Acta Agrophysica, 2006, 7(1), 7-15

CHARACTERISTICS OF WATER STATE IN SOME CHOSEN TYPES OF HONEY FOUND IN POLAND

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Abstract. The paper presents an analysis of the state of water in two chosen types of honey: rape and buckwheat honeys. In the research two different methods were used: the first one was based on the measurement of the activity of water in dependence on the moisture content, whereas the other one consisted in determining the rheological properties of honeys at low temperatures. The rheological measurements showed that at temperatures below zero degrees centigrade the analysed honey preserved its Newtonian properties although its viscosity considerably increased. The measured values of water activity in the honey depended linearly on the water content, although they were found to be different for either type of honey. The research work and measurements have shown that water found in the honey is bound by multi-layer adsorption. It has also been determined that in the case of buckwheat honey with a moisture content of 19.8% a critical value of water activity is reached at the temperature of 25 degrees. Above this critical point fermentation may occur. The results obtained in the investigations were compared with the current literature on the subject.

Keywords: water activity, honey viscosity

INTRODUCTION

Honey is a product made by bees from vegetable raw materials such as nectar and honeydew. It is a clear, sticky, aromatic and hygroscopic liquid of the density of around 1.38-1.45 g cm^{-3} [8]. Its chemical composition is dominated by glucose and fructose whose total quantity may exceed even 80% of the mass of the product [13]. Carbohydrates also include such disaccharides as maltose and sucrose, as well as trisaccharides such as melezitose [9]. Moisture content in honey usually amounts to 20%, reaching, in some exceptional cases, almost 23% in heather honey [12]. Apart from saccharides, honey contains enzymes, organic acids, mineral salts, vitamins, aromatic oils and flavonoids [20]. However, monosaccharides and water determine the physical properties of this product [9].

In general the characteristics of the moisture content depend on the activity of water in honey. In liquid honeys water activity reaches the values from a_w = 0.53 for 15.8% of water content up to a_w = 0.69 for 22.20% of water content [17]. Other reports state that this parameter ranges from 0.57 up to 0.622 for moistures from 16.5 to 19.4 %, respectively [16]. It is assumed that water activity is affected by the honey origin which in turn remains related to the chemical composition of the product [9]. It is often pointed out to the fact that going over the critical value i.e. a_w = 0.6 may be the cause of the fermentation of honey in its upper layers during storage [9,17]. This phenomenon was already observed some time ago, i.e. in 1977 when „Doner" discovered the dependence of honey fermentation on the increase of its activity in spite of the fact that its moisture content did not exceed the admissible limit [6]. In the literature on the subject we can find reports concerning problems connected with storing bee honeys satisfying qualitative requirements [21]. The problem refers mainly to buckwheat honey collected in "wet years" as it starts to ferment in liquid state. On the other hand, rape honey will cause problems mainly after its granulation as it begins to "grow" or "rise" giving off an unpleasant smell [10]. There are no reports in beekeeping bibliography concerning water activity in monofloral honeys. Nor are there any moisture content values or limits that would indicate safe honey storage at room temperature.

Another aspect related to the state of water in honey relates to the rheological properties of this product. There are a considerable number of publications available on this subject; however, they are mainly concerned with the measurements of honey viscosity at relatively high temperatures [3,9,14]. The investigations on the rheological properties of honey are usually conducted in the context of its hydraulic transport as well as its filtration, dosage and spilling processes, which are usually carried our at high temperatures. The investigations have shown in an unambiguous way that liquid honey has the properties of the Newtonian fluid and its dynamic viscosity is strictly dependent on temperature and moisture content. However, there have so far been no reports concerning the rheological properties of honey at low temperatures. There are some data concerning temperatures above 0 degrees C [4,14], but it would be most interesting to obtain some data on the rheological characteristics of the state of water in honey below zero degrees centigrade. It is well known that the determination of the properties of honey below zero degrees centigrade, i.e. the determination of its freezing temperature is one of the ways (methods) used to describe honey [13].

The purpose of this paper is to present a characteristic of the state of water in two types of Polish honeys depending on their moisture content. The investigations are concerned with the measurements of water activity and determination of the rheological properties of honey at low temperatures.

MATERIALS AND METHODOLOGY

Rape and buckwheat honeys have been selected as the materials for study. These two original types of honey were chosen due to the fact that they show substantial differences in their chemical compositions and also because they are very typical of Poland [12]. It can be assumed that they constitute two extreme cases between which all other nectar honeys are contained. Rape honey, first of all, constitutes a rich source of glucose and undergoes granulation relatively fast [5]. It has the ratio of glucose to fructose of about 1.1, with the content of reducing sugars equal to about 80 %. In buckwheat honey the dominant sugar is fructose and the amount of reducing sugars does not generally exceed 75%. This is why it undergoes the granulation process much more slowly [12].

In our investigations the rape honey of the following moisture contents was used: 17.4; 17.8; 18.3; 18.7; 19.0; 19.5%. Samples of the rape honey were characterized by the following parameters: 17.6; 18.1; 18.7; 19.1; 20.1 and 20.9%. The samples of the honey came from the author's own apiary and they were taken during (higher moisture content) and immediately after nectar flow from bee colonies that had been moved to the rape and buckwheat plantations.. In this way it was possible to avoid errors relating to the origin of the investigated medium. Moisture content in the honey was determined refractometrically by means of an Abbe refractometer [11]

Two research methods were used to determine moisture content in the honeys investigated. One involved measuring water activity in the liquid product. The investigations were conducted in thermo-stable conditions at 25°C making use of the device called AQUA LAB CX-2. The measurements were repeated three times for each test. The other method involved determining rheological properties of liquid honeys in the temperature ranging from 266 to 295 K. In order to obtain low temperatures, a special thermo-stabilizer with a refrigerating unit was used. The rheological measurements were carried out in the Searle rheometric flow by making use of Rheotest 2 and typical measuring procedures [8]. A significant constraint in the rheological investigations was the sensitivity (measurement resoslution) of Rheotest 2. As a result, the measurements of viscosity had to be concluded at the temperature of 266 K. The obtained results were analysed and compared with the available reports in the beekeeping bibliography.

RESULTS

Figure 1 gives some illustrative results of the measurements of the rheological properties of two honey samples investigated at 217 K and moisture content of 18.7 %. The figure shows the values of shear stress obtained at shear rates within the range of $\dot{\gamma} \in <0.167; 1> s^{-1}$. Approximating the results of measurements to the

form of a linear function it is possible to obtain regression equations of a relatively high coefficient of determination R^2 which amounts to above 0.99. It means that the honeys investigated are Newtonian fluids and their rheological properties can be described by a single parameter i.e. dynamic viscosity. It appears that buckwheat honey, compared to rape honey of the same moisture content and same temperature, has a higher viscosity by 2.2%. However, it should be noted that this difference is comparable to the measurement accuracy of the measuring instrument used.

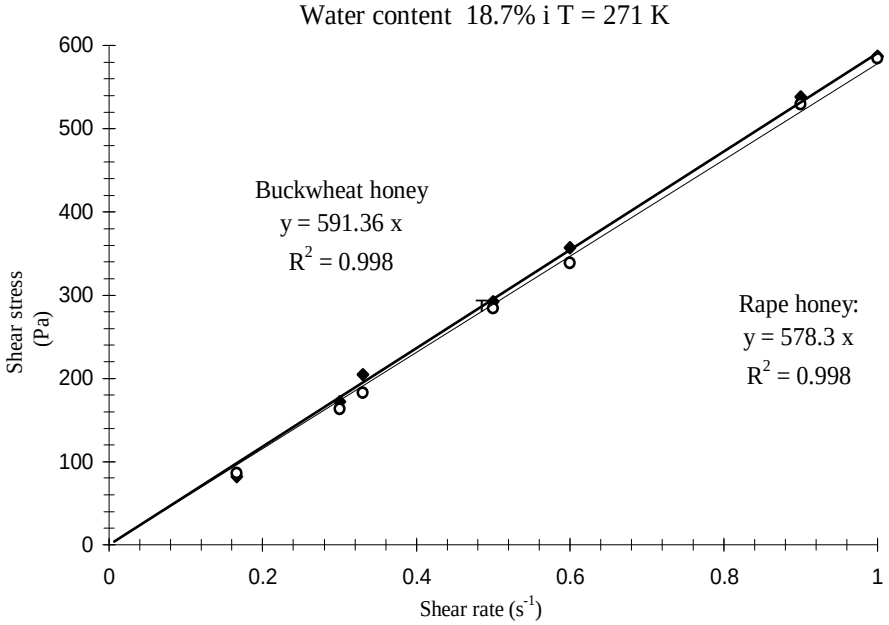

Fig. 1. Flow curves of the investigated honeys at 271 K and water content of 18.7%: ♦ – buckwheat honey, o – rape honey

The results of analogous measurements conducted between 266 and 275 K are presented in Table 1. However, due to the fact that the lowest temperatures could not be recorded by Rheotest 2 because if its measuring limitations, it was impossible to determine the viscosity values for all the samples investigated. The viscosity of the samples that were analysed varied from 3.8 to 1695 Pas. An interesting phenomenon here is a relatively high dependence of viscosity on temperature. It was found that below zero degree centigrade the values of viscosity considerably increased. It should be noted here that moisture content in honey also has a significant influence on its viscosity.

Table 1. Results of rheological measurements of the investigated honeys

T (K)	Rape honey viscosity (Pas)						Buckwheat honey viscosity (Pas)					
	Water content (%)						Water content (%)					
	17.4	17.8	18.3	18.7	19.0	19.5	17.6	18.1	18.7	19.1	20.1	20.9
295	14.4	16.9	11.4	13.0	6.85	7.0	11.3	10.4	11.4	9.6	5.6	3.8
293	19.4	16.9	16.4	14.6	8.9	9.1	16.5	16.2	15.0	13.3	7.1	4.5
291	26.1	22.6	19.3	17.2	12.1	12.0	20.8	22.4	20.5	18.2	9.2	6.0
289	33.0	29.3	25.8	19.5	15.2	14.2	29.4	29.4	26.8	23.1	12.4	7.7
287	39.2	38.5	29.6	25.5	20.8	21.9	40.0	37.6	35.7	32.2	15.2	12.9
285	60.5	56.0	46.6	36.8	30.5	30.5	54.9	50.0	49.7	48.6	21.4	17.4
283	80.9	79.7	64.3	51.6	40.1	40.6	75.5	70.4	67.9	62.2	28.3	24.2
281	117.6	104.9	92.2	76.5	52.6	53.4	104.0	93.6	94.9	85.2	40.2	32.2
279	170.7	151.6	122.6	108.6	72.4	75.2	149.1	138.1	135.7	124.0	52.4	40.5
277	214.5	217.0	179.2	227.0	104.8	109.2	210.3	197.4	176.2	175.5	74.7	56.3
275	360.5	317.7	261.6	232.0	146.5	151.0	320.1	285.6	268.8	248.0	106.4	78.6
273	545.5	490.9	391.4	344.2	215.5	224.3	456.4	429.9	395.3	367.9	149.4	110.8
271	845.9	715.4	595.7	578.2	305.5	321.8	685.8	647.7	591.4	563.7	206.8	159.6
269	1288	1048	881.4	840.4	457.6	479.0	1043	976.7	920.6	821.3	299.5	218.3
268	1587	1382	1148	1094	593.1	597.2	1235	1189	1104	1058	348.9	254.8
267					692.2	744.0					439.2	329.2
266					890.6	923.4					568.4	527.5

In all cases (samples) the investigated honeys showed the properties of the Newtonian fluid. It means that there was no change of state i.e. freezing of water within the temperature range in which the samples were analysed. A detailed study of the literature on this subject made it possible to state that the results were correct. There is no freezing process in honey [18]. Lowering the temperature of honey down to 233 K will not result in its change of state. Using the technique of differential scanning calorimetry (DSC) it was possible to observe, at the temperature of about 233K, the phenomenon of the so called glass transition. This clearly proves that water in honey can be found only in a strongly bound form.

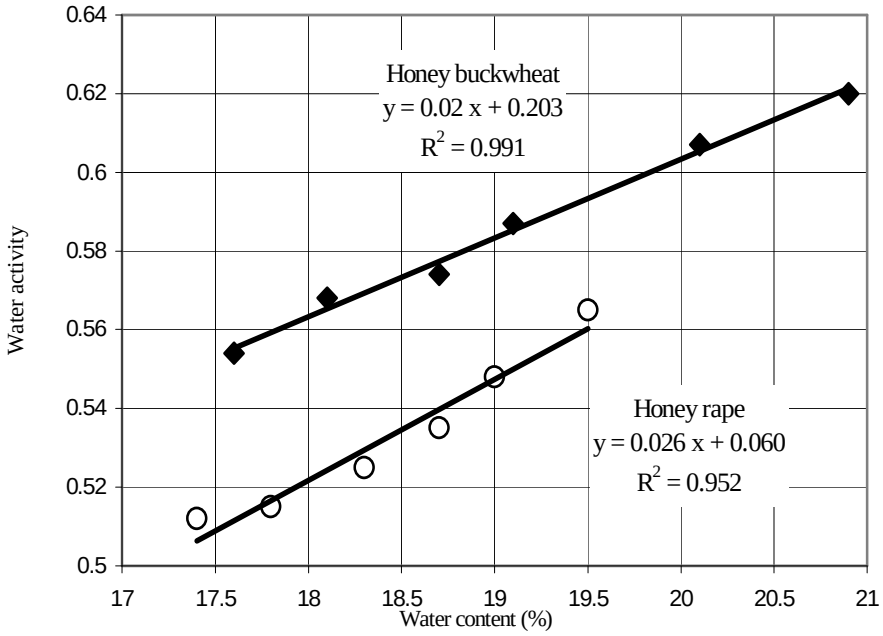

Fig. 2. Dependence of water activity on moisture content at 25°C in the investigated honeys

Figure 2 shows measurement results of water activity. Increase in the moisture content results in an increase of water activity and vice versa. The regression equations which express the dependence of the average values of water activity on moisture content in the investigated honeys are linear in character. Rape honey has a higher water activity than buckwheat honey of the same moisture content. This can be explained by the phenomenon of a stronger water binding activity of glucose in the solution and is in good agreement with the reports presented in the literature on the subject. [15]. The obtained results show that for buckwheat

honey the critical moisture value of water activity (a_w = 0.6) is reached below 20% of its moisture content (the value is admissible by the standards) and is equal to 19.83%. This implies that the honey whose water moisture rises above the critical value at the temperature of 25 degrees centigrade may start the fermentation process caused by the activity of osmophilic yeasts [17]. The above temperature value is found within the temperature range in which honey is kept for consumption in household conditions. These results confirm honey fermentation occurrences that satisfy quality standards and have been described in the beekeeping bibliography [10,21]. One way to protect honey against fermentation is to lower the storing temperature or, alternatively, acquire honey of moisture content below the critical limit. This will guarantee honey stability at room temperature. It should be noted, however, that during the storing period granulation takes place – the process that will additionally enhance water activity in the product [9]. Investigations carried out on various types of honey have shown that granulation additionally increases the value of water activity by about 0.032 [15], which creates good conditions for the development of osmophilic yeasts [17]. The most reliable way to counteract this negative phenomenon is to lower moisture content in honey. This is practically possible only by convincing honey producers to acquire honey products of lower moisture content.

RECAPITULATION

It follows from the results obtained that water remains strongly bound to honey and liquid honey has the property of the Newtonian fluid even at the temperature of 266 K. Although it does not freeze, its viscosity acquires considerable values, even up to a thousand Pa's. The measurements of water activity were confirmed by the results obtained from the rheological measurements. The values of water activity were found to be within the range of $a_w \in <0.539; 0.620>$ and were characteristic of water binding due to multilayer absorption [13]. It was shown that a_w for both buckwheat and rape honeys depended linearly on moisture content, which follows from the regression equations presented in the paper. Buckwheat honey is characterized by a higher moisture activity than rape honey at the same moisture content.

The value a_w<0,6 guarantees the stability of honey stored at room temperature [13,17]. The measurements showed that the critical value of water activity was surpassed in the case of liquid rape honey. The above results confirm the data from the literature on the subject indicating the occurrence of fermentation processes in honeys that satisfy the qualitative requirements of Polish standards. [10,11]. It seems to be purposeful to continue the investigations of water activity taking into account of the granulation processes in other types of monofloral honey. It would be also interesting to study the relationship between fermentation

processes and the degree of honey infection with the spores of osmophillic yeasts. The research should be able to determine safe water content levels at which the fermentation process would cease even after the granulation of the product.

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CHARAKTERYSTYKA STANU WODY W WYBRANYCH POLSKICH MIODACH PSZCZELICH

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Streszczenie. W pracy przedstawiono analizę stanu wody w dwóch wybranych, płynnych, polskich miodach odmianowych: rzepakowym i gryczanym. Dokonano tego wykorzystując dwie różne metodyki badawcze. Pierwsza polegała na pomiarze aktywności wody w zależności od zawartości wody. Druga sprowadzała się do określenia właściwości reologicznych miodów płynnych w niskiej temperaturze. Pomiary reologiczne wykazały, że w temperaturze poniżej 0°C miód ma nadal właściwości płynu newtonowskiego, wzrasta tylko znacznie jego lepkość. Zmierzone wartości aktywności wody w obu przypadkach wykazały liniowe zależności od zawartości wody, przy czym różniły się one znacznie między sobą. Przeprowadzone studia i pomiary wskazują, że woda w miodzie występuje w postaci związanej poprzez adsorpcję wielowarstwową. Ustalono również, że w przypadku miodu gryczanego przy zawartości wody 19,8%, w temperaturze 25°C zostaje przekroczona krytyczna wartość aktywności wody, powyżej której może wystąpić fermentacja. Wyniki badań skonfrontowano z doniesieniami z literatury branżowej.

Słowa kluczowe: aktywność wodna, lepkość miodu