complexa, regressão não linear.

KEYWORDS: Viscosity, complex viscosity, nonlinear regression.

1. INTRODUCTION

Honey is a complex semi-liquid food with high nutritional value. It is a natural sweetener whose composition includes a complex mixture of sugars, where the main constituents are fructose and glucose (approximately 60 – 85%), water (approximately 15 – 20%), amino acids, vitamins, minerals,
enzymes, wax, pollen, organic acids and pigments. It can be marketed in its pure form, mixed with propolis and plant extracts, or marketed as a raw material for industries (Al-Mahasneh, Rababah, Amer, & Al-Omoush, 2014).

The rheological behavior of honey and its accurate prediction during all processing steps, such as transport in pipes, centrifugation, filtration and heating, are of great importance in quality control of the final product and reducing economic losses in the process. The steady shear viscosity is a very important quality parameter in honey processing and is influenced by its composition, and consequently related to its floral origin, bee species, climate conditions of the production area, harvesting methods, processing and storage conditions (Turhan, Tetik, Karhan, Gurel, & Reyhan Tavukcuoglu, 2008; Yanniotis, Skaltsi, & Karaburnioti, 2006). Thus, there are many studies in literature which evaluated the viscosity of honey from different countries by means of the steady state shear rheological measurement (Al-Mahasneh et al., 2014; Dobre, Georgescu, Alexe, Esucredo, & Seijo, 2012; NayiK, Dar, & Nanda, 2015; Oroian, Amariei, Escrich, & Gutt, 2013; Oroian, 2012; Silva, de Carvalho, de Oliveira, Torres Filho, & de Resende, 2016).

The small amplitude oscillatory shear (SAOS) test can be used in honey to adequately describe its rheology without considerable changes to its structure (Ahmed, Prabhu, Raghavan, & Ngadi, 2007). The complex viscosity, measured by SAOS measurements, assesses the total resistance of the sample when subjected to a dynamic shear stress (Karasu, Toker, Yilmaz, Karaman, & Dertli, 2015). In mechanical spectra, the Newtonian nature of the material is confirmed if the complex viscosity is independent of the frequency (Witczak, Juszczak, & Gałkowska, 2011). This behavior is characteristic of liquid-like macromolecular solutions, such as honey (Kayacier, Yüksel, & Karaman, 2014).

The combined effect of temperature and total soluble solids concentration (°BRIX) (TSS) of honey plays an important practical role in the prediction of its steady shear viscosity (Oroian et al., 2013), given the ease of determining these variables. However, there is a gap in literature regarding the possibility of predicting the complex viscosity. Thus, the purpose of the study is to assess the combined effect of temperature and concentration of soluble solids (°BRIX) of these honeys on their steady shear viscosity and complex viscosity.

2. MATERIALS AND METHODS

Honey Samples

This study analyzed twenty-two samples of monofloral honey (Assa-peixe (Vernonia polysphaera) (3), Cipó-uva (Serjania lethalis) (5), Eucalyptus (Eucalyptus spp.) (7), and Orange blossom (Citrus sinensis) (7)) and eighteen samples of multifloral honey from the southeast (8), south (3), northeast (3), and center-west (4) regions of Brazil, which were obtained from beekeepers and supermarkets. The floral source of each honey was provided by the apiarist and was collected between the years of 2014 and 2015.

Concentration Analysis

Refractive indices of honey samples were measured using a refractometer (Reichert technologies, NY, USA) at 20 °C to calculate the °BRIX concentration based on Chataway tables (AOAC, 1995).
Rheological Measurement

Both small amplitude oscillation stress (SAOS) and steady shear rheological measurements were performed using a ReoStress 6000 rheometer (TermoHaake, Karlsruhe, Germany) with a 1-mm-gap parallel plate sensor (35-mm diameter). The rheometer has a Peltier plate at the bottom that controls the temperature in the range of –40 °C to 200 °C with an accuracy of 0.01 °C. The instrument was programmed for a set temperature and equilibrated for 10 min.

For steady shear rheological measurements, before being used the samples were warmed to 55 °C to dissolve any crystals, and kept in flasks at 30 °C for 48 h to remove air bubbles that could interfere with rheological studies (Mossel, Bhandari, D’Arcy, & Caffin, 2000). Steady shear rheology of each sample was investigated in the shear rate range of 0.1-100 s⁻¹ in 2 min by three cycles (upward, downward, and upward again) at 10 °C, 15 °C, 20 °C, 25 °C, 30 °C, 40 °C, 50 °C and 60 °C. Data referring to the temperatures between 10 °C and 30 °C was published by Silva et al. (2016) for rheological characterization of Brazilian honeys from different floral regions, while data in the temperature range between 40 °C and 60 °C was exclusively for this study. All rheological measurements were conducted in duplicate and the average values are reported here.

The linear viscoelastic region for SAOS tests was pre-determined by stress sweep tests for each honey sample. Oscillatory tests to obtain the complex viscosity were performed in a frequency (ω) range between 0.1 and 10 Hz at 10 °C, 15 °C, 20 °C, 25 °C, 30 °C, 40 °C, 50 °C and 60 °C (Ahmed et al., 2007).

The following models (Eq. 1 and 2) were investigated to evaluate the combined effect of temperature and concentration on steady shear viscosity and complex viscosity:

\[ \eta = \eta_0 \exp \left( D_1 C + \frac{E_a}{RT} \right) \]  
\[ \eta = \eta_0 C^{D_2} \exp \left( \frac{E_a}{RT} \right) \]

where C - sugar concentration in °BRIX, T – Temperature (K) and \( \eta_0, D_1, D_2 \) are parameters determined by non-linear regression analysis.

Statistical Analysis

The data corresponding to concentration (°BRIX) was analyzed by one-factor analysis of variance (ANOVA). Multiple comparisons were performed using the Tukey’s multiple-range test and statistical significance was set at \( \alpha = 0.05 \).

It should be mentioned that a nonlinear regression technique that uses the Levenberg-Marquardt method to solve nonlinear regression was used. The performance of derived models was evaluated using the statistical parameter root mean square error (RMSE – Eq. 3) in addition to \( R^2 \). These parameters can be calculated as follows:

\[ RMSE = \sqrt{\frac{1}{N} \sum_i^{N} (y_{exp,i} - y_{pred,i})^2} \]
where $y_{\text{exp},i}$ is the experimental data, $y_{\text{pre},i}$ is the predicted data by each nonlinear model, and $N$ is the number of data points. This statistical analysis was performed using version 9.1 of the SAS (Statistical Analysis System) software.

3. RESULTS AND DISCUSSION

Table 1 shows the results for the total soluble solids (TSS) content of the honeys. The multifloral-centerwest type presented a TSS content significantly lower ($p < 0.005$) than the assa peixe, cipó uva, orange blossom and multifloral-southeast types. The range of TSS values found in this study, 80.89 to 83.57%, is higher than that found in Mexican honeys, 77.0 to 80.67% (Viuda-Martos et al., 2010), honeys of India, 79.16 to 80.03% (Nayik & Nanda, 2015) and those produced in Rio Grande do Norte, Brazil, 70 to 81% (Costa, Moraes, Sobral, Gomide, & Carrer, 2013). However, it resembles the values obtained in honeys from Spain, 80.4 to 82.0 (Oroian et al., 2013), Romania, 79.8 to 81.94 (Oroian, 2012, 2013) and Israel, 80.5 to 83.2% (Cohen & Weihs, 2010). Anomalous TSS values may indicate product adulteration (Terrab, Recamales, Hernanz, & Heredia, 2004), which was not observed in this study.

Table 1 - Concentration (°BRIX) of selected Brazilian honeys.

<table>
<thead>
<tr>
<th>Type</th>
<th>BRIX (%)</th>
</tr>
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<tbody>
<tr>
<td>Assa Peixe</td>
<td>83.565 ± 0.69</td>
</tr>
<tr>
<td>Cipó Uva</td>
<td>83.572 ± 0.90</td>
</tr>
<tr>
<td>Eucalyptus</td>
<td>82.146 ± 0.86</td>
</tr>
<tr>
<td>Orange Blossom</td>
<td>83.527 ± 0.53</td>
</tr>
<tr>
<td>Multi-Southeast</td>
<td>82.902 ± 0.38</td>
</tr>
<tr>
<td>Multi-South</td>
<td>82.429 ± 0.36</td>
</tr>
<tr>
<td>Multi-Northeast</td>
<td>82.242 ± 0.86</td>
</tr>
<tr>
<td>Multi-Centerwest</td>
<td>80.889 ± 1.37</td>
</tr>
</tbody>
</table>

Values with different superscripts in one column indicate that average scores for the Brazilian honey are significantly different according to Tukey’s test ($p < 0.05$).

*Mean and standard deviation of the mean

According to the dynamic rheological behavior of Brazilian honeys, the $\eta^*$ is independent of frequency, indicating a liquid-like behavior of the honeys, reported by many authors in literature (Kayacier et al., 2014; Nayik et al., 2015; Oroian et al., 2013). The increase in temperature results in an increased kinetic energy of the honeys, causing a decrease in intermolecular forces and consequent reduction of $\eta^*$ (Recondo, Elizalde, & Buera, 2006). The honey cipó-uva presented, at 10 Hz, a variation of its $\eta^*$ between 151.33 Pa.s and 0.67 Pa.s at 10°C and 60°C, respectively. This honey showed the highest $\eta^*$ values, except at 60°C. At this temperature, the highest value of $\eta^*$ was equal to 0.84 Pa.s, referring to the honey assa peixe. On the other hand, the multifloral-centerwest honey showed the lowest $\eta^*$ values, in the range of 53.72 at 10°C and 0.42 Pa.s at 60°C.

With regards to the steady shear viscosity, results for the temperatures of 10 to 30°C have been reported in a previous study conducted by the authors (Silva et al., 2016). In temperatures of 40 to 60°C the honeys presented an excellent fit to the Newton model, with $R^2$ greater than 0.9995 and RMSE less than 1.7120, which confirms the results obtained in other studies (Dobre et al., 2012; Nayik et al., 2015; Oroian, 2012). Furthermore, just as $\eta^*$, $\eta$ decreases with increasing temperature for all honeys.

The combined effect of temperature and concentration presents an important practical application in determination of the rheological properties steady shear viscosity and complex viscosity.
of honeys. The values of the constants determined for the models with respect to equations 1 and 2 and their respective statistical parameters are shown in Table 2. The model that presented the lowest RMSE and highest R² was that of equation 1 for both properties. In evaluation of Spanish honeys the same equation was defined as the best model for determining the steady shear viscosity (Oroian et al., 2013), however its R² was equal to 0.8221, lower than the R² equal to 0.9540 obtained in this study, and its coefficients (η₁, D₁ and Eₐ) varied greatly from those presented in Table 2. The activation energy of the steady shear viscosity prediction models was lower than the complex viscosity, indicating that the latter is more sensitive to temperature changes. This demonstrates the increased sensitivity of measurements made by means of dynamic oscillatory testing and the efficiency in determination of physical and chemical changes of the materials (Oroian et al., 2013).

Table 2 – Combined effect of temperature and concentration to selected Brazilian honeys

<table>
<thead>
<tr>
<th>Modelo</th>
<th>ηᵢ</th>
<th>η₀</th>
<th>Dᵢ</th>
<th>Eₐ</th>
<th>R²</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ηᵢ = η₀exp\left(\frac{DᵢC + Eₐ}{RT}\right)</td>
<td>η</td>
<td>7.74.10⁻³²</td>
<td>0.447±0.01</td>
<td>92.277±2.01</td>
<td>0.9540</td>
<td>8.0020</td>
</tr>
<tr>
<td></td>
<td>η*</td>
<td>6.55.10⁻³²</td>
<td>0.427±0.02</td>
<td>96.752±2.59</td>
<td>0.9345</td>
<td>10.4432</td>
</tr>
<tr>
<td>ηᵢ = η₀C²exp\left(\frac{Eₐ}{RT}\right)</td>
<td>η</td>
<td>2.67.10⁻⁷⁸</td>
<td>32.700±0.78</td>
<td>91.220±0.49</td>
<td>0.9517</td>
<td>8.1998</td>
</tr>
<tr>
<td></td>
<td>η*</td>
<td>2.71.10⁻⁷⁸</td>
<td>32.285±1.06</td>
<td>95.739±0.66</td>
<td>0.9322</td>
<td>10.5258</td>
</tr>
</tbody>
</table>

i = 1 and 2.

4. CONCLUSION

Brazilian honeys presented liquid-like behavior in the mechanical spectrum (0.1 to 10 Hz) evaluated at temperatures of 10 to 60°C. Regarding the effect of concentration and temperature on the rheological parameters, η and η* were properly modeled by nonlinear models. The equations that defined the combined effect of temperature and concentration of the η and η* are useful for adequate processing and quality control of honeys and honey-based products.

5. ACKNOWLEDGMENTS

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6. REFERENCES


