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Rheological and Physicochemical Properties of Honeys as a Function of Temperature, Concentration and Moisture Content

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ABSTRACT: In this study the rheological and physicochemical properties of four types of honeys, two poly floral (Mountain, Forest) and two mono floral (Sunflower, Ivy), were investigated. Rheological characteristics of honeys were evaluated at different temperatures (10, 15, 20, 25 and 30ºC). All the honeys exhibited Newtonian behavior for shear rate in the range of 1.045-41.8 s^{-1}. The viscosity of samples varied between 1.70 and 270.48 Pa.s according to the kind of honey and the temperature of measurement. The temperature dependence of viscosity was described using the Arrhenius and the Vogel–Taumman–Fulcher (VTF) equations. The values of flow activation energy varied between 89.716 and 112.189 kJ/mol. Two models (Power Law and Exponential models) were also investigated to describe the concentration dependence of viscosity. The samples were found to be different from each other in moisture content, ºBrix, pH, ash, conductivity, free acidity, diastase activity, hydroxymethylfurfural content and sugar content values. The water content of honey samples was between 15.25–19.92 g/100 g.

Keywords: *Arrhenius Model, Honey, Physicochemical, Rheology, VTF Model*.

Introduction

Honey is a natural food product having a high nutritional and medicinal value. Honey contains a complex mixture of carbohydrates, mainly glucose and fructose other sugars (depending on the floral origin), organic acids, lactones, amino acids, minerals, vitamins, enzymes, pollen, wax, and pigments. Sensory and physical properties and chemical composition of honey depend on the botanical origin and the regional and climatic conditions of the area in which it is produced (Lazaridou *et al.*, *2004;* Ramzi *et al., 2015*).

Most honeys are supersaturated solutions of glucose, which have a tendency to crystallize spontaneously due to the formation of glucose monohydrate. It could happen, in a short time before extraction or longer. Crystallization of honey, commonly called granulation, is an undesirable process in liquid honey because it affects the textural properties, honey processing during extraction, filtration, mixing or bottling and it also reduces the honey appealing to the consumer. Moreover, in many cases, due to the crystallization of honey, the moisture content of the liquid phase will increase

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which can allow naturally occurring yeast cells to multiply causing fermentation of the product. Physical and chemical properties of different types of honey have been analyzed by many Researchers (de Rodrıǵuez *et al.*, 2004; Küçük *et al.*, 2007; Ouchemoukh *et al.*, 2007; Saxena *et al.*, 2010; Silva *et al.*, 2009). The composition highly depends on the type of flowers utilized by the bee as well as climatical conditions.

The knowledge of honey rheology is very important for its processing, quality control, process control, and selection of proper process equipment, storage, handling, and transportation and plays an important role in fluid heat transfer (Al-Mahasneh *et al.*, 2014; Dobre *et al.*, 2012; Salehi & Kashaninejad, 2014; Yoo, 2004; Zameni *et al.*, 2015). Rheological properties of honeys depend on many factors including composition, temperature, and amount and size of crystals (Bhandari *et al.*, 1999). Water content is one of the major factors affecting the rheology of honey. The water content of honeys varied between 10.6 and 29 g/100 g (Ajlouni & Sujirapinyokul, 2010). Generally, the viscosity decreases as water content increases due to the plasticizing effect of water (Yanniotis *et al.*, 2006). It is known that the more water content; the lower is the viscosity of honey. Viscosity was also reported to be inversely proportional to temperature, especially at temperatures below 30ºC. Viscosity decreases as temperature increases, due to less molecular friction and reduced hydrodynamic forces (Mossel *et al.*, 2000).

Although the Newtonian behavior of honey has been reported in several studies few authors reported a non-Newtonian behavior for certain types of honeys. For example pseudo plastic for Galician (Spanish honey) and Jordanian wild flowers honeys, thixotropy for group of Karvi, Heather, Manuka, and Buckwheat, and dilatancy for Eucalyptus and Nigerian honeys (Al-Mahasneh *et al.*, 2014; Gómez-Díaz *et al.*, 2006; Mossel *et al.*, 2000). Several researches have studied the rheological behavior of honey varieties produced from different countries, such as those from Brazil (Sabato, 2004), Germany (Smanalieva & Senge, 2009), Poland (Witczak *et al.*, 2011) and Korea (Yoo, 2004).

Different kinds of honeys with various floral origins (such as Rosa, Thyme, Astragalus, Trifolium, sunflower, Medicago, alfalfa and etc.) are produced in different regions of Iran. In this study, some physicochemical and rheological properties of four Iranian honeys from Golestan provience were investigated.

Materials and Methods

- *Sample collection*

All honey samples were collected directly from beekeepers in Golestan Province, Iran, in different seasons of 2012. The samples were two monofloral (Sunflower, Ivy) and two polyfloral (Mountain, Forest) honeys.

- *Physiochemicalanalysis*

Moisture content of honey samples were determined by measuring the refractive index at 20ºC using a digital refractometer (ABBE Refractometer, CETi, BELGIUM). The water content and ºBrix concentration was fixed based on a Chataway table (Bogdanov *et al.*, 2002). Hydroxymethylfurfural content (HMF), diastase activity, pH, ash, free acidity, and electrical conductivity were determined by the harmonized methods of the International Honey Commission (AOAC, 2010). pH was measured by pH-meter (Denver Instrument UltraBasic pH Meters, UB-10) in a solution containing 10 g of honey in 75 mL of distilled water. Free acidity was determined by the titrimetric method, the solution containing 10 g of honey in 75 mL of distilled water was titrated with 0.1 N NaOH until the pH reached to 8.3 and the results were expressed as equiv./kg (Bogdanov *et* *al.,* 2002). Ash content was obtained by heating 5 g of honey samples at 550ºC for 6 h in a muffle furnace (Nabertherm GmbH, B 150, Germany). The electrical conductivity of a solution of 20 g dry matter of honey in 100 ml distilled water was measured at 20ºC using an electrical conductivity cell (WTW cond 720). The determination of the electrical conductivity is based on the measurement of the electrical resistance, of which the electrical conductivity is the reciprocal (Bogdanov *et al.*, 2002).

Hydroxymethylfurfural was determined after clarifying the samples with Carrez reagents (I and II) and the addition of sodium bisulfate and distilled water to the reference solution and the sample solution, respectively; absorbance was determined against a reference solution at 284 and 336 nm in a 1 cm quartz cuvette in a spectrophotometer (PG Instruments Ltd, T80+ UV/VIS Spectrometer). Results were expressed in milligrams of HMF per kg of honey.

Diastase activity was measured using a buffered soluble starch solution and honey, which was incubated in the thermostatic bath at 40ºC. The absorption was determined using a T80+ UV/VIS Spectrometer and a chronometer. By using regression (without using the data point at 0 min), lines were fitted to the absorption data and the diastase number was calculated from the time taken for the absorbance to reach 0.235.

The amylase activity is usually expressed as diastase number, symbol DN, and also known as Gothe units. A Gothe unit is defined as ml of 1% starch solution hydrolysed at 40 ^{0}C for one hour by the enzyme present in 1 g of honey (Bogdanov *et al.*, 2002).

The reducing sugars (fructose and glucose) and sucrose content were determined by the Lane and Eynon (old Fehling) method. In this method the amount of total sugars and reducing sugars were determined using titration method by the solutions of Fehling A and B before and after hydrolysis. The sucrose concentration in honey samples was calculated using the equation: sucrose (%) = (total sugar-total reducing sugar) × 0.95. The results for each sugar were represented as gram per 100 g honey. All experiments performed in three replicates and the data was presented as a mean ± standard deviations of each experiment.

- *Rheological properties*

- *Sample preparation*

Since the presence of crystals and air bubbles can influence the viscosity of honey, all honey samples were heated to 55ºC for 1 h in a water bath to dissolve any crystals that might be present and then to ensure complete removal of air bubbles, the preheated honey samples were stored in an incubator (model BINDER, USA) at 30ºC for 48 h.

- *Rheological measurements*

The rheological measurements were carried out on the honey samples at eighteen rotations, ranging from 5 to 200 rpm at five temperatures, ranging from 10 to 30ºC, using Brookfield viscosimeter, model RVDV- II+ pro, manufactured by Brookfield Engineering Laboratories, USA. A water bath (Model ULA-40Y, Brookfield, Inc. USA) was employed to maintain the constant temperature in range of 10 to 30ºC in the viscometer during different experiments (Salehi & Kashaninejad, 2015). The viscosity and shear stress curves of the honeys were drawn in the shear rate range 1.048- 41.81 s^{-1}betweenthe temperatures of 10 to 30ºC for every 5ºC intervals. All the measurements were performed in two replicates and the data presented as mean ± standard deviation for each experiment.

Arrhenius model (Eq. 1) was used for the evaluation of the dependence of viscosity on temperature:

$$\mu = \mu_0 . exp\left(\frac{E_a}{RT}\right) \quad (1)$$

Where μ_0 is constant, E_a is the activation energy (J/mol), R is the gas constant = 8.314 (J/K. mol) and T is the temperature in K. This relationship can be linearized to facilitate theanalysis by taking the natural logarithm of both sides as follows:

$$Ln(\mu) = Ln(\mu_0) + \left(\frac{E_a}{RT}\right) \quad (2)$$

Therefore, a plot of ln (μ) versus 1/T will yield a straight line with a slope= $\left(\frac{E_a}{R}\right)$ from which E_a can be obtained.

The temperature dependence of viscosity was also described using the Vogel–Taumman–Fulcher (VTF) model:

$$\mu = \mu_\infty . exp\left(\frac{B}{T-T_0}\right) \quad (3)$$

where μ_∞ is the viscosity at T=∞ and T_0 is the temperature at which the relaxation time relevant to molecular displacements becomes infinite. The value T_0 was fixed at 184 K, that was estimated from the data reported by Oroian *et al.* (2013)for aqueous sugar systems of similar concentration, and B was calculated as the slope of the linearized form of equation of VTF.

The concentration dependence of viscosity was described using the Power law (Eq. 4) and Exponential models (Eq. 5):

$$\mu = \mu_1 C^{b_1} \quad (4)$$

$$\mu = \mu_2 . exp(b_2 C) \quad (5)$$

where, μ_1, μ_2, b_1, and b_2 are constants, and C is the concentration in ºBrix.

- *Statistical analysis*

Standard statistical packages (SAS Version 9.00 and Excel 2010), were used for relevant analysis. Means comparison of the physicochemical and rheological parameters was performed by Duncan multiple range test.

Results and Discussion

- *Physicochemical properties*

The results of physicochemical parameters of studied honeys are presented in Table 1. The moisture content of honey depends on various factors such as the harvesting season, the degree of maturity reached in the hive, moisture content of original plant and climatic factors. Honey moisture is a quality criterion that determines the capability of honey to remain stable and to resist spoilage by yeast fermentation; therefore it affects storage life and processing characteristics (Omafuvbe & Akanbi, 2009; Perez-Arquillué *et al.*, 1994). The refractive index at 20ºC for different types of honeys varied from 1.4867 to 1.4985, and then using the Chataway table the value of moisture was obtained between 15.25% and 19.92% (Table 1). The highest and lowest moisture contents were related to the samples Ivy and Forest, respectively. All honeys met the requirement for moisture content as defined by the Codex Alimentarius and Iranian Standards (Commission *et al.*, 2003) (max 20%). In general, the moisture content in different varieties of honeys may be as low as 10.6% for Homebrand sample (Ajlouni & Sujirapinyokul, 2010) and as high as 29% for Acacia sample (Junzheng & Changying, 1998). The moisture content values reported by other researchers for some honeys are: 15.4-18.3% (Perez-Arquillué *et al.*, 1994), 13-18.9% (Lazaridou *et al.*, 2004), 17.2-21.6% (Saxena *et al.*, 2010), 16.2-20.1% (Yoo, 2004), 16.1-17.3% (Al-Mahasneh *et al.*, 2014).

Table 1. Some physico-chemical parameters of honey samples

Parameter	Forest	Mountain	Sunflower	Ivy
Moisture content (g/100 g)[a]	15.25[d]±0.002	16.08[c]±0.002	19.49[b]±0.001	19.92[a]±0.001
[0]Brix	82.70[a]±0.002	81.9[b]±0.002	78.7[c]±0.001	78.2[d]±0.001
Diastase activity (DN)	10.25[b]±0.310	8.38[d]±0.22	9.36[c]±0.056	18.61[a]±0.3
HMF (mg.kg^{-1})	10.63[a]±0.150	9.43[b]±0.3	7.78[c]±0.15	5.34[d]±0.23
pH	3.69[b]±0.015	3.91[a]±0.023	3.61[c]±0.015	3.54[d]±0.011
Free acidity (meq .kg^{-1})	15.17[d]±0.29	18.00[c]±0.50	38.67[a]±0.58	34.67[b]±0.58
Ash	0.20[c]±0.010	0.21[c]±0.005	0.40[a]±0.010	0.31[b]±0.008
Conductivity (µS .cm^{-1})	219.13[d]±0.58	272.12[c]±0.0	691.41[a]±0.58	508.68[b]±1.0
Total suger	76.11[a]±0.99	74.18[b]±0.37	73.19[bc]±0.38	72.29[c]±0.5
Total reducing sugar	73.25[a]±0.73	73.25[a]±0.64	68.89[c]±0.67	70.44[b]±0.9
Sucrose	2.71[b]±0.240	0.88[d]±0.34	4.08[a]±0.38	1.76[c]±0.35
Fructose	41.72[a]±0.99	39.92[b]±0.47	35.25[d]±0.42	38.0[c]±0.30
Glucose	31.53[a]±1.56	33.34[a]±0.9	33.64[a]±1.04	32.44[a]±0.9
Fructose/glucose ratio	1.326[a]±0.093	1.198[b]±0.044	1.049[c]±0.045	1.172[b]±0.036

[a] Results are expressed as mean values ± standard deviation. Means in a row with different letters are significantly different (P<0.05)

Diastase activity is a parameter used to qualify the honey if it has been widely heated during processing, because the enzyme is sensitive to heating and storage factors (Silva *et al.*, 2009). The amylase activity ranged from 8.38 to 18.61 Gothe in the studied honeys (Table 1). These values were in agreement with those reported by Codex (Commission *et al.*, 2003). A high quality honey is expected to have high diastase activity. The Ivy sample had the highest DN value (18.61). Low DN values in some honey samples may indicate exquisite heat treatments that caused significant decrease in amylase contents. As found by Tosi *et al.* (2008), the diastase number of honey decreases with increased temperature up to 100ºC when the activity of the enzyme decays. According to the report by other researchers, the plant type used by Honeybee significantly influences the Diastase content (Küçük *et al.*, 2007). For Indian, Turkish, Argentian and Australian honeys, the amylase activity ranged from 31.4 to 42.9 Gothe, 5 to 10.9 Gothe, 11.2 to 25.8 Gothe and 9.43 to 25.4 Gothe, respectively (Ajlouni & Sujirapinyokul, 2010; Kaur *et al.*, 2015; Tosi *et al.*, 2008).

Hydroxymethylfurfural (HMF) content is an indicative factor for honey freshness. HMF can be formed either by Maillard reaction (heating of reducing sugars in the presence of proteins), or by dehydration under acidic conditions (Ajlouni & Sujirapinyokul, 2010). The content of HMF in the studied honeys ranged from 5.34 to 10.63 mg/kg (Table 1). These results were in agreement with those reported by Codex (Commission *et al.*, 2003). Since the high HMF concentration and low diastase number were not observed in any of the honey samples simultaneity, it could be an indication for suitable heat treatment and storage conditions for examined samples. The HMF content of Argentinian, Polish and Spanish honeys have been found to vary between 1.1 to 44.8 mg/kg, 0.36 to 74.9 mg/kg and 3.12 to 14.85 mg/kg, respectively (Finola *et al.*, 2007; Juszczak & Fortuna, 2006; Oroian *et al.*, 2013).

In general, honey is acidic in nature irrespective of its variable geographical origin. Its acidity is due to the presence of organic acids, mainly gluconic acid, in equilibrium with their corresponding lactones or internal esters, and to inorganic ions, such as phosphate, sulphate and chloride (Finola *et al.*, 2007; Silva *et al.*, 2009). All studied honey samples were acidic in nature and the pH values varied from 3.54 to 3.91 (Table 1). Moreover free acidity values were obtained between 15.17 and38.67 meq/kg. Free acidity was within the limits of Codex (Commission *et al.*, 2003)(below 40 meq/kg), indicating the absence of undesirable fermentation.

The ash content is a quality criterion for honey botanical origin. The mineral content of honey depends on the type of soil in which the original nectar bearing plant was located (Saxena *et al.*, 2010; Silva *et al.*, 2009). The ash content of the studied honey samples were between 0.2 to 0.4% (Table 1). The maximum value is found for the Sunflower honey (0.4%), followed by the Ivy honey (0.31%). All the values are in the range determined by Codex (Commission *et al.*, 2003) (max. 0.6). Other researchers also reported the same results such as 0.1776-0.5669% (Malika *et al.*, 2005) and 0.19-0.36% (Omafuvbe & Akanbi, 2009).

The electrical conductivity is related to the ash, organic acids, proteins, some complex sugars and polyols content and varies with botanical origin (Juszczak & Fortuna, 2006; Terrab *et al.*, 2004). The electrical conductivity values of the honey samples were between 219.13 µS/cm and 691.41 µS/cm. These values are below the maximum limit indicated by Codex (Commission *et al.*, 2003) for nectar honey (800 µS/cm). The results of the examined samples are quite similar to Spanish, Tunisian and Portuguese honeys for which the electrical conductivity values ranged from 288 to 559 µS/cm, 314 to 618 µS/cm and 114.7 to 636.5 µS/cm, respectively (Silva *et al.*, 2009; Terrab *et al.*, 2004).

In the present study, the increase of ash content of the honey samples was attended by the increase of electrical conductivity. The coefficient of correlation between electrical conductivity and ash content was 0.9943 (Figure 1).

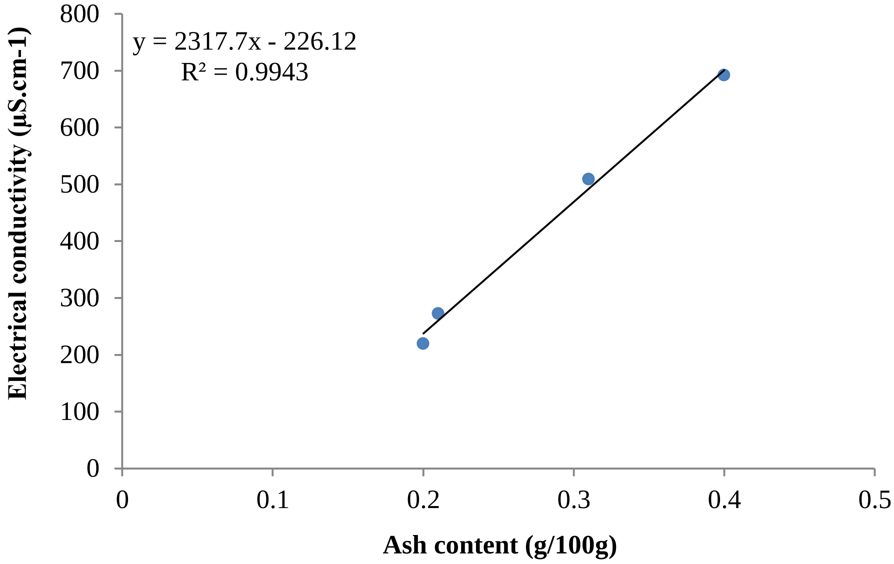

Fig. 1. The linear relationship between electrical conductivity and ash content of honeys

The total sugar and the total reducing sugar contents in the honey samples ranged from 72.29 to76.11% and 68.89 to 73.25%, respectively (Table 1). The data indicates that sugars are the main components of honey. The values of total reducing sugar were in agreement with those reported by Codex (Commission *et al.*, 2003) (min. 65). The sucrose contents in the samples were between 0.88 to 4.08%. The values of sucrose in all the honey types were less than the maximum allowable limit of 5% purposed by Codex (Commission *et al.*, 2003). A high sucrose concentration of honey could be related to reasons such as overfeeding of honeybees with sucrose syrup, adulteration, or an early harvest of honey, because sucrose has not been fully transformed into glucose and fructose by the action of invertase (Küçük *et al.*, 2007). Some unifloral honeys like Banskia, Citrus, Hedysarum Medicago and Robinia contain up to 10% sucrose, whereas, up to15% sucrose has been reported for Lavandula honeys (Saxena *et al.*, 2010).

The major sugars present in honey are reducing sugars mainly fructose and glucose. The actual proportion of fructose to glucose, in any particular honey, depends largely on the source of the nectar (Küçük *et al.*, 2007). The fructose/glucose ratio was estimated for all samples from 1.049 in Sunflower honey to 1.326 in Forest honey. This ratio gives information about the crystallization state of honey. Honey with high fructose/glucose ratio would remain liquid for longer times because of the modification of the saturated level of glucose by the presence of the larger amount of fructose. The ratio of fructose/glucose might have an influence on honey flavour since fructose is much sweeter than glucose (Ajlouni & Sujirapinyokul, 2010; Finola *et al.*, 2007).

The reported fructose/glucose ratio for some Venezuela, German and Australian honeys are in the range of 1.19 to 1.39, 0.95 to 1.75 and 1.1 to 1.27, respectively (Ajlouni & Sujirapinyokul, 2010; Smanalieva & Senge, 2009).

- *Rheological behaviour*

Rheological properties of honey samples at various temperatures (5, 10, 15, 20, 25 and 30ºC) were studied and the results are presented in Table 2. The values of the torque and speed rate (rpm) were converted into the shear rate and shear stress according to the methodology proposed by Mitschka (1982). The values of shear rate calculated in the range of 1.045 to 41.8 s^{-1}. The values of viscosity varied between 1.7 to 270.48 Pa.s according to the kind of honey and the temperature of measurement.

Table 2. Moisture content and viscosity of honeys at different temperatures

Honey	**Moisture Content (g/100g)**[a]	**Viscosity (Pa.s)**				
		10ºC	**15ºC**	**20ºC**	**25ºC**	**30ºC**
Forest	15.25±0.002	270.48[a]±0.45	103.05[c]±0.52	45.50[e]±0.25	23.52[h]±0.17	11.12[l]±0.13
Mountain	16.08±0.002	181.75[b]±0.21	75.99[d]±0.54	35.10[f]±0.13	18.07[j]±0.21	7.95[o]±0.07
Sunflower	19.49±0.001	32.35[g]±0.34	16.80[k]±0.24	8.69[n]±0.20	4.52[q]±0.08	2.55[s]±0.04
Ivy	19.92±0.001	22.14[i]±0.27	10.43[m]±0.21	5.87[p]±0.23	3.28[r]±0.14	1.70[t]±0.01

[a] Results are expressed as mean values ± standard deviation. Means in the table with different letters are significantly different (P<0.05)

Figure 2 (a- d) shows the flow curves and Figure 3 (a- d) represents the relationship between viscosity and shear rate for honey samples at different temperatures, respectively. According to the curves, it was observed that the shear stress (τ) dependence on the shear rate (γ) was linear and the viscosity did not change by increasing the shear rate and it remained nearly constant for all type of honeys. These results show that the studied samples of honey are Newtonian fluids (τ=μγ), but the value of viscosity substantially decreased as the temperature was increased for all the samples. These results are consistent with the findings reported by other researches on different types of Chinese, Australian, Greek and Romania honeys (Bhandari *et al.*, 1999; Dobre *et al.*, 2012; Junzheng & Changying, 1998; Lazaridou *et al.*, 2004).

Figure 4 represents the relationship between viscosity and temperature of honey samples evaluated in this study. Viscosity decreased with an increase in temperature for all honey samples. According to Figure 4, the decrease in viscosity is more pronounced at lower temperatures while at higher temperatures decrease in viscosity is much slower. This observation is clearly seen in the scientific works (Sopade *et al.*, 2003; Yanniotis *et al.*, 2006). Oroian *et al.* (2013) showed that the temperature effect on viscosity is greatest at lower temperatures

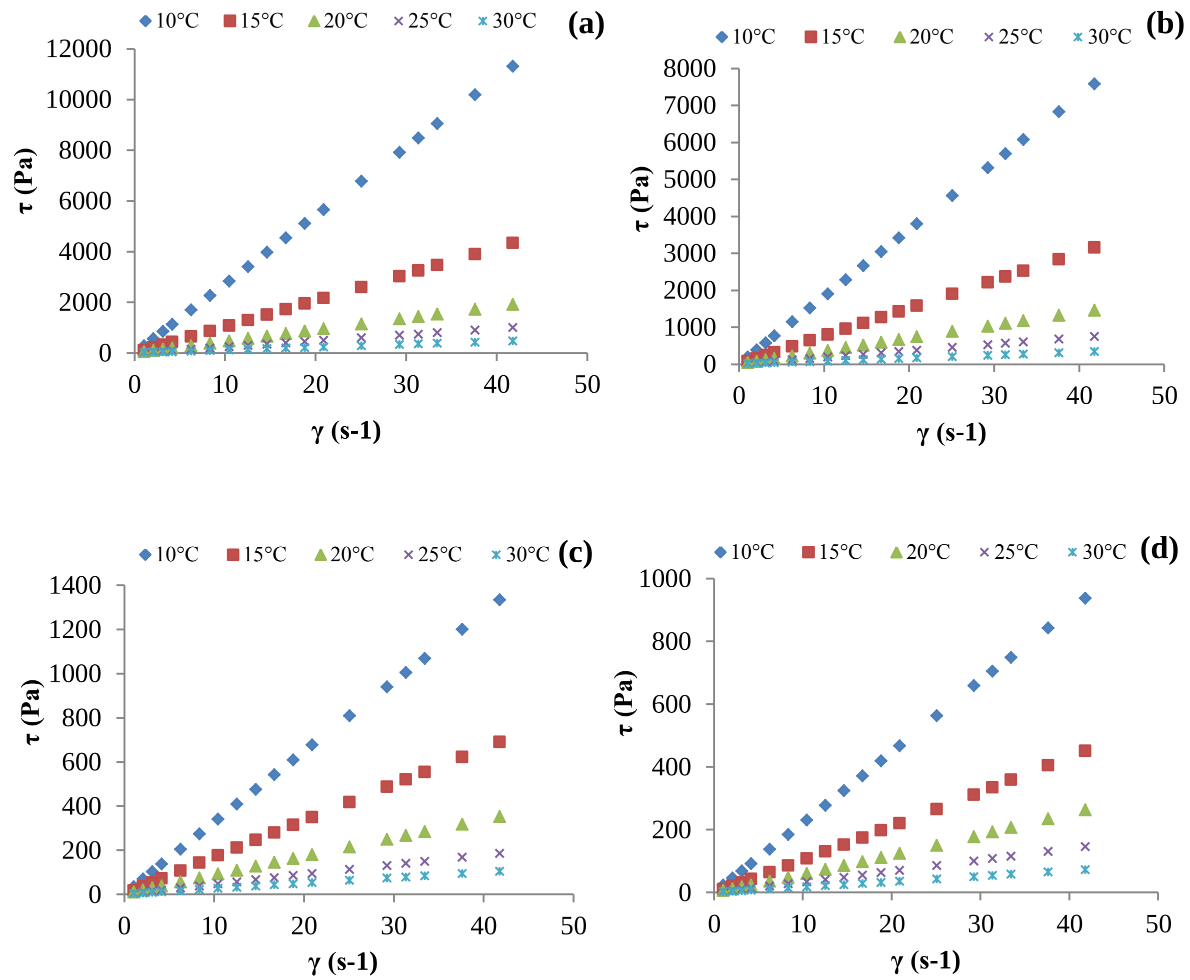

Fig. 2. Flow curves of honeys at different temperatures: **a:** Forest, **b:** Mountain, **c:** Sunflower, **d:** Ivy

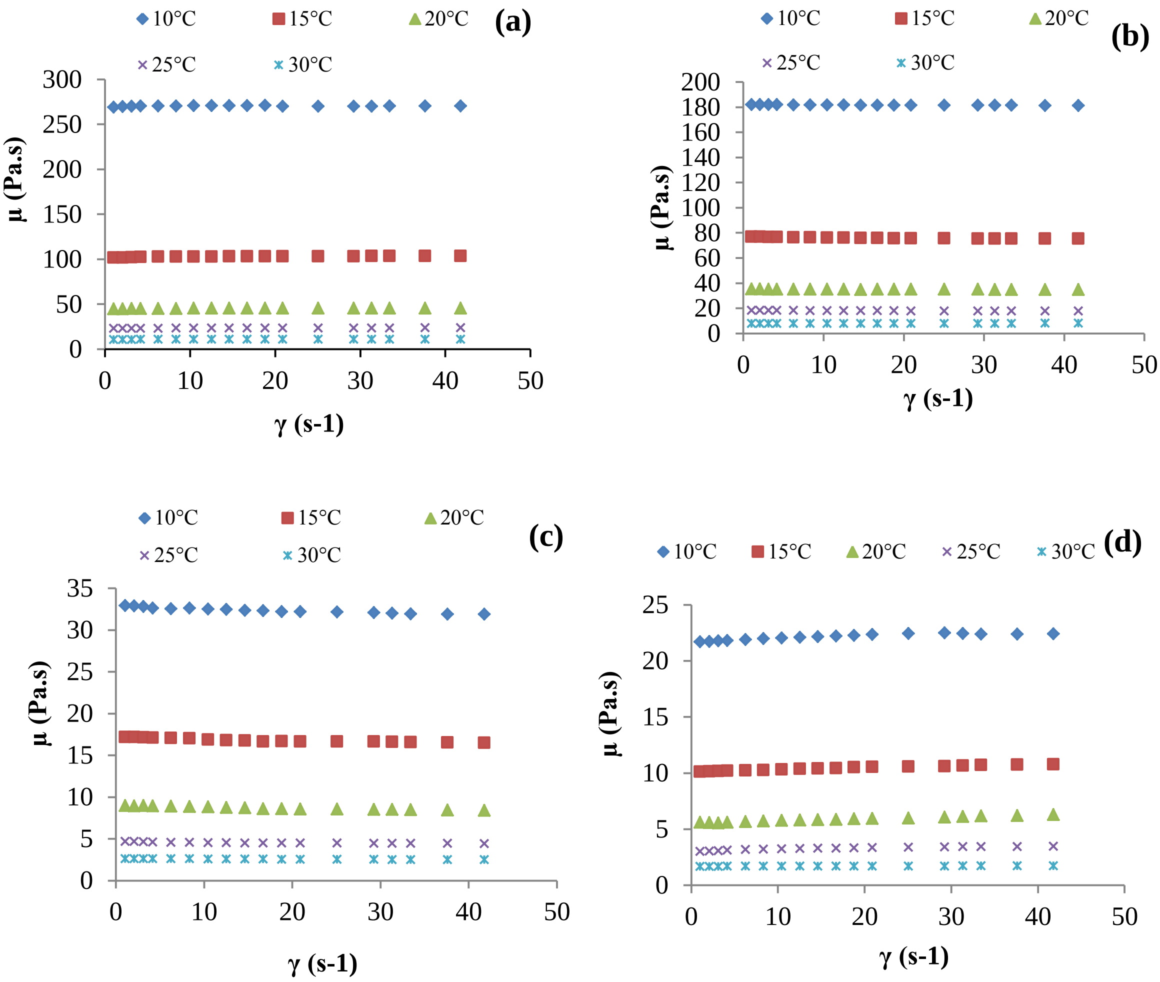

Fig. 3. Effect of shear rate and temperature on viscosity of honey samples: **a:** Forest, **b:** Mountain, **c:** Sunflower, **d:** Ivy

(below 15ºC), and heating above 30ºC has a little effect of practical importance. Generally, as the temperature increases the average velocity of the molecules in honey increases and the amount of the contact time with adjacent molecules decreases; thus, the average intermolecular forces decrease and therefore the viscosity decreases.

In this study the temperature dependence of viscosity was described using Arrhenius and VTF models. Application of the Arrhenius model on the honey samples is shown in Figure 5. A linear relationship of ln (μ) vs. (1/T) was observed. From this equation activation energy (E_a), μ_0, and the determination coefficients (R^2) for all honeys were determined by the use of regression analyses which the results are presented in Table 3.

The values of R^2 for all samples were greater than 0.997. This indicates that the viscosity dependence on temperature can be fitted using an Arrhenius equation adequately.

The values of activation energy (E_a) ranged from 89.315 to 112.189 kJ/mol. These data were similar to the results reported for Jordanian, Australian and Polish honeys(Al-Malah *et al.*, 2001; Juszczak & Fortuna, 2006). Activation energy indicates the sensitivity of the viscosity to temperature changes. Higher activation energy means that the honey viscosity is relatively more

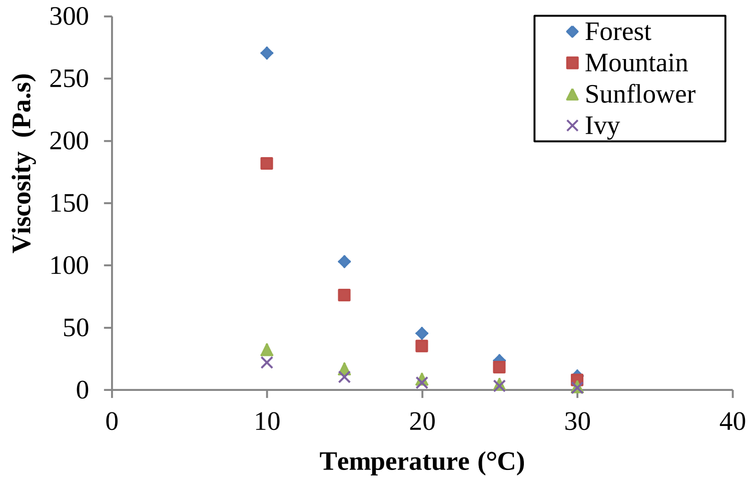

Fig. 4. Viscosity of honey samples as a function of temperature

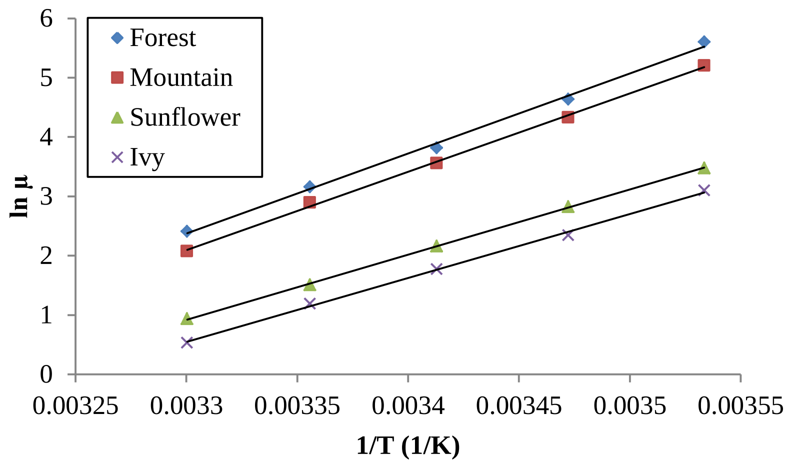

Fig. 5. Arrhenius plot of viscosity vs. temperature

Table 3. Parameters of Arrhenius and VTF models for different honeys

Honey	Arrhenius model			VTF model		
	μ_0 (Pa.s)	E_a (kJ/mol)	R^2	μ_∞ (Pa.s)	B (K)	R^2
Forest	4.91×10^{-19}	112.189	0.9971	1.908×10^{-6}	1855.4	0.9990
Mountain	9.81×10^{-19}	109.745	0.9987	2.073×10^{-6}	1812.5	0.9979
Sunflower	4.799×10^{-16}	91.188	0.9998	8.363×10^{-6}	1505.8	0.9987
Ivy	5.92×10^{-16}	89.716	0.9983	7.027×10^{-6}	1481.8	0.9977

sensitive to a temperature change (Lazaridou *et al.*, 2004). Thus, among the honey samples investigated in this study, Ivy honey is the least sensitive (lowest activation energy value) and Forest honey is the most sensitive (highest activation energy value) to temperature. In deed the highest and least activation energy values was obtained for forest honey with lowest moisture content and Ivy honey with highest moisture content, respectively. There was an inverse linear relationship between E_a and moisture content (R^2=0.9958) for studied samples (Figure 6). These results show the inverse relationship between the moisture content and the sensitivity of the viscosity to temperature changes.

A linear plot of ln(μ) versus (1/T-T_0) was drawn for the VTF model. The values of constant B and determination coefficients (R^2) for the individual samples calculated using the regression analyses are shown in Table 3. The values of constant B obtained for different honeys varied from 1481.8 to 1855.4 K. Recondo *et al.* (2006) and Oroian *et al.* (2013) reported similar values for constants B, 1535 K for the Argentina honey and 1595 to 1954 for the spanish honeys, but Sopade *et al.* (2003) found B values in the range of 4.5 to 12.9K for Australian honeys. This difference is due to the fact that Sopade *et al.* (2003) used the value of T_g (The glass transition temperature) for the constant T_0.

Coefficient of determination for all honey samples was greater than 0.997 that indicates the VTF model is a good model to describe the temperature dependence of honey viscosity in this research. Comparison between the two used models shows that the Arrhenius model to be the most suitable model for Mountain, Ivy and Sunflower honeys and VTF model would be the best for honey of Forest.

Besides temperature, honey composition, the moisture content has an important influence on viscosity variation. Examples of viscosity curves were plotted at 20ºC for all honey samples in Figure 7. Forest honey with the lowest moisture content exhibited the greatest values of viscosity over all shear rate range, while Ivy honey with the greatest water content had the lowest ones. This result confirms earlier data concerning dependence of honey viscosity on water content. Honeys with greater water content

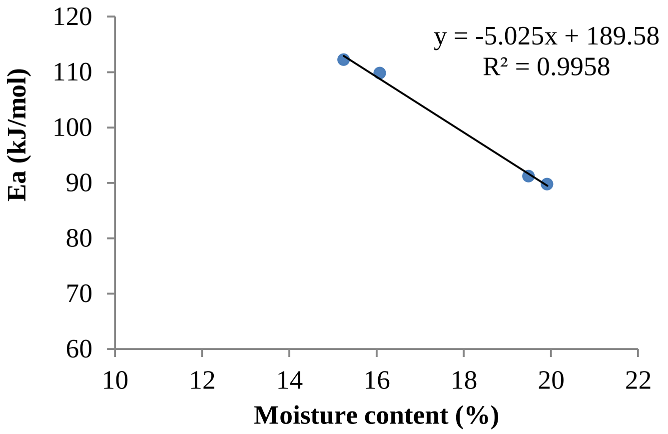

Fig. 6. Activation energy as a function of moisture content

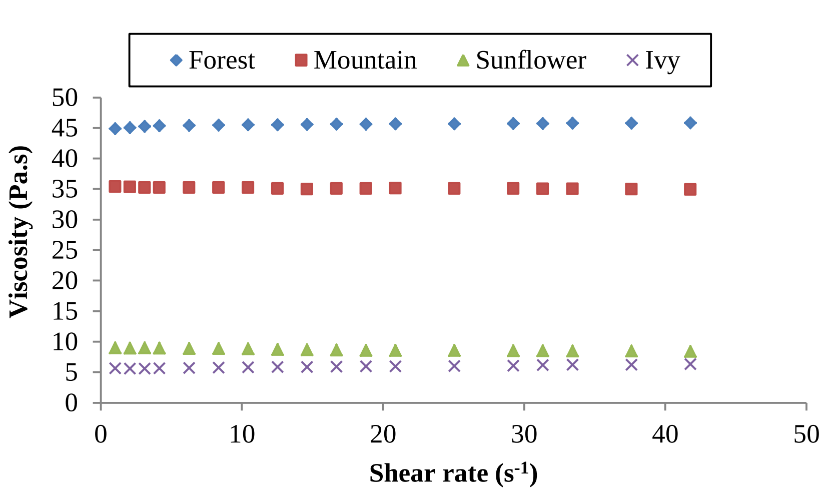

Fig. 7. Viscosity of honey samples vs. shear rate at 20ºC

are less viscous because of plasticizing and diluting effect of water, which reduces intermolecular friction on food products. In this study, both Power Low and Exponential models were used to describe dependence of honey viscosity on soluble solid content (C, ºBrix) (Oroian *et al.*, 2013).

The curves of μ vs. C (ºBrix) and lnμ vs. C (ºBrix) were plotted for Power law and Exponential models, respectively and the model constants including μ_1, μ_2, b_1, b_2 determined using regression analyses. The calculated parameters are presented in Table 4.

The values of R^2 for the two models obtained more than 0.99 for all the samples. Thus, both models were suitable for describing the concentration dependence of viscosity but it can be seen that the Power Law model was better than the Exponential model. Activation energy values that were calculated for different samples varied. The greatest values of activation energy were obtained for the samples with the highest concentration and lowest values were obtained for the sample with the lowest concentration.

Therefore the following models are presented (Oroian *et al.*, 2013):

$$E_a = A_1 C^{B_1} \quad (6)$$

$$E_a = A_2 \exp(B_2 C) \quad (7)$$

where A_1, A_2, B_1, and B_2 are constants. For the equation 6, the curve of E_a vs. concentration was plotted and for the equation 7, the curve of $\ln(E_a)$ vs. concentration was plotted and the model parameters calculated by the regression analyses (Table 5). The values of R^2 exhibited that the Exponential model was more appropriate than the Power law model to describe the concentration dependence of E_a.

Conclusion

Some physicochemical characteristics and rheological behavior of four honey samples produced in Iran was investigated in the present study. Physicochemical parameters (moisture, ^{0}Brix, pH, ash, conductivity, total acidity, diastase activity, hydroxymethylfurfural content, total sugar content, total reducing sugar content, fructose and ratio fructose /glucose) and rheological properties varied significantly among studied samples. This study demonstrated that floral source has important role in quality parameters related to processing and storage. Rheological behavior of honey varieties was determined in the temperature range 10- 30^0 C. All studied samples exhibited Newtonian

Table 4. Parameters of Power law and Exponential models at different temperatures

T (ºC)	Power Law model			Exponential model		
	μ_1 (Pa.s)	b_1	R^2	μ_2 (Pa.s)	b_2 (Brix^{-1})	R^2
10	5×10^{-83}	44.207	0.9989	4.956×10^{-18}	0.5498	0.9986
15	5×10^{-75}	39.797	0.9925	1.82×10^{-16}	0.4949	0.9919
20	5×10^{-68}	35.982	0.9944	4.07×10^{-15}	0.4474	0.9938
25	2×10^{-66}	35.000	0.9973	5.713×10^{-15}	0.4353	0.9969
30	1×10^{-60}	31.809	0.9912	6.876×10^{-14}	0.3956	0.9909

Table 5. Influence of the total soluble solids (C, °Brix) on the activation energy

Parameter Model	A_i	B_i	R^2
$E_a = A_1 C^{B_1}$	9×10^{-7}	4.2119	0.9943
$E_a = A_2 exp(B_2 C)$	1.1465	0.0557	0.9973

i=1,2

behaviour. The viscosity was independent of shear rate, but strongly affected by temperature and moisture content and varied significantly among studied samples. Arrhenius and VTF models were fit to describe the relationship between temperature and viscosity. The calculated activation energies for flow were inversely related to the moisture content. The maximum of activation energy obtained for Forest sample with lowest moisture content and highest viscosity, indicating that the viscosity is more sensitive to temperature changes at low moisture contents.

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