The Hidden Property of Arrhenius-type Relationship:
Viscosity as a Function of Temperature

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Abstract: *In this paper, an equation to replace the well-known Arrhenius-type relationship was derived. This is because the activation energy constant is not yet in its fundamental form. The model maintains the traditional properties of activation energy and infinite-temperature viscosity constants, and it contains a new constant that is the zero-temperature viscosity. The ration of zero- and infinite-temperature represents the value of fundamental activation energy. This model was tested using six vegetable oils and has proven its accuracy (R-squared, 0.999). Viscosity – temperature stability refers to the difference between the zero- and infinite-temperature viscosities, rather than the activation energy.*

Keywords: viscosity, Arrhenius-type relationship, temperature, rheology

Abstrak: *Dalam penulisan ini, satu persamaan untuk menggantikan hubungan jenis Arrhenius telah diterbitkan. Ini adalah kerana pemalar tenaga keaktifan daripada persamaan itu bukan dalam bentuk asas. Persamaan baru ini mengekalkan sifat asal tenaga keaktifan dan kelikatan pada suhu tidak terhingga, dan ia merangkumi pemalar baru, iaitu kelikatan pada suhu sifar. Nisbah kelikatan pada suhu sifar dan kelikatan pada suhu tidak terhingga merupakan nilai asas untuk pemalar tenaga keaktifan. Model ini telah diuji dengan enam minyak sayur-sayuran dan kejituannya terbukti (R kuasa dua, 0.999). Kestabilan kelikatan – suhu merujuk pada perbezaan kelikatan pada suhu sifar dan kelikatan pada suhu tidak terhingga, bukan nilai tenaga teraktifan itu sendiri.*

Kata kunci: kelikatan, hubungan jenis Arrhenius, suhu, reologi

1. INTRODUCTION

Viscosity is one of the most important physical properties of a fluid system. Studies on viscosity have been performed on polystyrene, protein, pineapple juice, vegetable oil, dark beer, etc.[1–5] Viscosity changes with shear rate, temperature, pressure, moisture, and concentration; all these changes can be modelled by equations.

The effect of temperature is normally fitted with the Arrhenius-type relationship that is shown below:[6–8]

$$\eta = Ae^{\frac{E_a}{RT}} \tag{1}$$

Where η is dynamic viscosity (Pa.s); A is the pre-exponential factor (Pa.s); E_a is the exponential constant that is known as activation energy (J/mol); R is the gas constant (J/mol/K) and T is the absolute temperature (K).

The value of A can be approximated as the infinite-temperature viscosity (η_∞), which is exact in the limit of infinite temperature. Hence, equation (1) can be rewritten in the following form:[9]

$$\eta = \eta_\infty e^{\frac{E_a}{RT}} \tag{2}$$

Equations (1) and (2) are basically equivalent. Although equation (1) normally appears in the literature, equation (2) gives a more accurate representation of the fluid since the pre-exponential value is better defined there. However, equation (2) is not yet in its simplest form. In addition to this, E_a, which is used to represent the stability of the liquid system, is reported as unreliable in discriminating oil viscosity – temperature stability.[10]

The aim of this work is to model the changes in viscosity as a function of temperature. The objectives are to: (1) derive the simplest form of an equation that incorporates zero- and infinite-temperature viscosity parameters and has a relation to the activation energy constant; and (2) to determine a reliable indicator of the viscosity – temperature stability of oil from the comparison of the activation energy constant and the experimental data.

2. EXPERIMENTAL

2.1 Liquids Used in the Experiments

Several types of vegetable oils were used in the experiment. They were: coconut oil, crude palm kernel (CPK) oil, olive oil, sesame oil, soy oil, and sunflower oil. These oils were purchased from the respective manufacturers of Felda Kernel Products Sdn. Bhd., Basso Fedele e figli s.r.l., Lee Kum Kee (Xinhui) Food Co., Ltd., Celestial Ventures Sdn. Bhd., and Lam Soon Edible Oils Sdn. Bhd. Coconut oil was manually produced in the laboratory.

2.2   Instrumentation Set-up and Viscosity Measurements

A Brookfield (Viscometer model DV-I+, Brookfield Engineering Laboratories Inc., Massachusetts, USA) rotational-type viscometer was used to measure the viscosity of the oil samples. Before use, the viscometer (accuracy: ± 1% full-scale range; repeatability: 0.2% full-scale range) was calibrated with a 4.7 cP Brookfield silicone viscosity standard. The viscosity of the oils was measured in triplicate at 100 rpm (revolutions per min). The highest speed was selected in order to increase the accuracy of the measurement because a lower speed would have increased the fluctuation of the viscosity readings. A temperature controller (temperature accuracy of ±1°C) was used to increase the temperature of the oil samples from 50°C to 100°C with an increment of 10°C. For each 10°C increment, the oil samples were left for 15 min until steady-state heat transfer was achieved.

2.3   Derivation of the Viscosity – Temperature Model

It is widely accepted that natural logarithmic viscosity is directly proportional to the reciprocal value of the temperature. To increase the flexibility of this equation, constants a and b are introduced into equation (3) as shown below:

$$\ln(\eta) + a = \frac{b}{T} \tag{3}$$

By knowing that viscosity decreases with increasing temperature and has a curve concave upward when a viscosity versus temperature graph is plotted, $\eta \approx \eta_{T_\infty}$ when temperature is approximating infinity. Similarly, a decreasing temperature would increase the viscosity of a fluid body and thus, temperature at T_o would give $\eta \approx \eta_{T_o}$ in which $\eta_{T_o} > \eta_{T_\infty}$. Based on the above-mentioned conditions, equation (3) can be rearranged into the following form:

$$\eta = \eta_{T_\infty} \left(\frac{\eta_{T_o}}{\eta_{T_\infty}} \right)^{\frac{T_o}{T}} \tag{4}$$

The E_a can be obtained as the following after comparing equations (2) and (4):

$$E_a = T_o R \ln\left(\frac{\eta_{T_o}}{\eta_{T_\infty}} \right) \tag{5}$$

Equation (5) has a similar value and unit to that of equation (1). R is the gas constant, and is equal to 8.314 J/mol/K. η_{T_o} is the viscosity at temperature T_o which, in this study, has been taken as the zero-temperature viscosity.

2.4   Model Regression of the Newly Derived Viscosity – Temperature Model

Equation (4) can be linearised by taking the natural logarithm on both sides of the equation:

$$\ln(\eta) = \ln\left(\eta_{T_\infty}\right) + \frac{T_o}{T}\ln\left(\frac{\eta_{T_o}}{\eta_{T_\infty}}\right) \tag{6}$$

Equation (6) can be solved by plotting $\ln(\eta)$ versus $1/T$ and thus, $\ln(\eta_{T_\infty})$ is the intercept at the $\ln(\eta)$-axis and $T_o \ln\left(\frac{\eta_{T_o}}{\eta_{T_\infty}}\right)$ is the slope of the linear graph. Viscosity data for the six points from 50°C to 100°C at 100 rpm for each vegetable oil was fitted with equation (6) using Microsoft Office Excel and zero-, infinite-temperature viscosity, and the E_a, and the R-squared value was estimated.

2.5   Shifting Experimental Data of Viscosity and Temperature to Investigate the Reliability of E_a in Indicating the Stability of Viscosity – Temperature Relation

The reliability of the E_a in indicating a reliable observation for the viscosity – temperature relation was carried out using the viscosity of coconut oil, which was randomly selected from the collection of oils used in this study. The viscosity – temperature curve line (M-type) was plotted as shown in Figure 1. This line was then shifted to the left, right, top and bottom from its original position (M-type) by taking $T - 10$ K, $T + 10$ K, $\eta + 0.003$ (Pa.s) and $\eta - 0.003$ (Pa.s), respectively, which resulted in the respective L-, R-, T- and B-shifted lines. These lines were curve-fitted by equation (6), and its determined model constants were compared to graphical observations in order to justify any reliable trend.
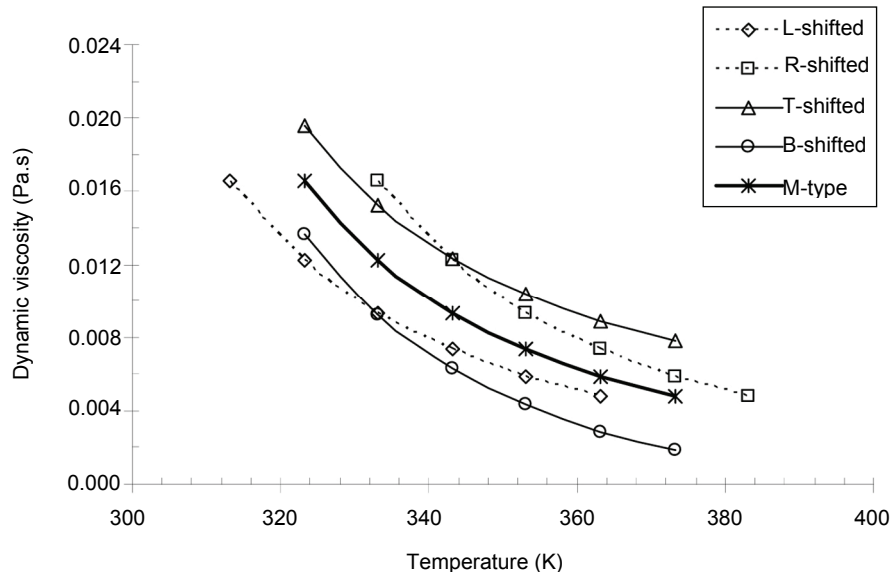
Figure 1:   Dynamic viscosity versus temperature for coconut oil at 100 rpm.

Notes: M-type is the original viscosity data from experiment; L-shifted is the left-shifted curve after the temperature was reduced by 10 K; R-shifted is the right-shifted curve after the temperature was increased by 10 K; T-shifted is the top-shifted curve after the viscosity was increased by 0.003 Pa.s; and B-shifted is the bottom-shifted curve after the viscosity was reduced by 0.003 Pa.s.

3.   RESULTS AND DISCUSSION

3.1   Viscosity – Temperature Relationship

The viscosity of all of the vegetable oils decreased as the temperature increased. This could be due to the energy obtained to overcome the resistance to flow, which may be due to the attractive forces among the oil molecules. A similar behaviour is also observed for various fluids, such as lemon juices, wine, honey, sweet sorghum and vegetable oil fuel.[11–15] From Figure 2, one can see that the reduction of the viscosity is greater at the initial stage of the temperature increment, and subsequent increases in the temperature during the latter part had less influence on reducing the viscosity, as was observed for all of the vegetable oils.

Olive and sunflower oil is the most and least viscous, respectively, from all six vegetable oils measured. The other vegetable oils are ranged between these two viscous limits in descending order as follows: sesame > soy > CPK > coconut. The high oil viscosity could be attributed to the stronger attraction force between oil molecules. Hence, sunflower oil is the liquid with the weakest in terms of its resistance to flow in relative comparison to the other five oils.
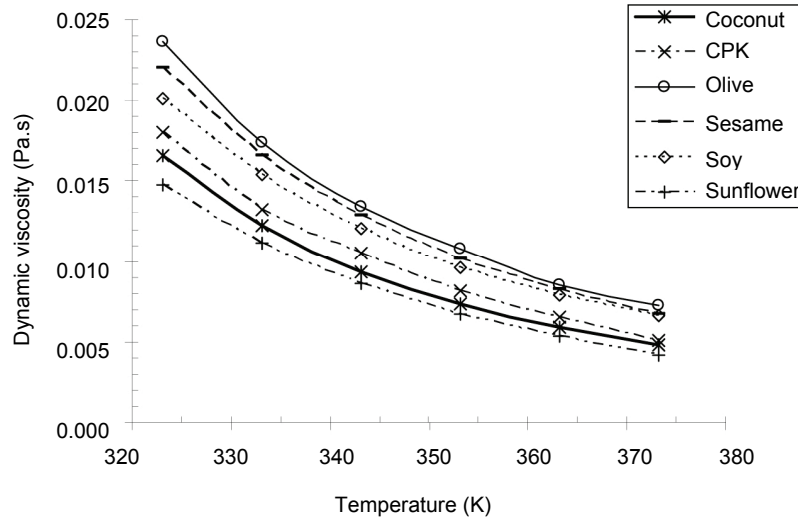
Figure 2: Dynamic viscosity of vegetable oils versus temperature at 100 rpm.

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3.2   Zero-, Infinite-temperature Viscosity and E_a

Figure 3 shows that the experimental viscosity data is in close approximation to the viscosity value estimated from equation (6). This observation is supported with an overall R-squared value of 0.999 and a mean squared error (MSE) of 3.47×10^{-8}. A high R-squared value of around 0.999 is also observed for individual vegetable oil (Table 1). This suggests that the experimental data is well-fitted by the current proposed model.

Zero-temperature viscosity indicates the value of the viscosity right before the temperature influences it, whereas infinite-temperature viscosity indicates its internal resistance to flow that is free from the influence of temperature. The ratio of zero- and infinite-temperature viscosity has an influence on the E_a, as indicated by equation (5). This suggests that a greater difference, in terms of value, between η_{T_o} and η_{T_∞} would give a high $\eta_{T_o}/\eta_{T_\infty}$ ratio, which would result in high E_a values. Thus, a smaller E_a indicates an oil viscosity that is less sensitive to temperature.
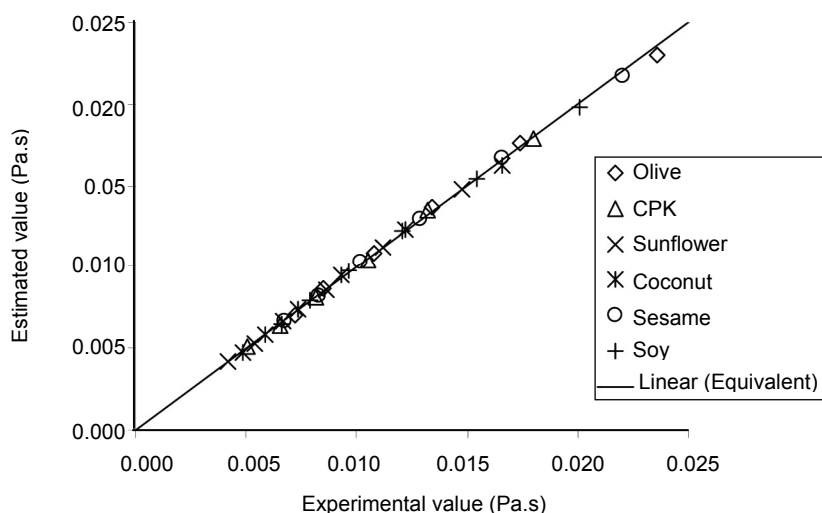
Figure 3:   The comparison between the experimentally derived value and the estimated value from equation (6). R-squared and MSE was calculated as 0.999 and 3.47×10^{-8}, respectively.

Table 1: Zero-, infinite-temperature viscosity, E_a and R^2 value of vegetable oils.

Vegetable oils	η_{T_O} (PA.S)	η_{T_∞} (PA.S)	E_a (J/MOL)	R^2
Coconut	8.75E–02	1.63E–06	2.47E+04	0.999
CPK	9.83E–02	1.62E–06	2.50E+04	0.999
Olive	1.16E–01	3.28E–06	2.38E+04	0.997
Sesame	1.09E–01	3.21E–06	2.37E+04	0.999
Soy	9.07E–02	4.87E–06	2.23E+04	0.999
Sunflower	8.22E–02	1.27E–06	2.52E+04	1.000

The E_a is ranked in a descending order as follows: sunflower > CPK > coconut > olive > sesame > soy (Table 1). This trend indicates that the viscosity of soy and sunflower is respectively the least and the most sensitive to the influence of temperature. This observation is not in consistent to the trend of $\left| \eta_{T_o} - \eta_{T_\infty} \right|$ value on each vegetable oil. The oil with the greatest sensitivity to temperature effect should possess the highest value of $\left| \eta_{T_o} - \eta_{T_\infty} \right|$ and this belongs to olive oil which has the largest value. The rests of $\left| \eta_{T_o} - \eta_{T_\infty} \right|$ value are in the following sequence in descending order: sesame > CPK > soy > coconut > sunflower. The disagreement between E_a and the difference between zero- and infinite-temperature viscosities is indicating the failure of the E_a to capture

viscosity – temperature stability observation and this problem is explained in the following section.

3.3   Justification on the E_a Suitability in Indicating Viscosity – Temperature Stability

The viscosity – temperature stability was investigated by comparing its original and shifted curve-lines such as the M-type, L-, R-, T- and B-shifted types for coconut oil, as shown in Figure 1. Each of the shifted curve-types was carried out with a constant value of viscosity added or removed from all of the experimental viscosity data in shifting the curve-line to the top (T-shifted) or to the bottom (B-shifted) from its original graph (M-type). A similar step was carried out by shifting the experimental temperature data either to the left (L-shifted) or to the right (R-shifted) from its original graph. Overall, the zero- and infinite-temperature viscosity changes depended on the shifted type, and this indicates that shifting the experimental data in different locations in the graph gives different E_a values (Table 2).

Table 2: Zero-, infinite-temperature viscosity, E_a and R^2 value of L-, R-, T- and B-shifted curves of coconut oil.

Type	η_{T_o} (Pa.s)	η_{T_∞} (Pa.s)	E_a (J/mol)	R^2
L	6.03E–02	2.08E–06	2.33E+04	0.999
R	1.29E–01	1.27E–06	2.62E+04	0.998
T	6.60E–02	2.03E–05	1.84E+04	0.993
B	2.16E–01	5.27E–09	3.98E+04	0.995

Note: Constants value for M-type is similar to that of coconut oil in Table 1

As mentioned in the previous section, the E_a is composed of the zero- and infinite-temperature viscosity value, as indicated by equation (5). Understanding the changes in these two constant values would lead to a better understanding of the changes in the E_a. Observation of the trend of the curve-line from the left (L-shifted) to the right (R-shifted), shows an increasing slope value and a decreasing intercept value (Fig. 4). Since the slope and intercept values relate to the E_a and the infinite-temperature viscosity, observing the L- to R-shifted curve-lines, shows an increasing value in the E_a but a decreasing value in the infinite-temperature viscosity. Similarly, this is observed from T- to B-shifted curve-lines. The $\left| \eta_{T_o} - \eta_{T_\infty} \right|$ is also increasing from L- to R-shifted, and T- to B-shifted curve-lines. The effort of shifting the experimental data for viscosity and temperature does not explain the failure of the E_a in indicating the viscosity – temperature stability. Therefore, it can be concluded that the activation energy is not a good representation of the viscosity – temperature stability in terms of taking the difference of the viscosity value between two points. Activation energy

can only be used to indicate viscosity – temperature stability when the ratio for a viscosity value that is over other viscosity values is required.
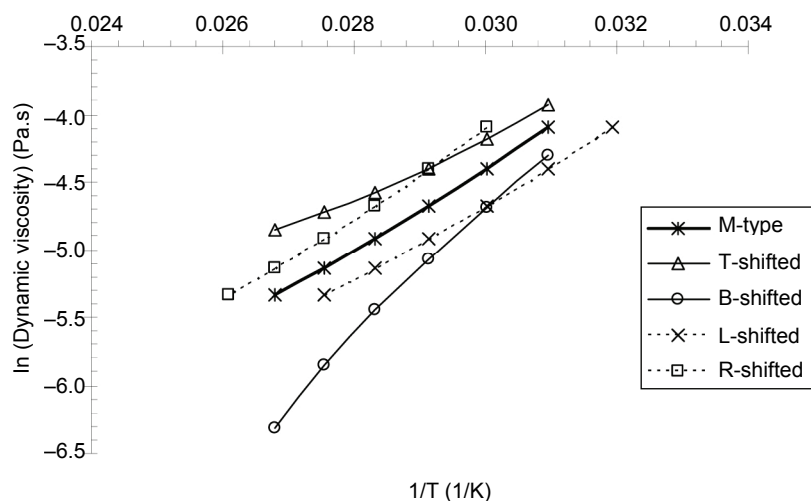

Figure 4: Natural logarithmic on dynamic viscosity versus temperature reciprocal for M-type, L-, R-, T- and B-type curve-lines of coconut oil at 100 rpm.

4.   CONCLUSION

A newly-derived equation from the simple correlation between the natural logarithm of dynamic viscosity and the temperature reciprocal is validated using six vegetable oils that give very good curve-fitting results, with an overall R-squared of 0.999. Viscosity, in nature, from vegetable oils is found to decrease as the temperature increases. The zero-temperature viscosity constant is introduced into the newly-derived equation and, together with the infinite-temperature viscosity constant, represents the fundamental value of the E_a constant. The stability of the viscosity – temperature observation is best indicated by the difference between zero- and infinite-temperature viscosities when the subtraction is more important than the ratio between any two points of viscosity.

5.   ACKNOWLEDGEMENTS

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