Investigation of the Reliability of Activation Energy in the Stability of Viscosity – Temperature Model

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Abstract

In search for the fundamental form of the molar activation energy constant, a new equation relating the dynamic viscosity and the absolute temperature was derived. The new equation contains a new constant known as the zero – temperature viscosity in addition to the activation energy and infinite - temperature constant in the well known Arrhenius- type equation. The ratio of zero – temperature viscosity / infinite – temperature viscosity represents the value of fundamental activation energy. The model was tested using five vegetable oils within an accuracy of 1.1%. Viscosity – temperature stability refers to the difference between the zero and infinite – temperature viscosities, rather than the activation energy.

Keywords: Temperature, viscosity, rheology, Arrhenius-type equation, activation.

Introduction

A liquid is a body which has definite volume but do not have elasticity of form (absence of a shear modulus). Liquids are distinguished for their strong molecular interactions and as a result, low compressibility. The low compressibility of liquids is evident since small reduction in the already small intermolecular distances give rise to large intermolecular forces of repulsion. A liquid is simply identified by its colour or odour without undergoing laboratory experiment. In the laboratory, liquids of like colour or odour are usually distinguished by studying their physical properties such as viscosity, density, melting point, boiling point and so on.

Viscosity is one of the most important physical properties of a liquid. Studies on viscosity have been performed on many liquids (Adeosun et al., 1997; Gyani and Murari, 1956,1983; Tabor, 1979; Fasina and Colley, 2008; Severa et al., 2008); Magerramov et al., 2009; Yanniotis et al., 2007; Toth et al., 2007; Yerima, 2005). It is widely accepted that viscosity changes with temperature, shear rate, pressure, moisture, size and entanglement of molecules, concentration and so on. All these changes can be modeled by equations.

The effect of temperature is given by the Arrhenius equation of the form (Thodesen et al., 2009; Saeed et al., 2009; Adeosun et al., 1997)

$$\mu = Ce^{\frac{G_a}{RT}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

where μ is the dynamic viscosity, C is the pre-exponential factor, G_a is the molar activation energy, R is the universal gas constant and T is the absolute temperature. The constant C is the exact value of viscosity (t) in the limit as T tends to infinity. Thus, equation (1) can be rewritten as (Wan Nik et al., 2005)

$$\mu = \mu_\infty e^{\frac{G_a}{RT}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Although equations (1) and (2) are basically the same, equation (2) gives a more accurate representation of the liquid since C is better defined there. However, equation (2) is not yet in its simplest form. In addition to this, G_a which is to represent the stability of the liquid system is reported as unreliable in discriminating oil viscosity-temperature stability (Goh et al., 2009).

In this paper, we want to model the changes in viscosity as a function of temperature in form of an equation that incorporates zero- and infinite-temperature viscosity parameters which has a relation to the activation energy constant. In addition to this, determine a reliable indicator of the viscosity-temperature stability of oil from the comparison of the activation energy constant and the experimental data.
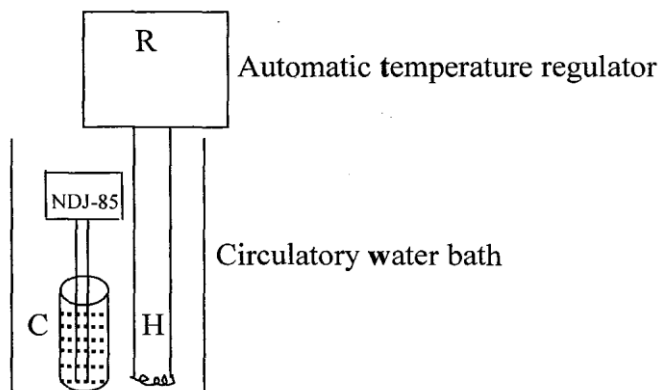
Experiment

Figure 1. Schematic diagram for viscosity measurement

The following vegetable oils namely palm kernel (pko), palm oil (pmo), coconut oil (cco), cotton seed oil (cso) and walnut oil (wno) were used in the experiment. These oils were manually produced in the laboratory. A computerized rotary viscometer (NDJ-85 model) was used to measure the viscosity of the oil samples. Before use, the viscometer (accuracy: ±2 % full-scale range; repeatability: 0.2 % full scale range) was calibrated with a 4.7 cp Brookfield silicone viscosity standard. The dynamic viscosity, i of the oil samples at various temperatures (285-343K) were measured with the viscometer rotor immersed in oil inside a cylinder C placed in a temperature (± 1 °C) controller of circulatory water bath. The cylinder containing oil sample was placed in the bath with its brim above the level of water in the bath but the

level of oil below the water level. An automatic electric heater H with stirrer room temperature. The values of the viscosity of oil sample were determined at shear rate of 30 rpm (revolutions per minute) at various temperatures. For high accuracy, a calibrated thermocouple of accuracy of ± 1 °C was placed in the oil to ascertain that the oil was at the same temperature with the water in the bath before readings were taken and contamination of oil sample with water and other impurities was avoided.

Viscosity-Temperature model

A host of authors have reported that the natural logarithm of dynamic viscosity (μ) is directly proportional to the reciprocal of the value of the absolute temperature T (Utah et al., 1989; Rakshit, 1997; Yavorsky and Detlaf, 1980)

$$\ln(\mu) + A = \frac{B}{T} \quad \dots\dots\dots\dots\dots\dots\dots 3$$

where A and B are constants.
If the viscosity decreases with increasing temperature in such a way that viscosity versus temperature curve is concave upward, then as $T \to \infty$, $\mu \approx \mu_{T\infty}$ Similarly, a decreasing temperature would increase the viscosity of a liquid body in a way that at a temperature T_o, $\mu \approx \mu_{To}$ such that $\mu_{TO} > \mu_{T\infty}$,• Therefore, substituting the boundary condition

Equation (7) represents a straight line which can be obtained by plotting $\ln(\mu)$

Viscosity data for the five points from 285 K to 353 K at 30 rpm for five vegetable oils were fitted with equation

attached to the temperature regulator was used to heat the oil sample above $\mu \approx \mu_{T\infty}$ as T tends to infinity in equation (3) we have

$$A = -\ln(\mu_{T_\infty}) \quad \dots\dots\dots\dots\dots\dots\dots 4a$$

Where the term $\dfrac{B}{T_\infty} \to 0.$

Similarly, putting $\mu \approx \mu_{To}$ as $T \to T_o$ in equation (3) gives

$$\ln(\mu_{T_o}) + A = \frac{B}{T_o} \quad \dots\dots\dots\dots\dots 4b$$

Combining equations (4a) and (4b) we get

$$B = T_o(\ln\mu_{T_o} - \ln\mu_{T_o}) \quad \dots\dots\dots\dots 4c$$

Now substituting equations (4a) and (4c) in equation (3) we have

$$\mu = \mu_{T_\infty}\left(\frac{\mu_{T_o}}{\mu_{T\infty}}\right)^{\frac{T_o}{T}} \quad \dots\dots\dots\dots\dots 5$$

Comparing equations (2) and (5) we get

$$G_a = T_o R \ln\left(\frac{\mu_{T_o}}{\mu_{T\infty}}\right) \quad \dots\dots\dots\dots 6$$

where R = 8.314 J/mol/K is the universal gas constant and μ_{To} is the viscosity at temperature $T_o(=0°C)$ called zero-temperature viscosity.
Now linearising equation (6) by taking the natural logarithm on both sides of the equation gives

$$\ln(\mu) = \ln(\mu_{T_\infty}) + \frac{T_o}{T}\ln\left(\frac{\mu_{T_o}}{\mu_{T_\infty}}\right) \quad \dots\dots\dots 7$$

versus $\dfrac{1}{T}$ where $\ln(\mu_{T_\infty})$ is the intercept

on the 1nμ-axis and T_o1n $\left(\dfrac{\mu_{T_o}}{\mu_{T_\infty}}\right)$ is the

slope of the graph.
(7) using Microsoft Office Excel and infinite temperature viscosity and the G_a and the R-squared value was estimated.

Results and discussion

Table 1. Viscosity values of vegetable oils

T(K)	Viscosity of Oil Samples				
	Palm kernel oil (cp)	Palm oil (cp)	Coconut oil (cp)	Cotton seed oil (cp)	Walnut oil (cp)
303	58.46	79.06	35.47	81.81	50.10
313	47.58	58.17	25.93	60.41	30.80
323	37.55	38.84	17.24	40.74	25.10
333	27.26	28.61	10.15	30.93	18.00
343	19.72	21.74	7.65	23.65	11.47

The viscosity of all the vegetable oils decreased with increasing temperature. This behavior could be attributed to the energy gained to overcome the resistance to flow owing to the attractive forces among the oil molecules (Magerramov et al., 2009; Yanniotis et al., 2007). From Table 1, we can see that the decrease in the viscosity is higher 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. Cotton seed oil (cso) is the most viscous while coconut oil is the least. The other vegetable oils are ranged between these two viscous limits in ascending order as follows: walnut oil (wno) <palm kernel oil (pko) <palm oil (pmo). The high oil viscosity could be due to the strong forces of attraction among the oil molecu0les. Hence, coconut oil is the weakest in terms of its resistance to flow relative to the rest of the oils.

Table 2 Zero-temperature viscosity $(\mu_{T\infty})$, infinite-temperature viscosity $(\mu_{T\infty})$, molar activation energy (G_a) and R^2 value of vegetable oils.

Vegetable oils	μ_{To}(CP)	$\mu_{T\infty}$ (Cp)x10^{-5}	G_a (J/mol)	R^2
Palm kernel oils	173.1	555.0	23486.7	0.981
Palm oil	277.1	99.4	28458.1	0.997
Coconut oil	170.2	4.1	34560.6	0.988
Cotton seed oil	270.2	164.8	27250.6	0.997
Walnut oil	182.7	32.1	30078.2	0.982

Table 2 shows that experimental viscosity data is in close approximation in the viscosity value estimated from equation (7). This observation is supported with an average R-squared of 0.989 and a mean squared error (MSE) of 4.84×10^{-5}. A high average value of R-squared = 0.989 suggests that the experimental data is well-fitted by the current proposed model.

Zero-temperature viscosity shows 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 G_a as shown by equation (6). This suggests that a greater difference in terms of value, between μ_{To} and $\mu_{T\infty}$ would give a high ($\mu_{To}/\mu_{T\infty}$) ratio (Table 2), which would results in high G_a values. Thus, a

smaller Ga shows an oil viscosity that is less sensitive to temperature.

In Table 2, G_a is ranked in ascending order as follows: pko < cso < pmo < wno < cco. This trend shows that the viscosity of palm kernel oil is the least while that of coconut oil is the most sensitive to the influence of temperature. This observation is not consistent with the trend $|\mu_{To} - \mu_{T\infty}| \approx \mu_{To}$ values in Table 2. The oil with the greatest sensitivity to temperature effect should have the highest value of $|\mu_{To} - \mu_{T\infty}| \approx \mu_{To}$, and this corresponds to palm oil which has the largest value. The rest of $|\mu_{To} - \mu_{T\infty}| \approx \mu_{To}$, values are in the following sequence in ascending order: cco <pko <wno <cso. The inconsistence between G_a and the difference between zero- and infinite-temperature viscosities is showing the failure of the G_a to capture viscosity-temperature stability observation.
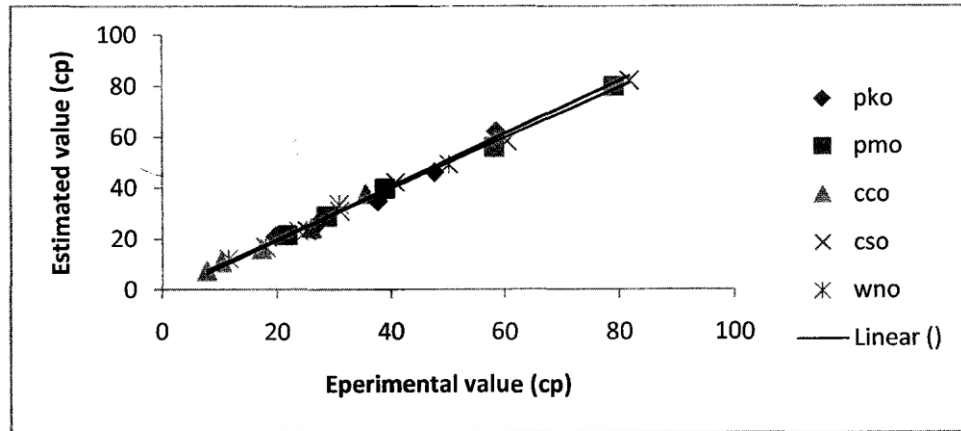

Fig. 2 The comparison between the experimentally derived value and the estimated value from equation (7). R-squared and MSE were calculated as 0.989 and 4.84×10^{-5}, respectively.

The viscosity-temperature stability was investigated by comparing its original and shifted lines such as the M-type, L-, R-, T-,, and B-shifted types for coconut oil (Fig. 3). Each of the shifted lines was

carried out with a constant value of viscosity added or subtracted from all of the experimental viscosity data in shifting the 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. On the overall, the zero-and infinite-temperature

viscosity changes depended on the shifted type, and this shows that shifting the experimental data in different locations in the graph gives different G_a values (Table 3).

Table 3. Zero-temperature viscosity, infinite-temperature viscosity, **Ga** and R2 value of L-, R-, T-, and B-shifted lines of coconut oil.

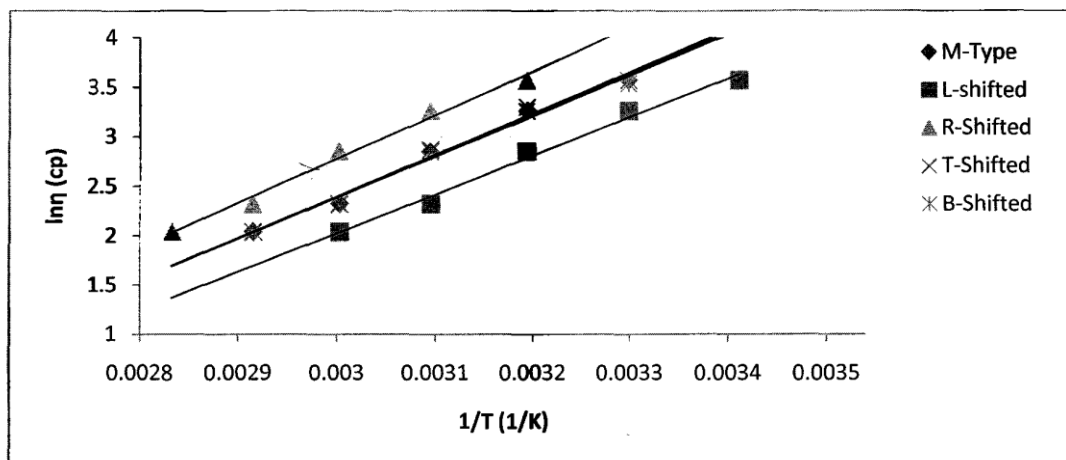| Type	$\mu_{To}(cp)$	$\mu_{T\infty}$ (cp)x10^{-5}	G_a (J/mol)	R^2
L	100.3	6.2	32449.4	0.988
R	299.3	2.8	36747.7	0.988
T	176.7	3.9	34802.4	0.984
B	163.9	4.8	34120.7	0.986

Fig. 3 Natural, logarithm of dynamic viscosity versus temperature inverse for M-, L-, R-, T-, and B-type lines of coconut oil at 30 rpm.

As before, for each shift-type, G_a was calculated substituting the zero-and infinite temperature viscosity value in equation (6). It is expected that the changes in these constant values would lead to a better understanding of the

changes in the Ga. The slope and intercept of the original graph M-type are 4157 and -10.09 respectively. The trend observed in the line shift from the left (L-shifted: slope = 3903; intercept = -9.69) to the right (R-shifted: slope

4420; intercept - 10.49), shows an increasing slope value and a decreasing intercept value (Fig. 3). Since the slope and intercept values relate to the G_a and the infinite-temperature viscosity, observed L- to R-shifted lines show an increasing value in the G_a but a decreasing value in the infinite-temperature (Table 3). Similarly, the trend observed in the line shift from the top (T-shifted: slope 4186; intercept = -10.16) to bottom (B-shifted: slope = 4104; intercept = -9.94), shows a decreasing slope value and an increasing intercept value. The $| \mu_{To} - \mu_{T\infty}|$ is also increasing from L- to R-shifted and decreasing from T- to B-shifted lines. The effort of shifting the experimental data viscosity and temperature does not account for the failure of the G_a in revealing the viscosity temperature stability. Therefore, it can be concluded that the molar activation energy is not a good representation of the viscosity value between two points. Activation energy can only be used to show viscosity-temperature stability when the ratio for a viscosity value that is over other viscosity value is required.

Conclusion

A newly derived equation from the simple correlation between the natural logarithm of dynamic viscosity and temperature reciprocal is validated using five vegetable oils that give very good line fitting results, with overall R-squared of 0.989. 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, together with the infinite-temperature viscosity constant, represents the fundamental value of the G_a constant. The stability of the viscosity- temperature observation is best showed by the difference between zero- and infinite-temperature viscosities when the subtraction is more important than the ratio between any two points of viscosity.

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