

A comparative study of texture and rheology of Argentinian honeys from two regions

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Running headline: Physical properties of honeys from two regions of Argentina

ABSTRACT

The rheological and textural properties of 26 eastern Argentinian honeys from two different regions (North and Central) were investigated. The viscosity curves of the samples were obtained using a rotational rheometer over a temperature range of 10 to 50°C. The viscosity decreased with temperature and all honeys showed a Newtonian behaviour. The temperature dependence of viscosity was described using the Arrhenius, Williams–Landel–Ferry, Vogel–Tammann–Fulcher and Power Law models. The glass transition temperatures of honeys were measured with differential scanning calorimetry and values ranged from -42.63 to -47.71°C. The glass transition temperature was also predicted with the Williams–Landel–Ferry model and no significant differences were observed with the experimental results. Rheological parameters were obtained by small amplitude oscillation experiments. Results indicated that the viscous modulus was higher than the storage modulus within all the frequency ranges assayed and honeys from the North region were more viscous. Results of the back extrusion test showed that honeys from the Central region are harder and both groups of honeys (North and Central) exhibited the same consistency and adhesivity.

KEYWORDS: Honey, Rheology, Texture, Glass transition, Viscosity

PRACTICAL APPLICATION

The honey chain production starts with the extraction of the product from the combs, pumping it through pipes and finishes at the packaging of the product. During all these stages, honey viscosity is a key parameter to ensure proper processing and quality control, preventing the waste of economic resources. Determining honey viscosity is of great importance for the industry to select the equipment such as pumps, mixers, filters, centrifuges, heat exchangers and optimization of industrial processes. The rheological and textural properties of honey are very important in terms of applications related to quality control and authenticity of honeys. Honey authenticity increases the trust of consumers to certified food products. Argentina is one of the leading honey producers and exporters in the world, but information on the rheological, thermal and textural characteristics of Argentinian honey is very poor in the scientific literature.

INTRODUCTION

Chemically, honey is comprised of sugars (80–85%), water (15–20%), and other minor constituents such as minerals, proteins, phenolic compounds, organic acids, and free amino acids (Akbulut *et al.* 2012). The composition is influenced mainly by the dominant flora around the apiaries (Silvano *et al.* 2014) and furthermore by the geographic region (Patrignani *et al.* 2015), weather, and type of soil (Oroian *et al.* 2013a). Temperature and moisture content have a strong influence on honey viscosity; however, factors like its chemical composition, are also important. The honey chain production starts with the extraction of the product from the combs, pumping it through pipes and finishes at the packaging of the product. During all these stages, honey viscosity is a key parameter to ensure a proper process. When honey is subjected to steady shear viscosimetry experiments, a Newtonian fluid behaviour is often found. However, there are few reports describing thixotropic and dilatant characteristics (Juszczak and Fortuna 2006; Osés *et al.* 2017). Dynamic measurements are also useful tools to analyse the rheological characteristics of honey without much alteration in the internal network structure. Kayacier and Karaman (2008), Da Silva *et al.* (2016) and Ahmed *et al.* (2007) used small amplitude dynamic oscillatory measurements on honey samples and observed a liquid-like behaviour with loss modulus greater than storage modulus within all the frequency range assayed.

As temperature increases, viscosity falls due to less molecular friction and reduced hydrodynamic forces (Juszczak and Fortuna 2006). Commonly, the Arrhenius equation has been used to describe temperature dependency of honey samples (Kayacier and Karaman 2008 in Turkish honeys; Da Silva *et al.* 2016 in Brazilian honeys; Juszczak and Fortuna 2006 in Polish honeys; Sopade *et al.* 2002 in Australian honeys; Belay *et al.* 2017 in Ethiopian honeys). However, this model renders a relatively higher value of activation energy (Al-

Malah *et al.* 2001). On the other hand, models like the William-Landel-Ferry (WLF), Vogel–Tammann–Fulcher (VTF) and Power Law, has been used successfully to describe the temperature dependence of honey viscosity (Sopade *et al.* 2002; Lazaridou *et al.* 2004; Juszczak and Fortuna 2006, Recondo *et al.* 2006, Oroian *et al.* 2013a,b). Glass transition is a phenomenon that occurs when a material changes from the rubbery state (viscous fluid) to the glassy state (mechanical solid) during cooling and it is a second order phase transition (Al-Malah *et al.* 2001; Sopade *et al.* 2002). The T_g can be experimentally determined by differential scanning calorimetry, but the high viscosity (10^7 - 10^{14} Pa.s, as reported by Sopade *et al.* 2002) of the glassy state makes the experimental determination of the η_{T_g} impossible. However, it is possible to use some extrapolation procedures to estimate the value of the η_{T_g} (Bhandari *et al.* 1999; Peleg 1992).

Moisture in honeys is a parameter related to the climatic conditions, geographical origin, handling, storage and degree of maturity. The Codex Alimentarius (2017) establishes a maximum acceptable moisture content of 20g/100g. However, water in honey could be as high as 29g/100g or as low as 13g/100g (Junzheng and Changying, 1998; White, 1975) A 1g/100 g change in water content has the same effect on honey viscosity as a 3.5°C change in temperature (Juszczak and Fortuna 2006). Thus, the higher the water content the lower the honey viscosity.

The objective of this study is to investigate the application of the viscosity-temperature describing models to honeys from two different phytogeographic regions of Argentina: The North and Central regions. The rheological behaviour at different temperatures and textural characteristics of honeys are also analysed.

MATERIALS AND METHODS

Honey samples

The present study was performed on 26 samples (13 from the East Central, Buenos Aires province and 13 from the North-East, Chaco province) of multiflora honeys. The selection of the beehives to obtain the samples was performed according to a simple random sampling design. Honey samples, harvested in January 2015, were obtained by cold extraction and immediately stored at 4°C in plastic containers until analysis. Before all determinations, samples were heated in closed containers during 1 hour at 45°C to melt any crystals that were present and to remove the air bubbles.

Moisture content, Brix degrees and sugars profile analysis.

Refractive index of honeys was measured at 20°C using an Abbe refractometer and the corresponding moisture content was calculated from the Chatway Table (AOAC 1990). The Brix degrees (°Brix) were measured with a portable refractometer (Hanna Instruments HI 96801, USA). Sugar analysis was performed as described by Silvano *et al.* (2014).

Differential scanning calorimetry

The glass transition temperature (T_g) of honeys was determined using a differential scanning calorimeter (DSC) (Thermal Analysis Instruments, New Castle, Delaware, USA) calibrated with indium. Twelve samples (six from the North and six from the Central region) of about 20 mg each were placed in aluminium DSC hermetic pans. . A sealed empty aluminium pan was used as a reference (Da Silva *et al.* 2018; Leo and Nollet, 2015). The experiment was performed as described by Lazaridou *et al.* 2004: the samples were heated from 20 to 50°C at

a heating rate of 10°C/min and kept at 50°C for 5min to ensure the melting of any crystals. The samples were then quench-cooled with liquid N₂ to -80°C and reheated to 50°C at the same heating rate. The T_g was determined, using the T_g command of the TA Instruments Universal Analysis 2000 software version 4.2E.

Rheological measurements

Rheological properties of honey were investigated with a RS 600 controlled stress rheometer (Haake, Karlsruhe, Germany) using a 1.0 mm gap parallel plate geometry. Samples were placed on the lower plate and temperature was regulated by a Haake (Karlsruhe, Germany) circulating water bath. After loading the sample, a waiting period of 5 min was necessary to allow the sample to recover and to reach the specified temperature. Small amplitude oscillation stress experiments were performed to obtain the storage (G') and viscous (G'') moduli and complex viscosity (η^*) at a strain level of 0.5% (within the linear viscoelastic range) and a range of angular frequencies (ω) of 0.4-600 rad s⁻¹ at 20°C. The flow behaviour was studied by measuring steady shear viscosity (η) and shear stress (τ) over a range of shear rates ($\dot{\gamma}$) of 0.1-400 s⁻¹ at 10, 20, 30, 40 and 50°C. For each sample, two independent replicates were assayed.

Temperature effects on η were analysed using the following models:

Arrhenius relationship:

$$\eta = \eta_0 \times e^{(E_a/RT)} \quad (1)$$

where η is the viscosity at temperature T , η_0 is a pre-exponential factor, E_a is the activation energy for flow, R is the perfect gas constant and T is the absolute temperature.

Willian-Landel Ferry model (Willian *et al.* 1955):

$$\log(\eta / \eta_{Tg}) = [-C_1(T - Tg)]/[C_2 + (T - Tg)] \quad (2)$$

where Tg is the glass transition temperature, η is the viscosity at temperature T , η_{Tg} is the viscosity of sample at Tg or glass viscosity and C_1 and C_2 are the WLF model constants.

The Vogel–Tausman–Fulcher model (Sopade *et al.* 2002).

$$\eta = A \times \exp(B/(T - Tg)) \quad (3)$$

where A is the pre-exponential factor Tg is the glass transition temperature. A and B were calculated as the slope of the linearized form of Eq. 3.

The Power Law model:

$$\eta = K \times (T - Tg)^{-m} \quad (4)$$

where K and m are constants estimated from linearization of Eq. 4.

Textural measurements: back extrusion

Back extrusion tests were carried out as suggested by Conforti *et al.* (2006) using a TA.XT2 Texture analyser (Stable Micro Systems Ltd., Surrey, UK) with a cylindrical container of 45mm internal diameter filled with honey, in which the compression probe (35mm diameter) moved at a speed of 0.5 mm/ s until 30% deformation. Sample hardness was defined as the maximum height of the peak of the force versus time/deformation curve. The area of first peak is the consistency of the sample. The negative force area obtained after the compression cycle is defined as the adhesivity (Figure 1). For each sample, three independent replicates were assayed.

Data analysis

Rheological data were fitted using the software Origin Pro 8 v8.0724 (Origin Lab Corporation, MA, USA).

Analysis of variance was performed and the least significant differences were calculated to compare the means of both groups of honeys (North and Central) at a 95% level using the Fisher test. A p -value of less than 0.05 was considered significant.

Cluster analysis was performed on the standardised data to classify samples based on the similarities of their rheological and textural parameters and moisture content. Clusters were calculated using the Euclidian distance and the Ward technique. The Infostat software 2014e version (Córdoba National University, Córdoba, Argentina) was used.

RESULTS AND DISCUSSION

Rheological characteristics

Fig. 1a,b shows the steady shear flow rheograms of selected honey samples at 20°C. Generally, the η did not change and τ linearly increased with γ indicating a Newtonian behaviour similar to Kayacier and Karaman (2008), Da Silva *et al.* (2016), Sopade *et al.* (2002) and Belay *et al.* (2017). Fig. 1c illustrates the mechanical spectrum of selected honey samples at 20°C. It was observed that G'' was higher than G' within all the frequency ranges assayed, except at very high frequencies in which both moduli have similar values. High values of G'' confirm the viscous nature of honey and the low values of G' suggest that there was no network formation in honey samples due to weak particle –particle interactions

(Ahmed *et al.* 2007). This response is typical of liquid-like materials, characterized as viscous fluids (Yamul and Lupano, 2009). As a result of the viscous nature of honey, changes in G'' with frequency provide more information than G' [Figure 1 here]. Honeys from the North region are more viscous ($p < 0.05$) than those from the Central as reflected by the results for η , G'' and η^* (Fig. 2 b,c,d). These differences could be attributed to natural variations in honey composition. The north of Argentina has a tropical climate with hot and wet summers, determining the flora of the area and, thus, the nectar composition used by bees to produce honey. In addition, higher temperatures and environmental moisture might also influence the maturation of honey in the beehive, affecting its physico-chemical properties and leading to differences in honeys from these different regions.

Figure 2e shows that the values of η and η^* of honeys from both regions are similar at equivalent numerical values of angular frequency and shear rate. This result suggests that these honeys follow the Cox-Merz rule (Cox and Merx 1958), which is expected for Newtonian liquids without particle–particle interactions. Lazaridou *et al.* (2004) reported a similar behaviour in Greek honeys. [Figure 2 here]

Moisture, which is a parameter related to several climatic conditions, handling of honey by the producer and degree of maturity (Silvano *et al.* 2014), decreased the viscosity of honey (Fig. 3). Honeys from the North (Fig. 3a) show a weak linear fit between viscosity and honey moisture content with an r^2 value of 0.6436, which is comparable to the r^2 value of 0.6369 obtained by Belay *et al.* (2017) in Ethiopian honeys. On the other hand, honeys from the Central region (Fig. 3b) show a greater dispersion of the data and it is not possible to fit them to a straight line with a satisfactory r^2 . It is interesting to note that Lazaridou *et al.* (2004) also found a decrease of the viscosity as water content increased but fitted data to a decreasing exponential function. [Figure 3 here].

Moisture content, sugar analysis, Brix degree and glass transition temperature of honeys.

The effect of moisture content on the T_g is shown in Table 1. Results show mean values of 17.95 gH₂O/100g and 18.55 gH₂O/100g for honeys from the North and Centre of the country, respectively. Samples shown in Table 1 agree with the requirements of the Codex Alimentarius (2017) which sets the maximum value of that parameter at 20 gH₂O/100g. Water is a universal plasticizer, which decreases the T_g due to its ability to weaken non-covalent interactions (Matveev *et al.* 2000). It is generally accepted that T_g is a function of both moisture and solid content. Sopade *et al.* (2002) and Lazaridou *et al.* (2004) found a strong dependence of T_g with water content in honeys from Australia and Greece, respectively. [Table 1 here]

Table 2 shows the composition of the most abundant sugars identified in the honey samples. As expected, fructose and glucose represent the main sugars, covering more than 65% of the total carbohydrates. Therefore, all honeys were in agreement with the requirements of the Codex Alimentarius (2017). Honeys from the Central region has significantly ($p \leq 0.05$) higher values of fructose and glucose content than honeys from the North, but no significant differences ($p \geq 0.05$) were obtained in the content of the disaccharides sucrose and maltose. Fructose/Glucose ratio is an indicator of honey granulation because glucose is less water soluble than fructose (Bentabol Manzanares *et al.* 2011). When this ratio is higher than 1.5 honey remains liquid for longer periods (Ouchemoukh. *et al.* 2010). Honeys from the northern region showed higher values of fructose/glucose ratio (1.54) suggesting that these honey samples remains liquid for longer times. [Table 2 here].

The °Brix is an estimation of the sugar (solid) content of an aqueous solution, thus, the higher the °Brix the lower the water content and the higher the T_g . Ahmed *et al.* (2007) found higher T_g values in honeys with higher solid content. Results in Table 1 show no significant differences ($p > 0.05$) in the mean values of T_g of honeys from both regions. This is an expected result because honeys also show no significant differences ($p > 0.05$) in the moisture content and °Brix. Venir *et al.* (2010), Recondo *et al.* (2006) and Oroian *et al.* (2013b) reported similar values of T_g at similar soluble solids content (80-81g/100g). In contrast, Ren *et al.* (2010) reported a lower value of T_g (-49.5°C) in Chinese honey containing 75g/100g of soluble solids.

Temperature dependence of viscosity: Arrhenius, VTF, Power law and WLF models.

As a Newtonian liquid, honey viscosity substantially reduced when temperature was increased (Fig. 1d). Viscosity values were similar to those obtained by Da Silva *et al.* (2004) and Sopade *et al.* (2002) at the same temperatures. The Arrhenius relationship (Eq. (1)) is a useful tool to estimate the temperature dependence of viscosity. Many authors used this model for diverse types of honeys (Kayacier and Karaman 2008; Nayik *et al.* 2016; Oroian *et al.* 2013b; Recondo *et al.* 2006). The E_a , which is derived from the Arrhenius formalism (Lazaridou *et al.* 2004), reflects the sensitivity of viscosity to temperature changes. Table 3 (supplementary material) shows no significant differences ($p > 0.05$) in the mean values of E_a suggesting that both types of honeys need the same energy to flow, in spite of the fact that honeys from the North are more viscous as suggested above. The mean values of E_a were 79.61 kJ mol⁻¹ and 82.09 kJ mol⁻¹ for North and Centre, respectively. These were similar to those reported in the literature (Oroian *et al.* 2013b; Recondo *et al.* 2006; Lazaridou *et al.* 2004; Sopade *et al.* 2002; Kayacier and Karaman 2008). The pre-exponential factor in the

Arrhenius equation, according to Al-Malah *et al.* (2001), represents viscosity at a temperature close to infinity. The values obtained were lower than those reported by Oroian *et al.* (2013b).

The viscosity vs. temperature relationship was also described using the VTF and Power law models. The values of the constants of both models (A , B , K and m , Table 3 supplementary material) were different from those reported by Recondo *et al.* (2006). The difference could be related to the fact that, these authors, used uniflora honey from *Bulnesia sarmientoi* (algarrobo), while we used multiflora honey.

Concentrated sugar solutions obey the WLF equation (Soesanto and William 1981), thus, honey due to its high sugar content could be adequately described using this model. Previous results (Lazaridou *et al.* 2004; Recondo *et al.* 2006; Sopade *et al.* 2002; Juszczak and Fortuna 2006) indicate that the WLF model has been useful to describe viscosity-temperature data of honeys from different origins. Compared to the Arrhenius relationship, the WLF equation is a more appropriate model to describe viscosity-temperature dependence between T_g and about $T_g + 100^\circ\text{C}$. Moreover, the WLF model specifies a much stronger temperature dependence of viscosity compared to that predicted by the Arrhenius formalism (Lazaridou *et al.* 2004). Viscosity data (η vs T) of 12 honey samples (6 from the North and 6 from the Centre region) were fitted to the WLF equation (Table 1). Using the universal values for the constants ($C_1 = 17.44$ and $C_2 = 51.6$ K; William *et al.* 1955), the results of the predicted T_g show good fits ($r^2 > 0.90$) in almost all samples analysed. Al-Malah *et al.* (2001) and Lazaridou *et al.* (2004) obtained similar fit when describing the temperature dependence of honey viscosity using the WLF equation. The predicted T_g values are not significantly different ($p > 0.05$) with the values obtained experimentally by DSC (Table 1, mean values of T_g). On the other hand, Lazaridou *et al.* (2004) explain that the differences between the

experimental and predicted values could lie on the fact that T_g reflects a range of temperatures and, thus depends on the technique and experimental conditions used for its determination. Recondo *et al.* (2006) obtained a T_g value much lower (-59.7°C , unifloral honey from *Bulnesia sarmientoi*) than our results (Table 1) probably due to the differences in the honeys analysed. However, when these authors used the reduced constants (i.e., constants calculated by the reduced model method, Recondo *et al.* 2006), they obtained a value of -45.2°C that is similar to our values of T_g .

The predicted η_{T_g} values ranged between $10^{10.34}$ and $10^{11.96}$ Pa.s for both regions and are similar to the values reported by Sopade *et al.* (2002) and lower than the values reported by Recondo *et al.* 2006. In contrast with the T_g , which could be measured by different techniques, the glass viscosity could be only estimated from the model because such high values are not accessible for any existing rheometer (Lazaridou *et al.* 2004).

The universal values for C_1 and C_2 are average values obtained from data on many glass-forming liquids and sometimes their use might not be successful with other samples. Sopade *et al.* (2002) claimed that C_1 and C_2 should not be fixed constants for comparison of the temperature sensitivity among different samples of honey. When the constants were allowed to vary (without using the universal values), and T_g from the DSC was used as the reference temperature (Table 1), very good fits ($r^2 > 0.96$) were obtained for C_1 and C_2 , except for 3 samples from the north region with r^2 ranging from 0.77 to 0.88. The mean values of C_1 and C_2 (shown in Table 1) for both regions are comparable to those obtained by Lazaridou *et al.* (2004). On the other hand, values of the η_{T_g} were much higher ($10^{18.29}$ Pa.s North and $10^{20.22}$ Pa.s Centre) than those obtained using the universal values for C_1 and C_2 ($10^{11.12}$ Pa.s North and $10^{11.07}$ Pa.s Central). These results do not likely represent the true values. Peleg (1992) reported that the magnitude of C_1 and C_2 might vary considerably from the universal values

depending on the material studied, the measured property and the reference temperature. In addition, it is interesting to note that, independent of the geographic origin of honeys, values of the predicted parameters using the WLF equation showed no significant differences ($p > 0.05$).

It is interesting to note that regardless of the model used some honeys from the North usually presented weaker fits to the models as reflected by those with r^2 values lower than 0.85 (Table 3 supplementary material).

Back extrusion test of honeys

Rheological properties of fluids or semisolid foods are typically assayed in a rheometer; however, the texture analyser could be used in these types of foods to carry out the back extrusion test. In this test, the sample is placed in a cylindrical container and subjected to compression to obtain the force vs time curve, which could be used to calculate the maximum force and adhesivity of the sample. Conforti *et al.* (2006) used back extrusion and Oroian *et al.* (2016, 2017) used texture profile analysis to study the fluid properties of honey. Figure 4a shows that honeys from the Central region are harder than those from the North, which is in agreement with the rheology results. The higher hardness would be, as suggested by Conforti *et al.* (2006), the result of a higher sugar concentration in samples from the Central region. This fact could be confirmed with the results of Table 2. Table 4 (supplementary material) shows a higher correlation between hardness and sugars (glucose, sucrose and maltose) in honeys from the Central region confirming the results above. The influence of fructose on hardness is insignificant in honeys from both regions. On the contrary, Oroian *et al.* (2016) found significant influence of fructose on textural parameters. It is interesting to note that maltose has the highest correlation with textural parameters of

honeys from both regions. Sugars depict a weak correlation with viscosity in honeys from both regions. The correlation of the ratio F/G with textural parameters is also higher in honeys from the Central region. The ratio F/G also has negative and positive associations with the viscosity of honeys from the Centre and North respectively. Consistency, which is related to 'thickness' or 'viscosity' of a liquid or semi-solid fluid, is commonly the textural property of dairy products, sauces and syrups. It is interesting to note that consistency shows a weak correlation with viscosity but a high correlation with hardness (Table 4 supplementary material). The results in Figure 4b show no significant differences ($p > 0.05$) in the consistency of honeys from both regions. Adhesivity is related to the negative extrusion force required for withdrawal of the probe away from the sample. Figure 4c shows that honey from both regions have no significant differences ($p > 0.05$) in their adhesive properties [Figure 4 here]. Figure 5a,b shows an inverse linear relationship obtained between the adhesivity and hardness of honey samples from both regions, with r^2 values of -0.928 and -0.910 for the North and Central regions, respectively. These results are similar to the Pearson correlation between adhesivity and hardness (Table 4 supplementary material). On the other hand, Oroian *et al.* (2016) also obtained a high Pearson correlation between these textural parameters but positively influenced one by the other. Honeys might adhere to the surface of the probe due to interatomic forces and non-covalent interactions. It is possible that in harder honeys the interactions with the metal of the probe are weaker due to stronger interactions in the honey structure. Conforti *et al.* (2006) found that honeys with higher values of hardness have lower moisture contents, which could be attributed to the higher sugar concentration in non-crystallised honey. However, our results (Fig. 5c,d) show a scattered point distribution with no clear trend between hardness and moisture

content.[Figure 5 here]. These results could be confirmed with the weak Pearson correlation obtained between hardness and moisture (Table 4 supplementary material).

Cluster analysis

The classification techniques based on groupings involves the distribution of study units in classes or categories in such a way that each class (conglomerate) brings together units whose similarity is recognizable under certain given criterion (Balzarini *et al* 2008). Figure 6 shows the cluster analysis and, at 75% (15) of the total range distance, two clusters are observed. One of them includes the samples from the North region and, the other one, the samples from the Central region Centre region. From 23 samples, some of them were misclassified using the cluster analysis. Samples C6, C10, C11 and C12 were included in the group from the North region. On the other hand, N3 and N8 were grouped as Central region samples. [Figure 6 here]

CONCLUSIONS

Honeys from the North and Centre of eastern Argentina behaved as Newtonian fluids, although some differences in their rheological behaviours were found. Honeys from the North were more viscous than those from the Central region as reflected by their η , E_a , G'' and η^* values. Moisture content decreased the viscosity of honeys from the North region, but its effect on honeys from the Central region was not well defined. Values of the glass transition temperature obtained from the DSC and those predicted by the WLF model were comparable for both regions. Arrhenius, WLF, VTF and Power Law models proved to be adequate to describe the viscous behaviour of honey as a function of temperature, except with some honeys from the North, which showed a weak fit to the models. The back-

extrusion test could be useful to analyse the textural characteristics of viscous foods like honey. On the other hand, the effect of moisture on hardness was not very clear. Cluster analysis showed a weak classification of honey samples based on rheological and textural parameters.

ETHICAL STATEMENT

The authors declare that they do not have any conflict of interest.

This study does not involve any human or animal testing

Written informed consent was obtained from all study participants.

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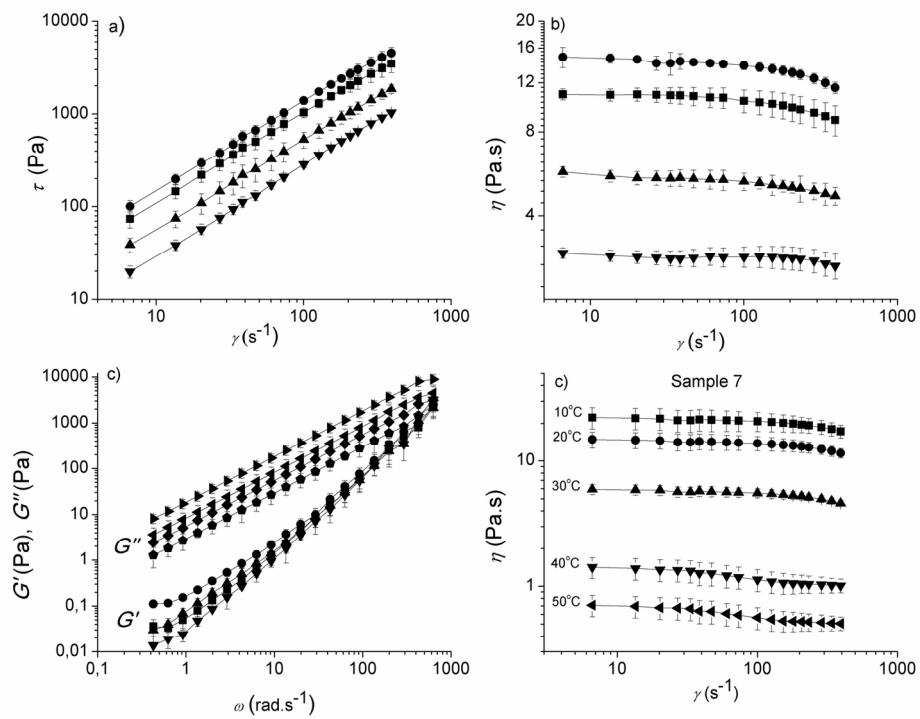


Figure 1. a) shear stress (τ), (b) steady shear viscosity (η), and (c) a representative mechanical spectrum (G' : storage modulus and G'' : loss modulus) of four honey samples (3 and 7 from the North region and 14 and 18 from the Central region) at 20°C; d) temperature effect (from 10°C to 50°C) on steady shear viscosity (η) of a representative honey sample. $\dot{\gamma}$ (shear rate) and ω (angular frequency). Samples symbol: 3(■), 7(●), 14(▲), 18(▼).

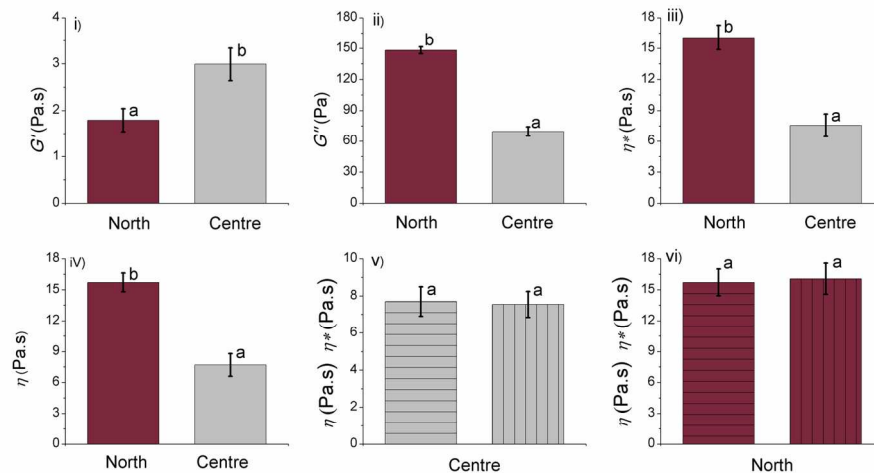


Figure 2. i) Storage modulus (G'); ii) Loss modulus (G''); iii) Complex viscosity (η^*) (measured at $\omega = 10 \text{ rad s}^{-1}$); iv), Steady shear viscosity (η); v) and vi) Comparative values of η and η^* at 20°C of honeys from both regions; η : bars with horizontal lines and η^* : bars with vertical lines. Values with the same letter in the same graph are not significantly different ($p > 0.05$).

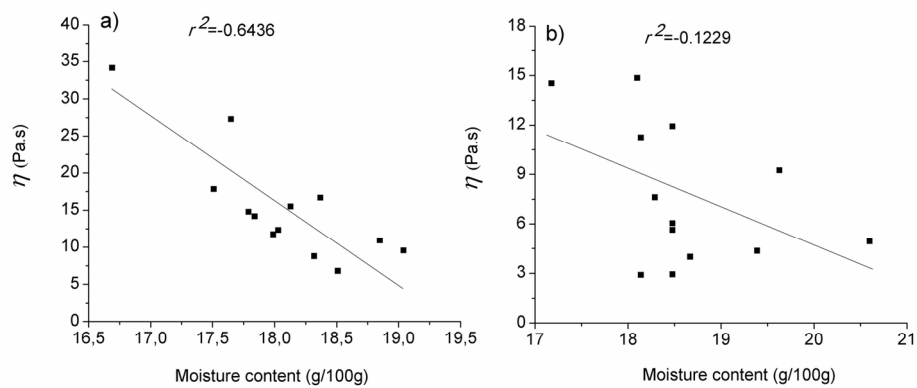


Figure 3. Linear fit showing the associations between steady shear viscosity (η) and moisture content of honeys. a) North region, b) Central region.

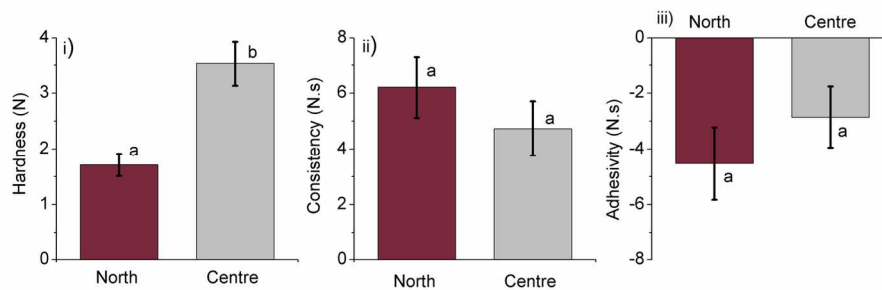


Figure 4. Textural parameters of honeys from both regions. Values with the same letter in the same graph are not significantly different ($p > 0.05$).

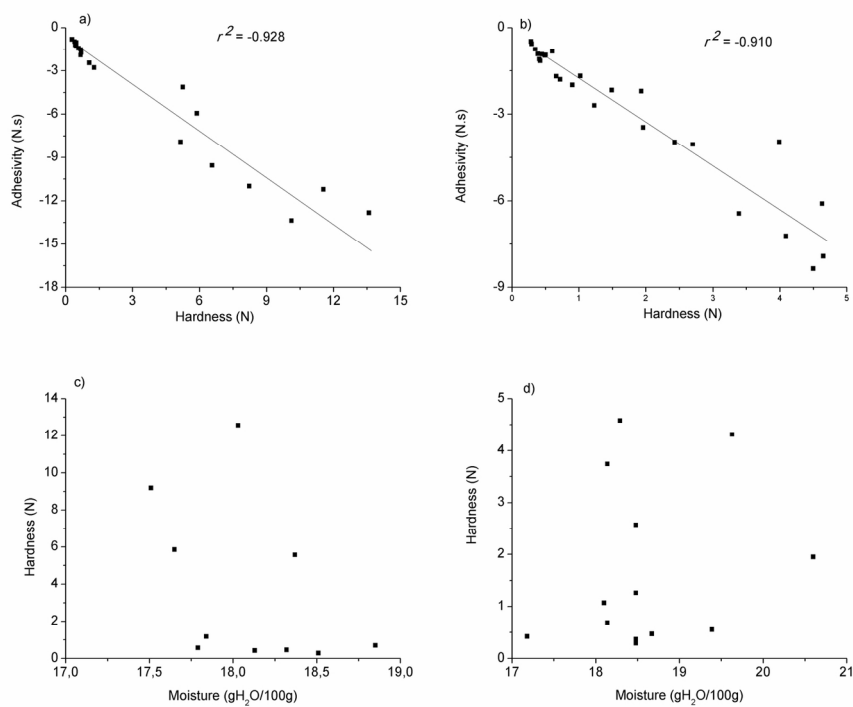


Figure 5. Linear fit showing the associations between adhesivity vs hardness (a and b) and hardness vs moisture content (c and d) of honeys. North region (a and c) and Central region (b and d).

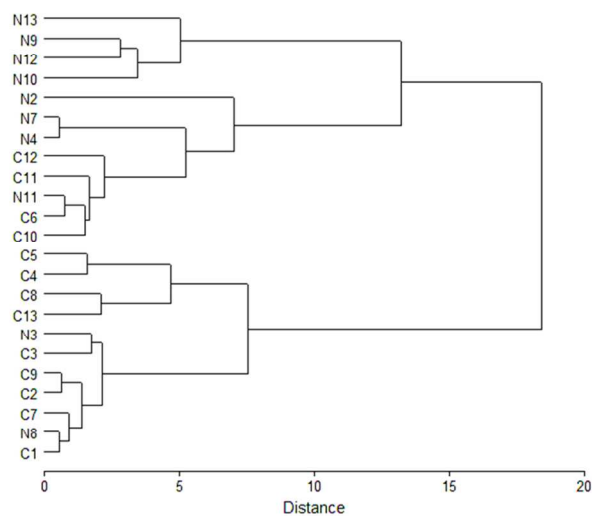


Figure 6. Dendrogram of cluster analysis. N: North region, C: Central region.

Table 1. Moisture content, °Brix, glass transition temperatures (Tg) and estimated parameters of the WLF model of honeys from North (N) and Central region (C) of Argentina. Values with the same letter in the same column are not significantly different ($p > 0.05$).

Sample	Moisture content (gH ₂ O/100 g)	°Brix (g/100g)	T _g , K (°C) experimental data from DSC	WLF using the universal values for C ₁ and C ₂			WLF using T _g from DSC experimental data			
				T _g (K) (predicted)	log(η_{Tg}) (Pa*s)	r ²	log(η_{Tg}) (Pa*s)	C ₁	C ₂ (K)	r ²
N1	16.69	81.80	229,85(-43.15)	240.44(-32.56)	10.34	0.91	16.33	12.47	26.26	0.99
N3	18.85	79.55	225,61(-47.39)	228.64(-44.36)	10.66	0.95	16.18	12.72	22.41	0.88
N5	19.04	79.35	226,45(-46.55)	216.97 (-56.03)	11.31	0.90	15.56	13.03	18.03	0.85
N7	17.79	80.65	230,2(-42.80)	208.01(-64.95)	11.96	0.81	16.36	13.69	17.17	0.77
N9	17.51	80.95	228,27(-44.73)	223.68(-49.32)	11.89	0.98	22.11	15.64	29.61	0.99
N11	17.84	80.60	229,66(-43.34)	229.82(-43.17)	10.58	0.99	23.19	14.97	35.10	0.98
Mean value	17.95^a	80.48^a	228.34(-44.66)^a	224.59(-48.46)^a	11.12		18.29	13.75	24.76	
C14	18.48	80.00	226,6(-46.40)	227.65(-45.35)	10.45	0.99	21.37	14.46	32.13	0.99
C16	19.39	79.05	225,51(-47.49)	222.46(-50.54)	10.96	0.97	19.83	14.47	26.49	0.99
C18	18.14	80.35	224,45(-48.55)	211.50(-61.50)	11.52	0.91	19.62	14.83	23.38	0.98
C20	18.48	80.00	227,2(-45.80)	229.44(-43.56)	10.34	0.98	19.61	13.89	28.85	0.96
C22	18.67	79.80	225,29(-47.71)	204.34(-68.66)	11.77	0.92	20.70	15.36	25.04	0.99
C24	18.14	80.35	230,37(-42.63)	227.09(-45.91)	11.35	0.97	20.19	14.77	26.17	0.99
Mean value	18.55^a	79.93^a	226.57(-46.43)^a	220.41(-52.59)^a	11.07		20,22	14.63	27.01	

Table 2

Sugar content of honeys from North (N) and Central region (C) of Argentina. Values with the same letter in the same column are not significantly different ($p > 0.05$).

Sample N°	Fructose (g/100g)	Glucose (g/100g)	Fructose/Glucose	Sucrose (g/100g)	Maltose (g/100g)
N1	41.5	23.5	1.77	1.6	5.3
N2	39.3	26.5	1.48	2.1	2.3
N3	39.5	26.0	1.52	1.7	4.8
N4	40.9	26.7	1.53	1.3	3.3
N5	39.3	28.1	1.40	0.9	3.5
N6	38.8	26.5	1.46	1.1	3.6
N7	41.2	25.1	1.64	1.3	6.2
N8	40.2	24.5	1.64	0.6	4.1
N9	42.1	24.1	1.75	1.5	6.2
N10	39.5	25.8	1.53	1.9	5.8
N11	39.8	27.8	1.43	1.2	3.0
N12	38.0	28.1	1.35	1.8	4.8
N13	39.6	27.2	1.46	1.6	3.8
Mean value	39.9^a	26.1^a	1.54^a	1.4^a	4.36^a
C14	43.2	31.9	1.35	1.5	4.4
C15	43.6	33.6	1.30	1.4	5.2
C16	43.3	33.0	1.31	1.6	3.0
C17	43.6	32.6	1.34	1.7	5.7
C18	43.0	32.0	1.34	1.7	4.9
C19	44.2	34.8	1.27	1.4	5.0
C20	43.2	33.0	1.31	0.9	3.7
C21	42.8	32.6	1.31	0.8	5.9
C22	43.9	34.6	1.27	1.2	2.3
C23	43.5	33.4	1.30	1.2	5.4
C24	43.0	33.1	1.29	1.1	3.1
C25	43.1	33.9	1.27	2.2	4.2
C26	43.4	33.2	1.31	1.4	6.3
Mean value	43.5^b	33.1^b	1.31^b	1.4^a	4.35^a

Table 3

Parameters calculated through the linearization of Arrhenius, VTF and Power Law models, for honeys from both regions (North and Central region). Values with the same letter in the same column are not significantly different ($p > 0.05$).

Sample	Arrhenius			VTF			Power law		
	E_a (kJ mol ⁻¹)	$\log \eta_0$ (Pa*s)	r^2	B (K)	A (Pa*s)	r^2	m	$\log K$ (Pa*s)	r^2
N1	82.92	8.12	0.978	190.70	-1.41	0.997	-0,0283	3,33	0,923
N3	72.30	8.22	0.625	169.82	-1.50	0.974	-0,0275	2,92	0,715
N5	80.62	7.57	0.521	155.04	-1.34	0.954	-0,0255	2,73	0,601
N7	81.78	7.92	0.776	169.15	-1.40	0.962	-0,0269	2,96	0,734
N9	79.59	11.30	0.979	246.11	-2.64	0.996	-0,0365	3,48	0,991
N11	80.47	11.9	0.912	257.53	-3.03	0.991	-0,0376	3,32	0,987
Mean value	79.61^a	10.06^a		198.06^a	-1.89^b		-0.0304^a	3.12^b	
C14	87,59	10,91	0,983	229.16	-2.83	0.994	-0,0341	2,93	0,972
C16	74,60	9,79	0,975	204.84	-2.59	0.997	-0,0304	2,55	0,988
C18	83,53	9,44	0,999	193.24	-2.52	0.966	-0,0291	2,37	0,991
C20	84,77	9,77	0,983	210.33	-2.57	0.981	-0,0306	2,66	0,993
C22	75,14	10,04	0,962	210.18	-2.69	0.999	-0,0310	2,57	0,915
C24	86,94	10,43	0,934	226.74	-2.57	0.997	-0,0333	3,09	0,976
Mean value	82.09^a	9.17^a		212.42^a	-2.63^a		-0.0314^a	2.69^a	

Table 4

Pearson correlation of textural and some physicochemical parameters of honeys from the North region (lower half of the main diagonal of the matrix) and Central region (upper half of the main diagonal of the matrix).

	Moisture	Fructose	Glucose	Sucrose	Maltose	F/G	Brix	Viscosity	Hardness	Consistency	Adhesivity
Moisture	1	-0.23	-0.24	-0.59	0.28	0.22	-1.00	-0.44	0.20	0.25	0.03
Fructose	-0.46	1	0.72	0.07	-0.04	-0.41	0.23	0.23	-0.06	-0.18	-0.06
Glucose	0.45	-0.76	1	0.01	-0.26	-0.92	0.25	0.47	-0.37	-0.47	-0.44
Sucrose	-0.23	-0.15	0.03	1	0.03	0.05	0.59	0.23	0.29	0.09	0.17
Maltose	-0.37	0.46	-0.60	0.14	1	0.35	-0.28	0.14	0.67	0.63	0.59
F/G	-0.50	0.89	-0.97	-0.08	0.59	1	-0.22	-0.52	0.49	0.55	0.56
Brix	-1.00	0.46	-0.45	0.23	0.37	0.50	1	0.44	-0.20	-0.25	-0.03
Viscosity	-0.82	0.22	-0.27	0.36	0.46	0.30	0.82	1	-0.02	-0.16	-0.01
Hardness	-0.43	-0.01	0.07	0.08	0.30	-0.02	0.43	0.37	1	0.95	-0.92
Consistency	-0.25	-0.05	0.09	0.29	0.24	-0.06	0.25	0.21	0.96	1	0.96
Adhesivity	-0.57	0.02	0.07	0.28	0.34	0.01	0.57	0.50	-0.93	0.86	1