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TEMPERATURE-TIME DEPENDENCE OF DIFFERENT ADULTERATED EGYPTIAN HONEY

Eman E. Mostafa, Manal A. Sorour, Salwa R. Mostafa
E-Mail Id: manal.sorour@yahoo.com
Department of Chemical Engineering, Faculty of Engineering, Cairo University, Egypt
Food Engineering and Packaging Department, Food Technology Research Institute, Egypt

Abstract- The effect of temperature on apparent viscosity of different types of Egyptian honeys (black seed honey, clover honey, desert honey and mountain flower honey) were investigated. Honey samples -each of volume 100ml- were adulterated with different volumes (2, 4, 6, 8 and 10 ml) of starch solution, glucose, molasses and distilled water respectively and were tested and compared to the pure sample. The results revealed that apparent viscosity decreases with the increase of temperature, activation energy of pure, purchased and adulterated samples were fitted to Arrhenius model; the results revealed that both pure clover and mountain flower honey had almost constant activation energy for all shear rates studied. Thixotropy effect for Egyptian honey was studied at different temperatures; the results demonstrated that only desert honey exhibited thixotropic behavior. Weltman model was studied to describe thixotropic effect for different honey samples.
Keywords: Honey, Adulteration, Thixotropy, Activation Energy

1. INTRODUCTION

Honey is a natural aromatic viscous fluid produced by bees using nectar of flowers. Honey bees convert nectar to honey by regurgitation and evaporation; it is stored as primary food source in wax honeycombs inside the bee hive. The sweetness of honey is basically from the two main monosaccharides it contains, fructose and glucose; and it is very similar to that of sugar.

Thixotropic fluids exhibits decrease in shear stress with the increase of time at constant shear rate. This would mean that the fluid will be less viscous. This behavior can be observed in cooling mud and in jam [1]. Thixotropy also includes materials that show isothermal reversibility while transforming from high to low viscosity, in form of gel. This transformation could be obtained by either by applying a constant shear rate for a certain time followed by a rest, or by increasing shear rate followed by a rest period [2]. For shear thinning fluids, thixotropy can be observed where equilibrium is reached between reforming and breaking down of the structure, so that the material goes through a permanent change due to shearing [3]. One of the factors with direct effect on the value of apparent viscosity of a fluid is temperature; as temperature increases kinetic energy of molecules in a fluid increases and they start to move faster easing the flow of the fluid, which result in the reduction in the values of apparent viscosity. [4]

2. EXPERIMENTAL SETUP

2.1 Materials

Different types of honey were collected from the Ministry of Agricultural out let El-Dokki, Giza governorate between November 2015 and April 2016 except Desert honey due to unavailability were purchased from the local market for comparison. Honey types selected were as follows:

- Black Seed Honey.
- Clover Honey.
- Desert Honey.
- Mountain Flowers Honey.

Materials used for adulteration were Distilled Water, Glucose, Molasses and Starch Solution.

2.2 Preparation of Adulterated Honey Samples

Starch solution (4%) was prepared by adding 4 gram of starch to 100 ml distilled water; the solution was gently stirred before heating the sample in the microwave to insure that the starch is completely suspended -gelatinized- in water. [5]

Pure honey was divided into equal volume of 100 ml, each adulterant was added to the different types of honey with different volumes (2, 4, 6, 8 and 10 ml) separately. A volume of 100ml was also taken of the honey purchased from local market from all honey types studied.

2.3 Rheological Properties of Samples

Apparent viscosity of honey samples were measured using Brookfield digital rheometer (DVIII Ultra) Spindle HA-07 was used as well as a thermostatic water bath to maintain temperature constant during measurement. Apparent viscosity was directly obtained from the rheometer whilst shear rate and shear stress were calculated. Shear rate was calculated using the following equation: [6]

$$\gamma = \frac{2\pi R_c^2}{60(R_c^2 - R_b^2)} * rpm \qquad 2.1$$

Where: γ = the shear rate in s^{-1}.

Rc = the radius of container cm.

Rb = the radius of spindle cm.

rpm = the revolutions per minute of the spindle.

Thixotropic properties of different honey types were characterized by hysteresis experiments consisting of two steps operation -forward curve and backward curve-. The hysteresis loop is obtained by increasing the speed from 10-100 rpm and then reversing the procedure measuring from 100-10 rpm. This procedure was repeated at 20oC, 30oC, 40oC and 50oC using thermostatic water bath, for samples with no coinciding forward and backward graphs at temperatures of 20oC and 50oC, viscosity was measured again at different time intervals until the viscosity reaches constant with ascending speed of spindle (10-100 rpm). [7]

The effect of temperature on apparent viscosity of different honey types was fitted according to Arrhenius equation: [1]

$$\mu = k e^{\frac{Ea}{RT}} \qquad 2.2$$

Where: μ: is the viscosity in Pa.s.

k: is a constant.

Ea: is activation energy in J/mol.

R: is the universal gas constant in $m^3.Pa.K^{-1}.mol^{-1}$.

T: is the temperature in K.

In order to obtain activation energy of honey, viscosity was measured with ascending speed of the spindle (10-100 rpm) at the temperatures of 20°C, 30°C, 40°C and 50°C using thermostatic water bath.

3. RESULTS AND DISCUSSIONS

The results revealed that as the temperature increase the values of apparent viscosity of pure, purchased and adulterated honey decreased for all shear rates studied. The same trend was exhibited for all honey types with different adulterants as shown in fig. 3.1 to 3.4. [1]

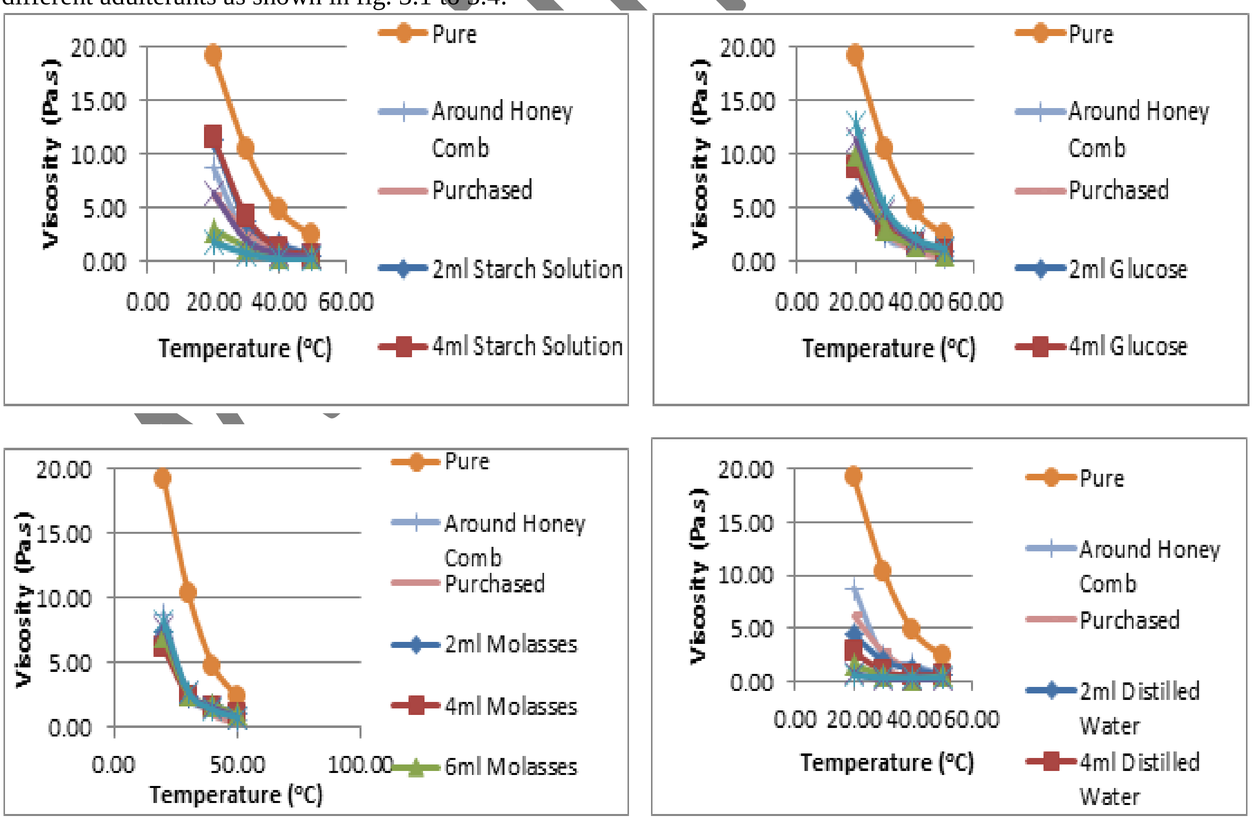

Fig. 3.1 Effect of Temperature on Apparent Viscosity of Pure and Purchased Black Seed Honey Compared to Different Adulterants at Shear Rate 4.1976 s^{-1}

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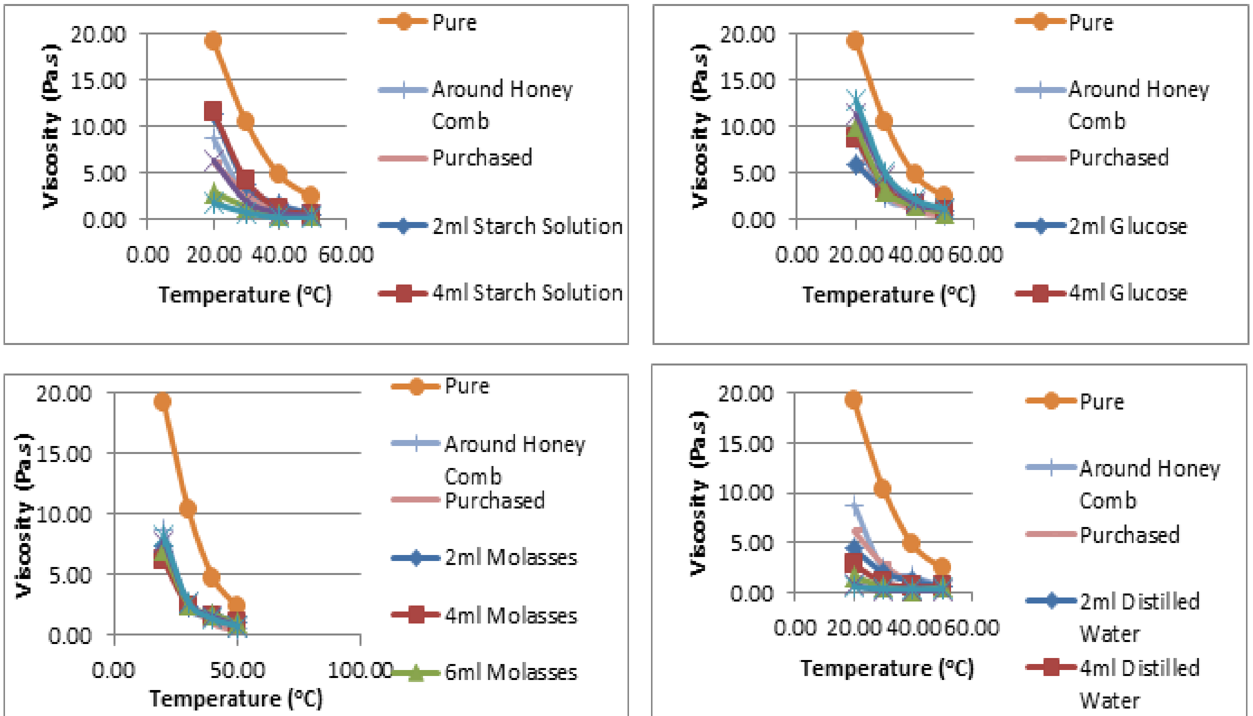

Fig. 3.2 Effect of Temperature on Apparent Viscosity of Pure and Purchased Clover Honey Compared to Different Adulterants at Shear Rate 4.1976 s^{-1}

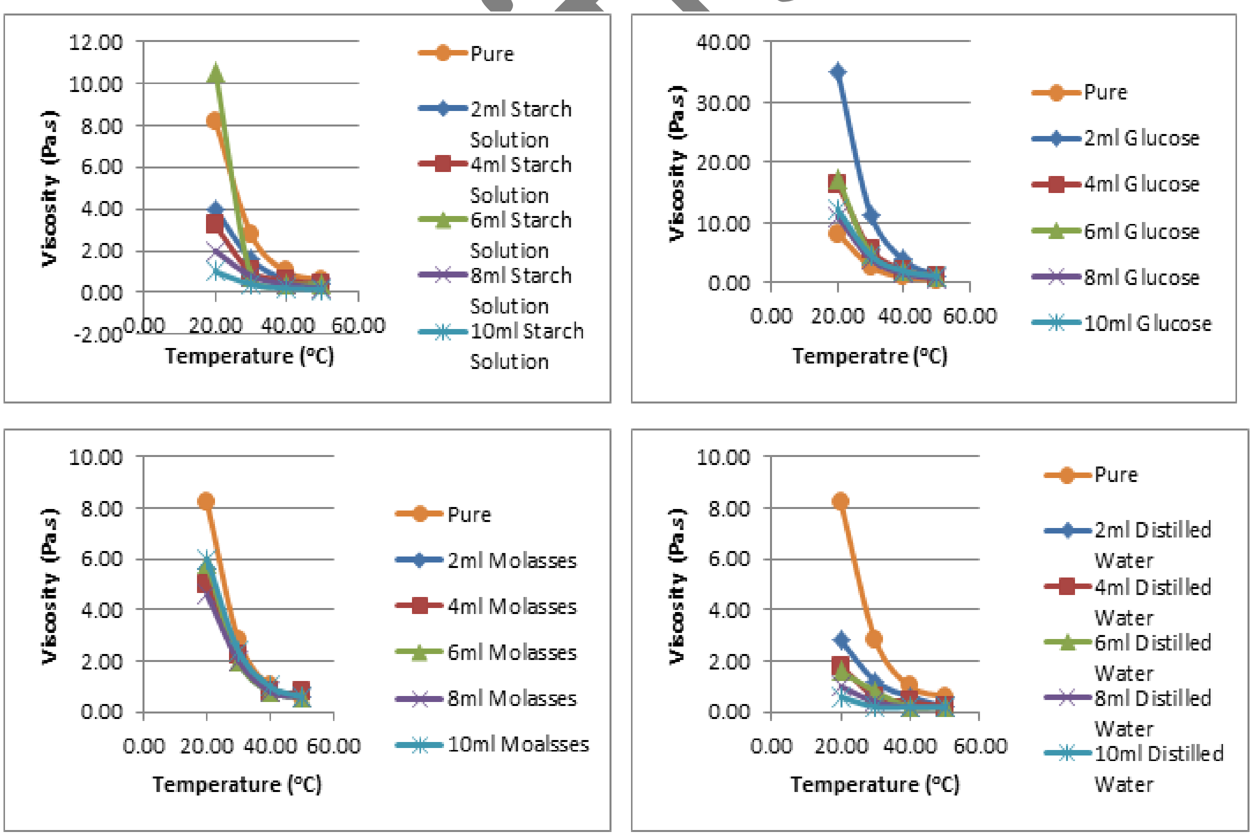

Fig. 3.3 Effect of Temperature on Apparent Viscosity of Pure Desert Honey Compared to Different Adulterants at Shear Rate 4.1976 s^{-1}

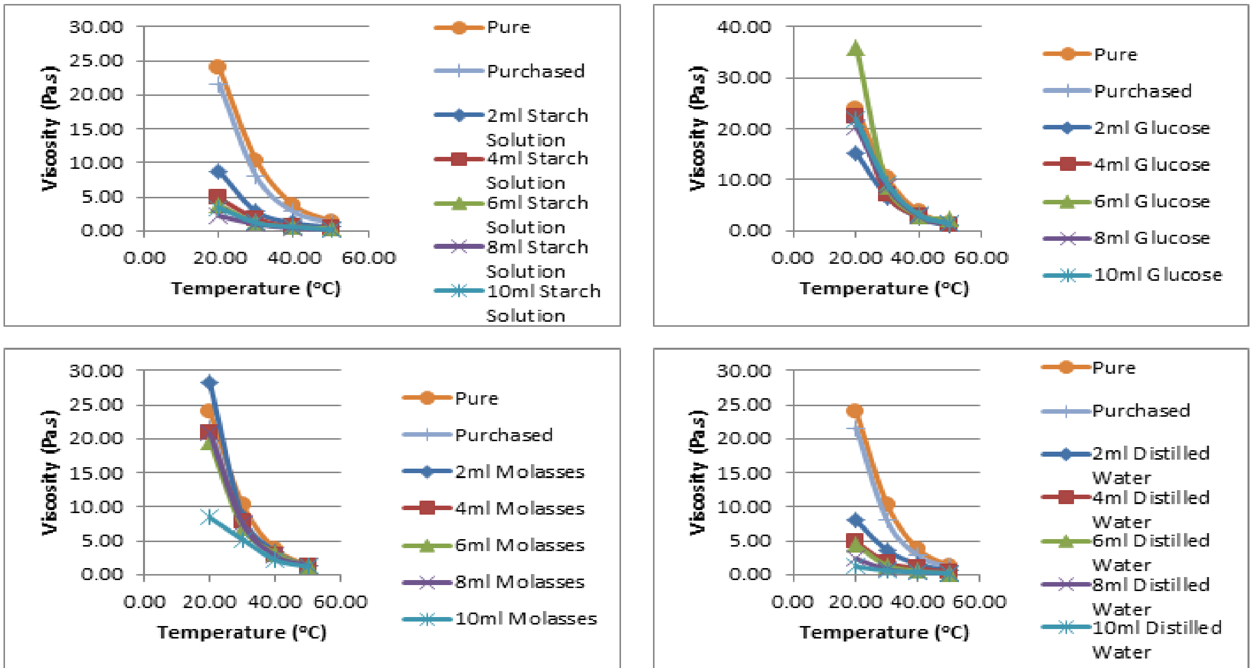

Fig. 3.4 Effect of Temperature on Apparent Viscosity of Pure and Purchased Mountain Flower Honey Compared to Different Adulterants at Shear Rate 4.1976 s^{-1}

The following linearization was carried out to ease the plotting of Arrhenius equation and the calculation of activation energy:

$$\ln(\mu) = \ln(k) + \frac{Ea}{R}.\frac{1}{T} \quad 3.1$$

Natural logarithm of apparent viscosity was plotted against the reciprocal of temperature; the slope of the line was then multiplied by the universal gas constant to determine the activation energy of the sample. The activation energy reflects the sensitivity of the viscosity to temperature change, the higher the values of activation energy the more sensitive the fluid is to temperature change. [8, 9, 10]

The results indicated that activation energy of pure black seed honey was higher than that of purchased honey for all the shear rates studied, activation energy for samples adulterated with 4% starch solution remained approximately constant for 2 and 4ml, it then decreased being lowest at 8ml then increased again at 10ml for all shear rates studied. Activation energy for samples adulterated with glucose slightly decreased with the increase of the volume of glucose for all shear rates studied, except for shear rate 2.1016 s^{-1} for 10ml of glucose where it abruptly increases. Activation energy for samples adulterated with molasses increased until 4ml of molasses then started to decrease for all shear rates studied, except for 8ml of molasses where a sudden increase in activation energy occurred at shear rate 1.0494s^{-1}. For 2 and 4ml of distilled water then decreased continuously for all shear rates studied, except for shear rate 4.1976s^{-1} where activation increase until 4ml then decreases continuously as shown in figures (3.5,3. 6).

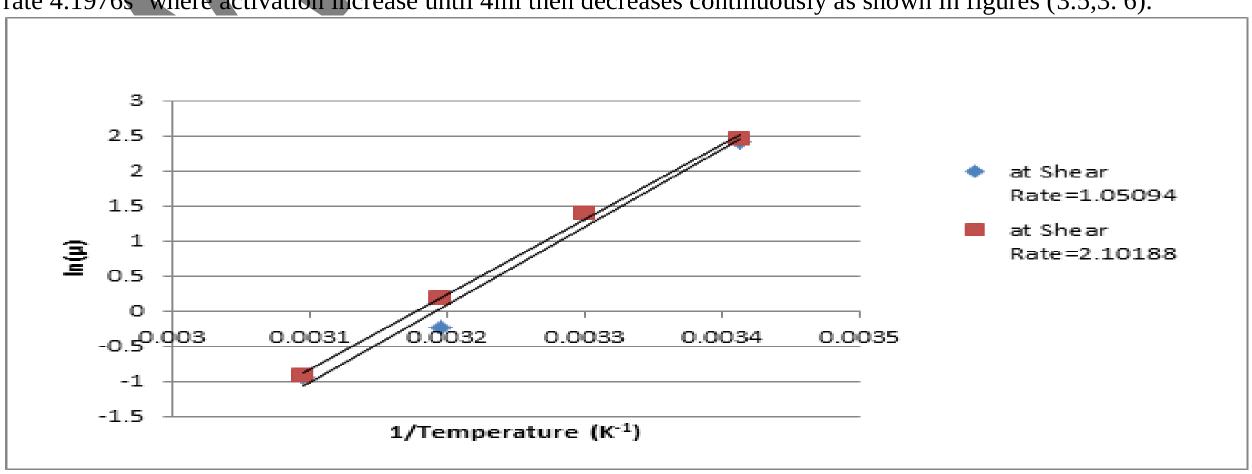

Fig. 3.5 Fitting of Data to Arrhenius Equation

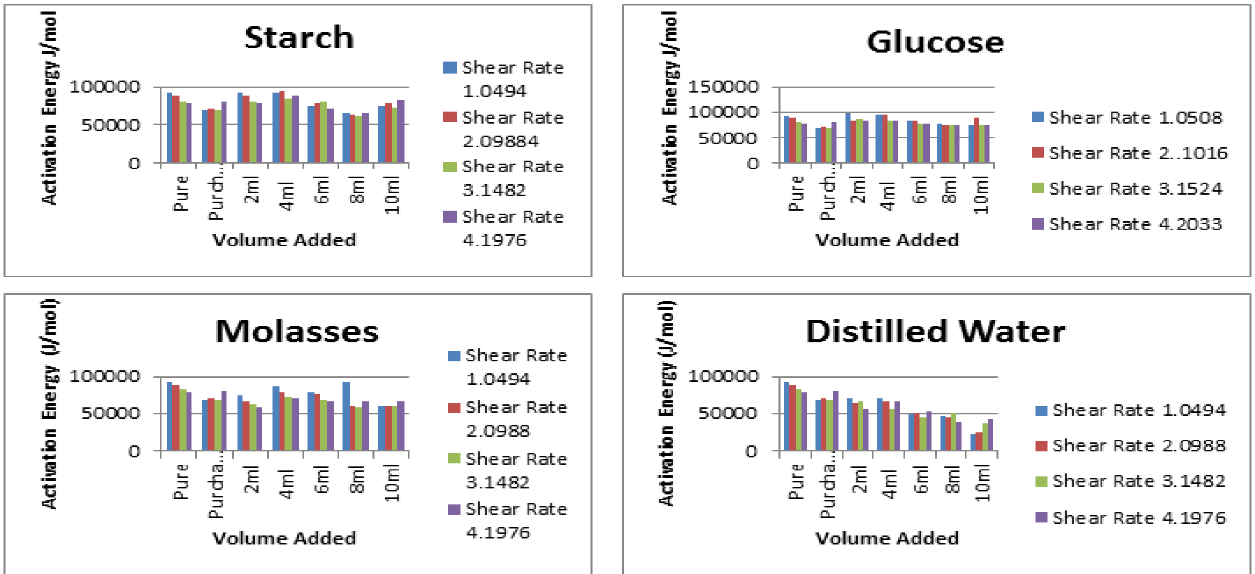

Fig. 3.6 Activation Energy of Black Seed with Different Adulterants

The activation energy of pure clover honey was approximately constant for all shear rates studied; it was also lower that the activation energy of honey around honey comb and purchased honey for all shear rates studied. Activation energy for samples adulterated with 4% starch solution increase until 4ml then decreased at 6ml then increased again at 8ml before it decreased at 10ml of 4% starch solution for all shear rates studied. Samples adulterated with glucose increase until 4ml then slightly decreased for all shear rates studied, except for 4ml of glucose at shear rate $4.2033s^{-1}$ where it abruptly decreases. Activation energy for samples adulterated with molasses decreased until 4ml then increased for all shear rates studied, except for shear rate $1.0494s^{-1}$ where the activation energy remained approximately constant. Samples adulterated with distilled water decreased continuously with the increase of volume of distilled water for shear rates $1.0494\ s^{-1}$ and $2.0988\ s^{-1}$, while for the remaining shear rates activation energy increased until 6ml then decreased as shown in fig. (3.7).

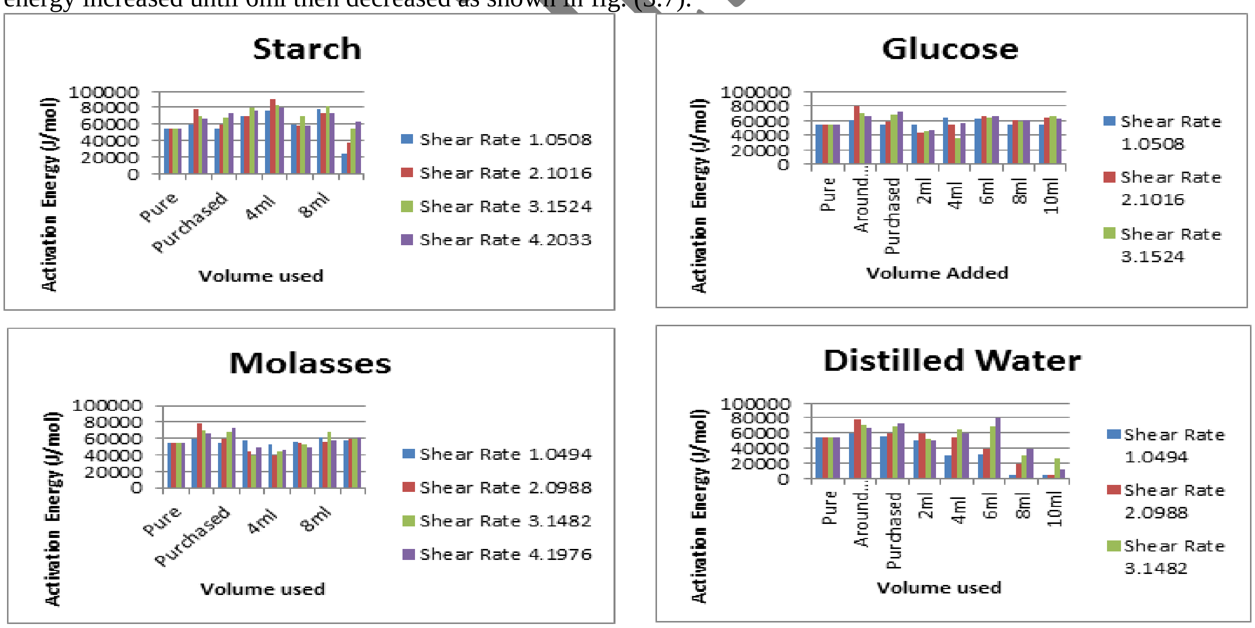

Fig. 3.7 Activation Energy of Clover Honey Adulterated with Different Adulterants

Activation energy of pure desert honey was in the range of 70072.6 – 81879.1 J/mol for all shear rates studied. Activation energy for samples adulterated with 4% starch solution decreased until 4ml then greatly increased at 6ml then decreased again with the increase of volume of adulterant for all shear rates studied. Samples adulterated with glucose decreased until 4ml then increased at 6ml then decreased again with the increase of volume of adulterant for all shear rates studied.

Activation energy for samples adulterated with molasses decreased until 8ml then increased again for all shear rates studied. Samples adulterated with distilled water decreased with the increase of the volume of distilled water for all shear rates studied, except for shear rate 4.1976s^{-1} where activation energy increased at 6ml then reduced again at 10ml of distilled water as illustrated in fig. (3.8).

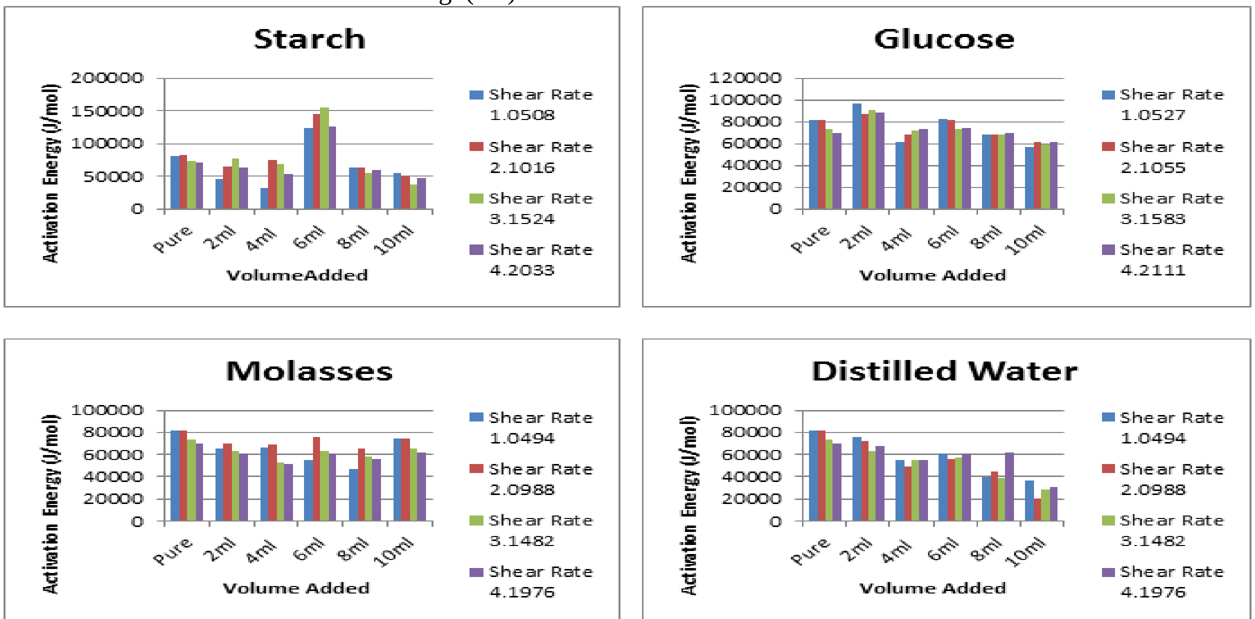

Fig. 3.8 Activation Energy of Desert Honey Adulterated with Different Adulterants

The activation energy of pure mountain flower honey was approximately constant for all shear rates studied, and it was more than that of purchased honey sample. Activation energy for samples adulterated with 4% starch solution increased until 4ml then decreased at 6ml then decreased again at 8ml for all shear rates studied, except for shear rate 3.1524s^{-1} where activation energy remained nearly constant but decreased at 8ml and increased again at 10ml of 4% starch solution. Samples adulterated with glucose increased until 4ml then decreased and remained constant for all shear rates studied, except for shear rate 2.1065s^{-1} where activation energy increase until 4ml then remained constant then increased at 8ml of glucose. Activation energy for samples adulterated with molasses decreased until 8ml then increased at 10ml for all shear rates studied, except for shear rate 2.1065s^{-1} where activation energy decreased with the increase of volume of molasses added. Samples adulterated with distilled water increased until 4ml then decreased at 6ml for all shear rates studied, except for shear rate 1.0514s^{-1} where activation energy decreased until 4ml then increased until 8ml then decreased again at 10ml of distilled water added as illustrated in figure (3.9).

Rheology of honeys could be informative about its composition, as previously mentioned, thixotropy is associated with the presence of proteins; whereas the presence of high-molecular weight dextran in honey can cause shear thickening. Newtonian behavior can usually be expected form a concentrated solution of low molecular weight compounds, indicating absence of macromolecules or particles in suspension or both. [11]

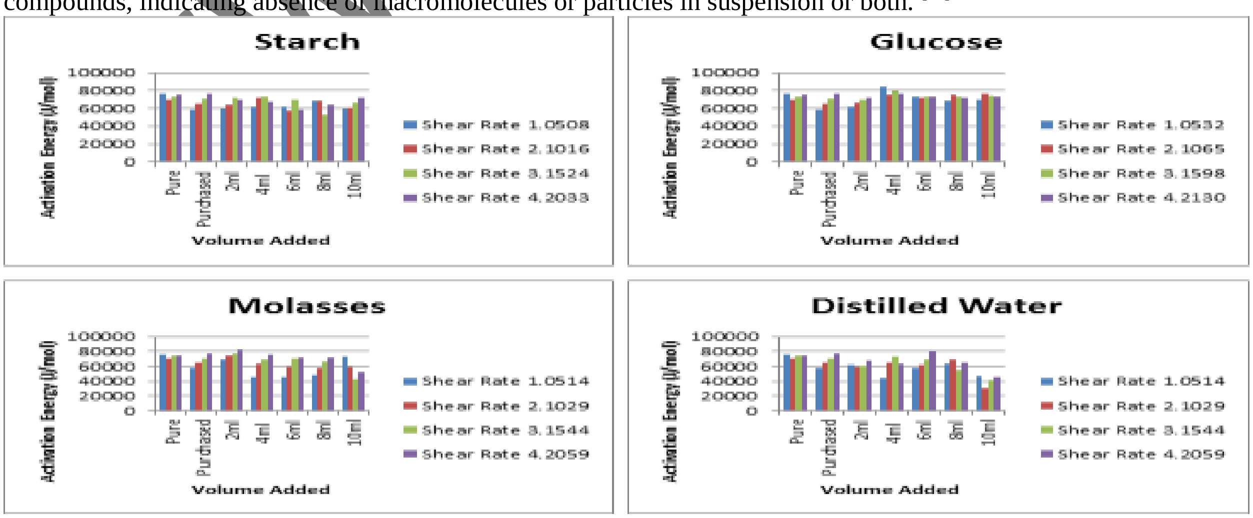

Fig. 3.9 Activation Energy of Mountain Flower Honey Adulterated with Different Adulterants

Thixotropic effect was studied for four different types of pure honey types -black seed, clover, desert and mountain flower- at room temperature and pressure as shown in figure (3.10). The results demonstrated that desert honey exhibited thixotropic behavior due to the gap between the forward and backward graphs unlike the other three types where the forward and backward lines almost coinciding.

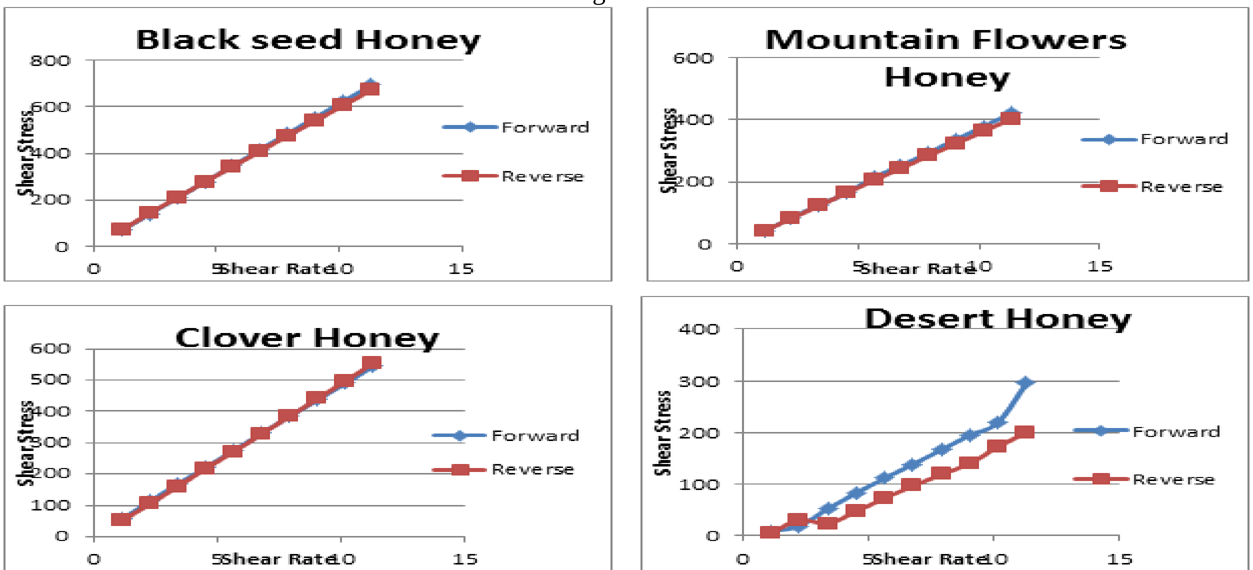

Fig. 3.10 Thixotropy Effect (Shear Stress - Shear Rate) of Different Honey Types at Room Temperature

CONCLUSION

The increase of temperature result in the decrease of apparent viscosity for all shear rates studied. The study of activation energy revealed that pure black seed honey had higher activation energy than that of purchased honey sample for all shear rates studied, pure clover honey had an approximately constant activation energy for all shear rates studied; the activation energy of clover honey around honey comb and purchased honey were higher than that of pure honey, pure desert honey sample had the activation energy of 70072.6 - 81879.1 J/mol for all shear rates studied and the activation energy of pure mountain flower honey was approximately constant for all shear rates studied, and it was more than that of purchased honey sample.

Thixotropic effect was studied for four different types of pure honey types -black seed, clover, desert and mountain flower- at room temperature and pressure, the results demonstrated that only desert honey exhibited thixotropic behavior.

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