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# EFFECT OF CRYSTALLIZATION ON THE WATER ACTIVITY OF HONEY

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## ABSTRACT

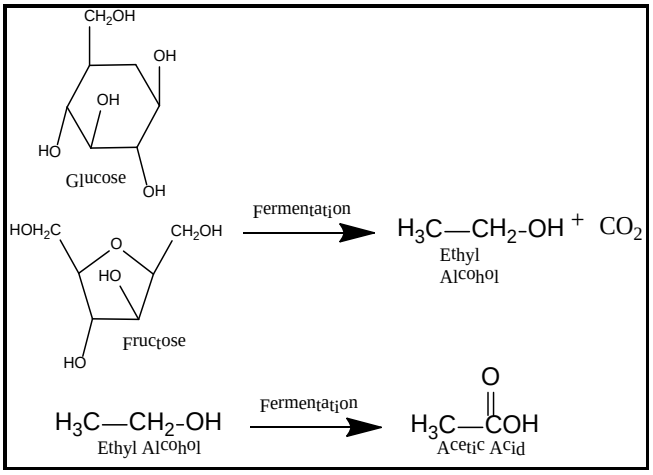
Honey is supersaturated solution of the sugars, particularly glucose, which tend to crystallize at room temperature in the form of glucose monohydrate. This crystallization results in lowering of the glucose concentration present in liquid phase and thus cause an increase in water activity $a_w$ of the honey. This increase in water activity facilitates naturally occurring yeast cells to multiply, which results in honey fermentation. In the present work we measured the water activity of 50 crystallized honey samples and change in water activity when samples were re-dissolved upon heating. Most samples show drop in $a_w$ (in rage of 0.03-0.04) when re-dissolved, thus confirming that crystallization of honey increases $a_w$ that helps the yeast cells to multiply.

**Key words:** Crystallization, Fermentation, Glucose, Honey, Water activity.

## INTRODUCTION

Honey can be defined as highly concentrated aqueous solution of glucose and fructose along with small amount of different other higher sugars (Alvarez et.al., 2010). Honey is composed of more than twenty five different types of sugar (monosaccharide's, disaccharides and oligosaccharides) which constitute about 95% of total dry weight of honey ( Weston, 1999). Among these sugars two monosaccharide's glucose and fructose are the major carbohydrates and typically constitute 80 to 85 % of total soluble solids of honey ( De La et.al., 2011). Other disaccharides (like glucose) and higher sugars are present in quite small amount. The final sugar composition varies with the floral source used by the bees as well it also depends upon geographic region and climatic conditions (Cotte et.al., 2004, de la et.al,., 2005 and Nozal et.al., 2005).

Osmotolerant yeast (naturally present in honey) act upon glucose and fructose resulting in fermentation of honey and formation of ethyl alcohol along with carbon dioxide. The ethyl alcohol is further oxidized to produce acetic acid and water and result in sour taste of fermented honey ( Gleiter et.al, 2006). Conventionally it is thought that spoilage of honey by fermentation depends upon total water content of honey. However, microbial activity is not depended upon water content it is controlled by water activity ($a_w$) of food system as demonstrated by many researchers (Troller, 2012, Beuchat, 1983, Lenovich, 1987 and Molan, 2006). Water activity is primary factor in preventing and limiting microbial growth ( Grant, 2004). Every microorganism require certain minimum water activity below which it can't grow and minimum water activity required for osmotolerant yeast found in honey is about $a_w$ = 0.61/0.62 (9). The $a_w$ of honey is usually below 0.6 which is enough to inhibit the growth of osmotolerant yeast present in honey ( Beckh et.al., 2004). Crystallization of glucose decrease the solute (glucose) concentration in the solution phase thus increase the water activity which allow naturally occurring yeast cell to grow that results in honey fermentation (Chirife et.al., 2006). Nearly all honey types crystallize but time period is different for different types.




The purpose of present study is to determine the $a_w$ of several crystallized honey samples collected from

different areas of Pakistan and $\Delta a_w$ of crystallized honey upon re-dissolving is measured.

## MATERIAL AND METHODS

Fifty crystallized honey samples of different floral and geographical origin were collected and used in the current study. Thirty samples were obtained from Honey Bee Research Institute and twenty were collected from the local market of Islamabad. The honey samples were of one of the two types a) completely granulated b) partially granulated i.e. mixture of liquid honey and crystallized honey. Honey collected from retail market were all partially crystallized honey while samples obtain from Honey Bee Research Institute composed of both type of crystallized form.

### DETERMINATION OF WATER ACTIVITY

Water activity ($a_w$) was determined by means of an AquaLab CX2 water activity meter (Decagon Device, USA) according to the procedure reported by Chirife, Zamora (14). The equipment was calibrated with saturated salt solutions in the $a_w$ range of 0.2 to 0.6. All the honey samples were first equilibrated at 25°C (±0.2°C) before measurement of $a_w$ by using an electronic chilling/ heating plate. All the analysis was done in replicates and the average reported; under these conditions accuracy of this meter is about ± 0.003 $a_w$.

## RESULT AND DISCUSSION

Water activity of honey depends upon the molal concentration of soluble compounds thus the substances which are present in very small amount like oligosaccharides, nitrogenous compounds, acids, flavor and minerals will have little effect on lowering of water activity ( Chirife et.al, 2006 and Chirief et.al, 1980). So water activity of honey is mainly depend upon the concentration of glucose and fructose in the water of honey to lesser extent on some disaccharide's like sucrose, maltose/isomaltose. The review of data available on the sugar composition of honey from different botanical and geographical sources ( Mateo et.al., 1998, Mendes et.al., 1998, Mossel et.al., 2003 and Ouchemoukh et.al., 2010) revealed that molal concentration of glucose + fructose ranges between 19m to 28m, while that of disaccharide's rages between less than 0.03-3

Any solute in a solvent above saturation eventually crystallizes out. Sugars also crystallize out from the honey if there concentration is above the saturation level and there is no hindrance that effect crystallization ( Bhandari, 2003). Since most honeys are supersaturated with respect to glucose, glucose has the tendency to crystallize out in the form of glucose monohydrate. There are number of factors on which rate of crystallization depends like viscosity of honey, storage temperature, presence of any foreign matter. But the most important factor on which rate of glucose crystallization depend is ratio of glucose/water ( Manikis, 2001). Figure 1 show the glucose concentration dissolved in water of honey (g glucose/ 100g of water) that was calculated from the data on honey composition reported from different countries (Mondragón et.al., 2013, Daniel et.al., 2009, Habib et.al., 2014, Buba, 2013 and Al-Khalifa, 1999).

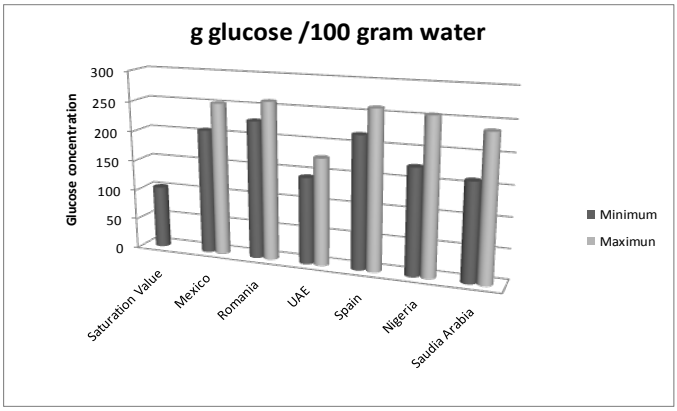



**Figure 1: Glucose concentration in water of honey, data was collected for different honeys from references (22-27)**

It can be observed that in all the cases examined concentration of glucose is well above the equilibrium saturation value i.e. 103.3g glucose / 100 g water at 25° C (28). On contrary fructose is always below its saturation value in all observed cases. The equilibrium saturation value of fructose is 405.1 g fructose /100 g of water (29). For example, values reported for fructose concentration in the water of honeys from different studies in different countries, were in the range of 125-300g fructose in 100 g water ((Mondragón et.al., 2013, Daniel et.al., 2009, Habib et.al., 2014, Buba, 2013 and Al-Khalifa, 1999).

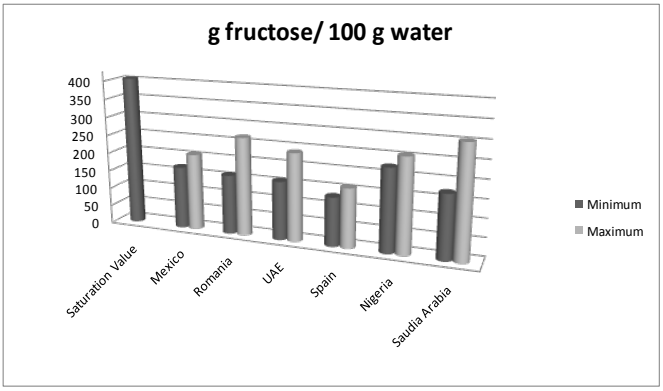



**Figure 2: Fructose concentration in water of honey, data was collected for different honeys from references (Mondragón et.al., 2013, Daniel et.al., 2009, Habib et.al., 2014, Buba, 2013 and Al-Khalifa, 1999).**

Every compound possess its own particular water activity value at saturation, and in case of glucose it is 0.891 (at 25° C); however water activity value decreases if a solution gets supersaturated. Since super-saturation is a thermodynamically non-equilibrium state, the extra solute will tend to crystallize out and as result water activity of the solution will increase up to the level of the saturation. Therefore, if we warm the crystallized honey to re-dissolve the glucose crystals, the water activity of this

supersaturated solution will decrease. Table 1 shows the water activity (at 25 ° C) of 50 samples of crystallized and re-dissolved honeys; and as expected the water activity of the re-dissolved samples is lower than that of the crystallized ones. It is important to note that honey samples in the liquid (re-dissolved) condition will be less susceptible to fermentation as their $a_w$ is about ≤ 0.61 (and minimum water activity required for osmotolerant yeast activity found in honey is about 0.62). While upon crystallization $a_w$ value increases to an unsafe range and honey will become more susceptible to fermentation.

**Table 1: Water activity of crystallized and re-dissolved honeys**

| Nr. of sample | Geographical origin | Botanical origin | Crystallization type | Water Activity $a_w$ | | $\Delta a_w$ |
|---|---|---|---|---|---|---|
| | | | | Crystallized | Re-dissolved | |
| **Honey bee research institute** | | | | | | |
| 1 | Peshawar | Mixed | Partially crystallized | 0.592 | 0.535 | 0.057 |
| 2 | | Mixed | Partially crystallized | 0.598 | 0.563 | 0.035 |
| 3 | | Mixed | Partially crystallized | 0.575 | 0.537 | 0.038 |
| 4 | Manshara | Acacia | Completely crystallized | 0.606 | 0.560 | 0.046 |
| 5 | Swabi | Citrus | Completely crystallized | 0.573 | 0.540 | 0.033 |
| 6 | Swat | Sider | Completely crystallized | 0.633 | 0.605 | 0.028 |
| 7 | | Sider | Completely crystallized | 0.601 | 0.578 | 0.023 |
| 8 | | Acacia | Completely crystallized | 0.610 | 0.581 | 0.029 |
| 9 | | Mixed | Completely crystallized | 0.620 | 0.599 | 0.021 |
| 10 | Islamabad | Mixed | Partially crystallized | 0.573 | 0.542 | 0.031 |
| 11 | | Mixed | Partially crystallized | 0.569 | 0.548 | 0.021 |
| 12 | Layyah | Brassica | Completely crystallized | 0.614 | 0.595 | 0.019 |
| 13 | | Citrus | Completely crystallized | 0.621 | 0.593 | 0.028 |
| 14 | | Citrus | Completely crystallized | 0.626 | 0.605 | 0.021 |
| 15 | | Citrus | Completely crystallized | 0.607 | 0.583 | 0.024 |
| 16 | Murdan | Acacia | Completely crystallized | 0.625 | 0.611 | 0.014 |
| 17 | | Acacia | Completely crystallized | 0.615 | 0.592 | 0.023 |
| 18 | | Acacia | Completely crystallized | 0.613 | 0.588 | 0.025 |
| 19 | Kark | Brassica | Partially crystallized | 0.589 | 0.562 | 0.027 |
| 20 | | Brasica | Completely crystallized | 0.618 | 0.597 | 0.021 |
| 21 | Chakwal | Mixed | Partially crystallized | 0.588 | 0.562 | 0.026 |
| 22 | | Mixed | Partially crystallized | 0.599 | 0.567 | 0.032 |
| 23 | Samryal | sunflower | Partially crystallized | 0.589 | 0.561 | 0.028 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 24 | | Sunflower | Partially crystallized | 0.579 | 0.551 | 0.028 |
| 25 | | Sunflower | Completely crystallized | 0.610 | 0.589 | 0.021 |
| 26 | Gilgit | Mixed | Partially crystallized | 0.573 | 0.549 | 0.024 |
| 27 | | Mixed | Partially crystallized | 0.573 | 0.552 | 0.021 |
| 28 | | Mixed | Partially crystallized | 0.577 | 0.551 | 0.026 |
| 29 | | Mixed | Partially crystallized | 0.581 | 0.558 | 0.023 |
| 30 | | Mixed | Partially crystallized | 0.587 | 0.561 | 0.026 |
| Local retail market of Islamabad | | | | | | |
| 31 | | Olive | Partially crystallized | 0.583 | 0.564 | 0.019 |
| 32 | | Olive | Partially crystallized | 0.579 | 0.552 | 0.027 |
| 33 | | Citrus | Partially crystallized | 0.598 | 0.562 | 0.036 |
| 34 | | Acacia | Partially crystallized | 0.601 | 0.573 | 0.028 |
| 35 | | Acacia | Partially crystallized | 0.583 | 0.559 | 0.024 |
| 36 | | Acacia | Partially crystallized | 0.587 | 0.561 | 0.026 |
| 37 | | Acacia | Partially crystallized | 0.585 | 0.569 | 0.016 |
| 38 | | Acacia | Partially crystallized | 0.610 | 0.581 | 0.029 |
| 39 | | Acacia | Partially crystallized | 0.608 | 0.595 | 0.013 |
| 40 | | Acacia | Partially crystallized | 0.613 | 0.588 | 0.025 |
| 41 | | Acacia | Partially crystallized | 0.601 | 0.579 | 0.022 |
| 42 | | Mixed | Partially crystallized | 0.589 | 0.575 | 0.014 |
| 43 | | Mixed | Partially crystallized | 0.581 | 0.564 | 0.017 |
| 44 | | Mixed | Partially crystallized | 0.562 | 0.549 | 0.013 |
| 45 | | Mixed | Partially crystallized | 0.591 | 0.572 | 0.019 |
| 46 | | Mixed | Partially crystallized | 0.595 | 0.581 | 0.014 |
| 47 | | Mixed | Partially crystallized | 0.579 | 0.565 | 0.014 |
| 48 | | Mixed | Partially crystallized | 0.587 | 0.569 | 0.018 |
| 49 | | Mixed | Partially crystallized | 0.593 | 0.575 | 0.018 |
| 50 | | Mixed | Partially crystallized | 0.598 | 0.570 | 0.028 |

[a] Average of three replicates

Histogram of $\Delta a_w$ shift is shown in fig 3. It can be seen that most honey samples show $\Delta a_w$ in the range of 0.02-0.035. Chirife, Zamora (2006) also studied the change in water activity and found $\Delta a_w$ of in the range of

0.03-0.04. While Ruegg and Blanc (1981) found the average water activity of liquid samples was 0.562±0.041 as compared to mean value of 0.589± 0.038 for the crystallized one.

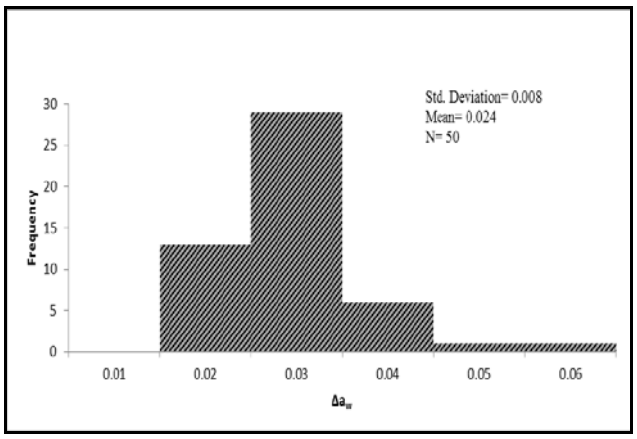



**Figure 3: Histogram of the $\Delta a_w$ for crystallized honeys**

## CONCLUSION

As the result of crystallization the water activity increases and so, the chance of honey fermentation. So honey crystallization is unfavorable process.

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