# ESTIMATION OF VISCOSITY ARRHENIUS PRE-EXPONENTIAL FACTOR AND ACTIVATION ENERGY OF SOME ORGANIC LIQUIDS

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*Abstract:* **Information concerning fluid's physico-chemical behaviors is of utmost importance in the design, running and optimization of industrial processes, in this regard, the idea of fluid viscosity quickly comes to mind. Models have been proposed in literatures to describe the viscosity of liquids and fluids in general. The Arrhenius type equations have been proposed for pure solvents; correlating the pre-exponential factor A and activation energy $E_a$. In this paper, we aim at extending these Arrhenius parameters to simple organic liquids such as water, ethanol and Diethyl ether. Hence, statistical method and analysis are applied using viscosity data set from the literature of some organic liquids. The Arrhenius type equation simplifies the estimation of viscous properties and the calculations thereafter.**

*Keywords:* **Viscosity, organic liquids, Arrhenius parameters, correlation, statistics.**

## 1. INTRODUCTION

All fluids are compressible and when flowing are capable of sustaining shearing stress on account of friction between the adjacent layers. Viscosity (η) is the inherent property of all fluids and may be referred to as the internal friction offered by a fluid to the flow. For water in a beaker, when stirred and left to itself, the motion subsides after sometime, which can happen only in the presence of resisting force acting on the fluid. The temporary resistance offered by fluids to the shearing stress is called viscosity. Viscosity is that behavior of fluids due to which they oppose relative motion between the adjacent layer. Liquids such as kerosene, alcohol and water etc which flows readily are said to be mobile while liquids such as tar, pitch etc which do not flow readily are said to be viscous. Liquids such as honey, heavy oils, glycerin etc are more viscous than tar. Some liquids, such as benzene, diethyl ether, gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as honey, heavy oils, glycerin, motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The viscosity of a liquid can be determined in two common ways; (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity of a liquid is expressed in units of kg m$^{-1}$ s$^{-1}$. However, the unit that is typically employed in practice is called the 'poise' (P) or gram cm$^{-1}$ s$^{-1}$ . Liquid viscosities are usually reported in centipoise, (cP) while gas viscosity are reported in micropoise (μP).

The viscosities of some common liquids show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due

to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.

There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become "tangled" with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

When a liquid flows in a tube, a viscous force opposes the flow of the liquid. Hence, a pressure difference is applied between the end of the tube which maintains the flow of the liquid. If all particles of the liquid passing through a particular point in the tube move along the same path, the flow of the liquid is called "streamed lined flow". This occurs only when the velocity of flow of the liquid in below a certain limiting value called the critical velocity, the flow is no longer streamed lined but becomes turbulent. In this type of flow, the motion of the liquid becomes zig-zag and edge currents are developed. Reynold's provided that the critical velocity for a liquid flowing, in a tube is (Shukla and Srivastava, 2006);

$$V_c = \frac{k\eta}{\rho a} \tag{1}$$

Where; $\rho$ = density, $\eta$ = viscosity, a = radius of the tube, k = Reynold's number whose value for a narrow tube and for water is about 1,000.

When the velocity of flow of the liquid is less than the critical velocity, then the flow will be controlled by the viscosity, the density having no effect on it. But when the velocity of flow is larger than the critical velocity, then the flow is mainly governed by the density, the honey, heavy oils, glycerin effect of viscosity becoming less important. It is because of the reason that when a volcano erupts, then the lava coming out of it flows speedily in spite of being very thick, rather very viscous.

To quantify viscosity, we will imagine our bulk fluid as consisting of a number of very thin layers. In order for the fluid to flow, a force will be required to slide these layers relative to one another. The amount of force (f) required is assumed to be directly proportional to the area (A) of the layers in contact with one another and the velocity difference (v) between the layers. Also, the force is inversely proportional to the distance (d) between the layers. Viscosity ($\eta$) can then be introduced as a constant of proportionally, yielding a force equation of the form;

$$f = \eta \frac{Av}{d}$$

What factors determine whether a given fluid has a high (or low) viscosity? Certainly the strength of intermolecular attractions has an influence; nitro-benzene has a much higher viscosity than regular benzene because the former is capable of dipole-dipole attractions which are considerably stronger than the dispersion forces of attraction present in bulk benzene. Other factors can contribute, such as the size and shape of molecules. For example, long chain molecules like polymers are capable of becoming entangled with each other which causes friction between the hypothetical layers of the fluid which translates into a large viscosity.

Viscosity varies with temperature, generally becoming smaller as temperature is elevated. This trend occurs because the increased kinetic motion at higher temperatures promotes the breaking of intermolecular bonds between adjacent layers. A considerable amount of research has been carried out in an attempt to understand the exact nature of the temperature variation of viscosity. One relatively simple model assumes that the viscosity obeys an 'Arrhenius-like' equation of the form

$$\eta = Ae^{\left(\frac{E_a}{RT}\right)}$$

where A is the frequency or the pre-exponential factor, E is the activation energy (to fit into this equation, it has to be expressed in Joules per mole and not in kilojoules per mole) for viscous flow, R is the gas constant (8.31 $JK^{-1}mol^{-1}$) and T is the temperature measured in Kelvin. The above expression is almost identical to the Arrhenius equation that describes the temperature variation of the rate constant (k) of a chemical reaction, except equation (3) does not have a negative sign

in the exponential which causes the viscosity to get smaller with increasing temperature. Equation (3) can be written in the logarithmic form

$$In\ \eta = \left(\frac{E_a}{R}\right)\frac{1}{T} + In\ A$$

If a fluid obeys equation (4), then a plot of viscosity versus inverse of absolute temperature should be a linear graph and the slope can be used to determine the activation energy $E_a$ and the pre-exponential factor A for viscous flow as follows;

Activation Energy $E_a$ = Slope S x Gas Constant R

And

The Pre − exponential Factor A = Antilog $\left[\frac{Intercept\ on\ the\ vertical\ axis}{2.30257}\right]$

## 2. METHODS

**VISCOSITY DETERMINATION:**

The Ostwald viscometer is commonly used for comparing the viscosities of two liquids or the same liquid at different temperatures such a viscometer is shown in plate 1
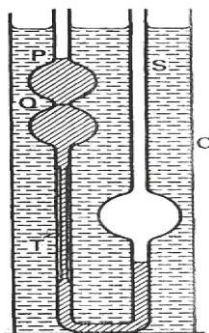


**Plate 1: Schematic diagram for measuring viscosity**

**PROCEDURES:**

A number of experimental methods are available for measuring viscosity. Many are based upon measuring the amount of time (t) it takes for a given amount of fluid to flow through a thin glass tube or to drain from a vessel that has a small opening in the bottom. An equivalent measurement is carried on a fluid of known viscosity. The liquid sample was introduced at point S, drawn by suction above P and the time $t_1$, taken for the liquid level to fall between the fixed marks P and Q will be observed. The same experiment will be repeated with the same volume of water and the time $t_2$ for the liquid level to fall from P to Q will be recorded. Suppose the liquids have respective densities $\rho_1$, $\rho_2$ then, since the average lead h of liquid falling through T is the same in each case, the pressure excess between the ends of $T = h\rho_1 g$, $T = h\rho_2 g$ respectively. If the volume between the marks P, Q is V, then, from Poiseuille's formula, we obtain that;

$$\frac{V}{t_1} = \frac{\pi(h\rho_1 g)a^4}{8\eta_1 L} \qquad\qquad (3.1)$$

Where 'a' is the radius of T, $\eta_1$, is the coefficient of viscosity of the liquid sample and L is the length of T. Similarly for the second liquid.

$$\frac{V}{t_2} = \frac{\pi(h\rho_2 g)a^4}{8\eta_2 L} \qquad\qquad (3.2)$$

Dividing equation (3.2) by (3.1) we have (Oyekunle *et. al.*, 2007);

$$\eta_1 = \frac{\eta_2 t_1 \rho_1}{t_2 \rho_2} \qquad\qquad (3.3)$$

Where:

η = Viscosity of the liquid samples

t = Time taken for the liquid sample to fall from P to Q

ρ = Density of the liquid sample

Thus, knowing $t_1$, $t_2$ and the densities $\rho_1$, $\rho_2$, the coefficients of viscosity can be compared. Further, if a pure liquid of a known viscosity such as water is used, the viscosity will be used to measure the coefficient of viscosity of the mahogany seed oil. Since viscosity varies with temperature, the viscometer will be used in a cylinder surrounded by water at a constant temperature. With the aid of an attached water bath, it will be possible to determine the viscosities of the mahogany seed oil with respect to the water at various temperatures (30 °C, 40 °C, 50 °C, 60 °C, 70 °C and 80 °C).

## 3. RESULT AND DISCUSSION

### Table 1: Viscosity of Water in Centipoise (Cp)

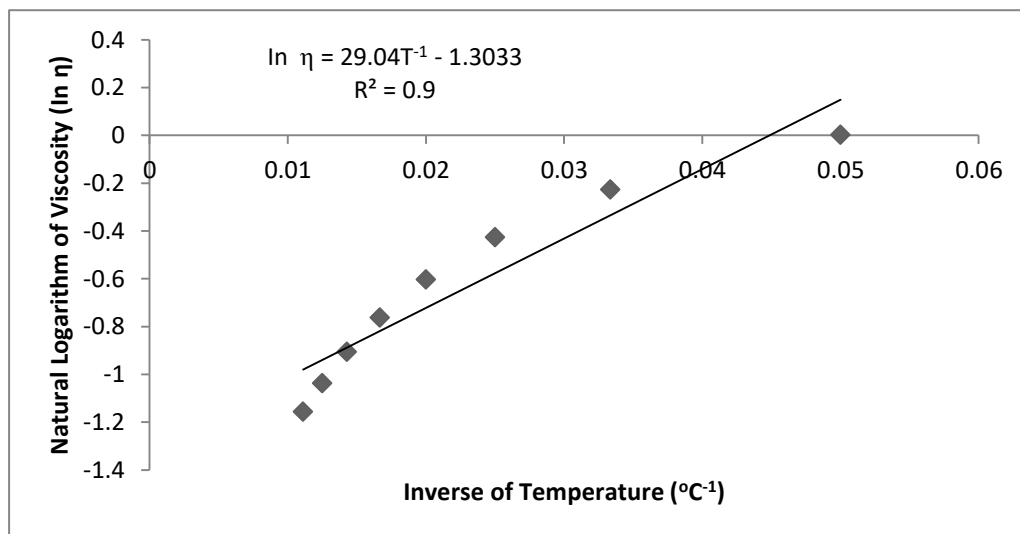| Viscosity η (cP) | In η | Temperature T (°C) | 1/T (°C⁻¹) |
|---|---|---|---|
| 1.002 | 0.001998003 | 20 | 0.05 |
| 0.7975 | -0.226273444 | 30 | 0.033333333 |
| 0.6529 | -0.426331301 | 40 | 0.025 |
| 0.5468 | -0.603672174 | 50 | 0.02 |
| 0.4665 | -0.762497259 | 60 | 0.016666667 |
| 0.4042 | -0.905845474 | 70 | 0.014285714 |
| 0.3547 | -1.036482917 | 80 | 0.0125 |
| 0.3147 | -1.156135475 | 90 | 0.011111111 |



Figure 1: Variation of Natural Logarithm of Viscosity (In η) of Water with Inverse of Temperature (°C⁻¹)

### Table 2: Viscosity of Ethanol in Centipoise (cP)

| Viscosity η (cP) | In η | Temperature (°C) | 1/T (°C⁻¹) |
|---|---|---|---|
| 1.773 | 0.572673027 | 0 | |
| 1.466 | 0.382537603 | 10 | 0.1 |
| 1.2 | 0.182321557 | 20 | 0.05 |
| 1.003 | 0.002995509 | 30 | 0.033333333 |
| 0.834 | -0.181521877 | 40 | 0.025 |
| 0.702 | -0.353821875 | 50 | 0.02 |
| 0.592 | -0.524248644 | 60 | 0.016666667 |
| 0.504 | -0.685179011 | 70 | 0.014285714 |

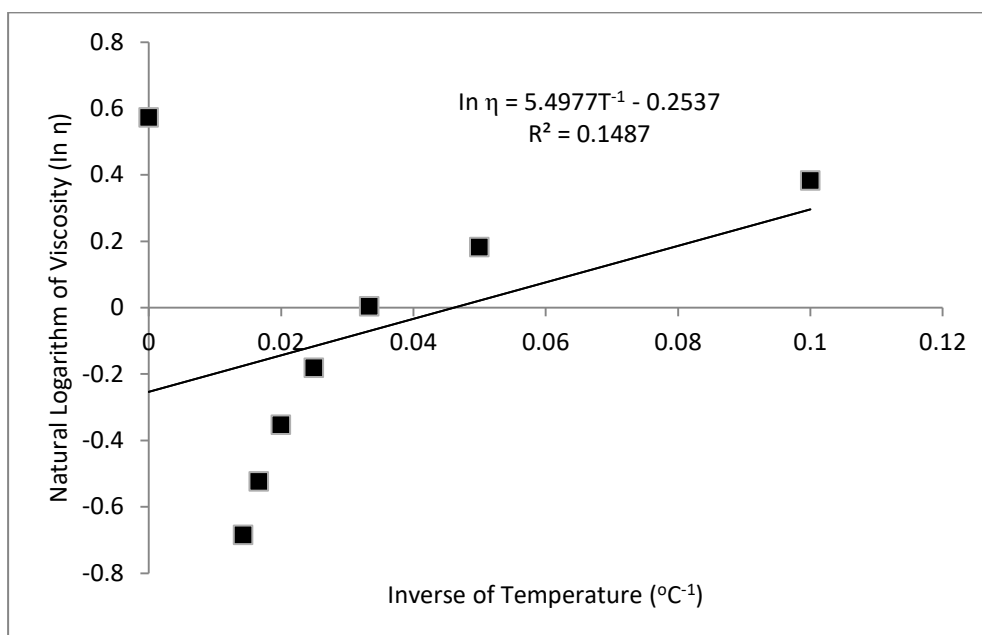**Figure 2: Variation of Natural Logarithm of Viscosity (In η) of Ethanol with Inverse of Temperature ($^{o}C^{-1}$)**

**Table 3: Viscosity of Diethyl ether in Centipoise (Cp)**

| Viscosity η (cP) | In η | Temperature T ($^{o}C$) | 1/T |
|---|---|---|---|
| 0.362 | -1.016111067 | -20 | -0.05 |
| 0.2842 | -1.258077063 | 0 | |
| 0.2332 | -1.455858825 | 20 | 0.05 |
| 0.222 | -1.505077897 | 25 | 0.04 |
| 0.197 | -1.62455155 | 40 | 0.025 |
| 0.166 | -1.795767491 | 60 | 0.016667 |
| 0.14 | -1.966112856 | 80 | 0.0125 |
| 0.118 | -2.137070655 | 100 | 0.01 |



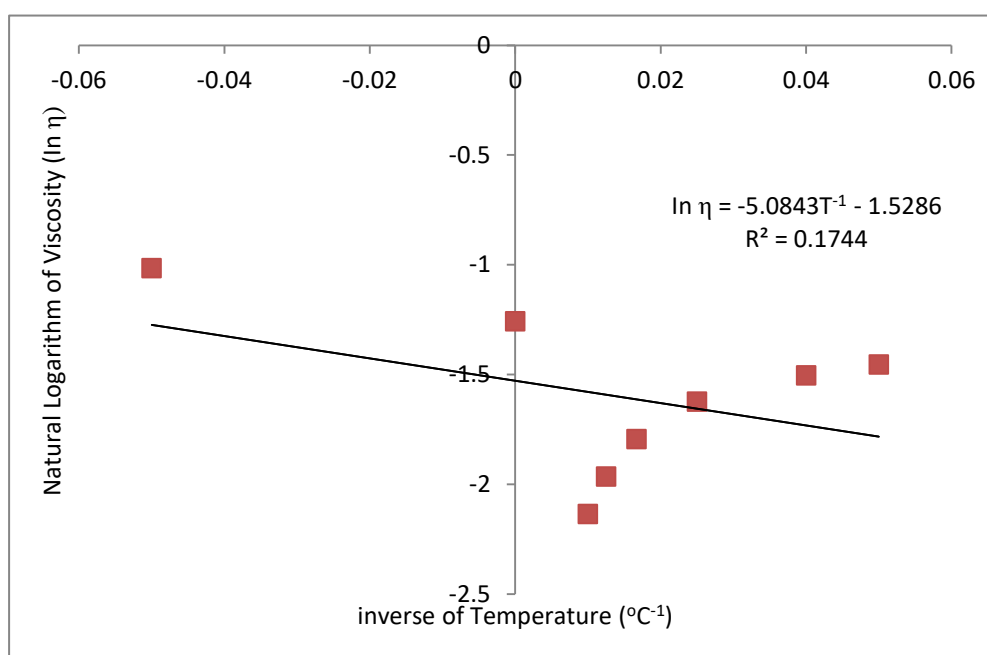**Figure 3: Variation of Natural Logarithm of Viscosity (In η) of Diethyl ether with Inverse of Temperature ($^{o}C^{-1}$)**
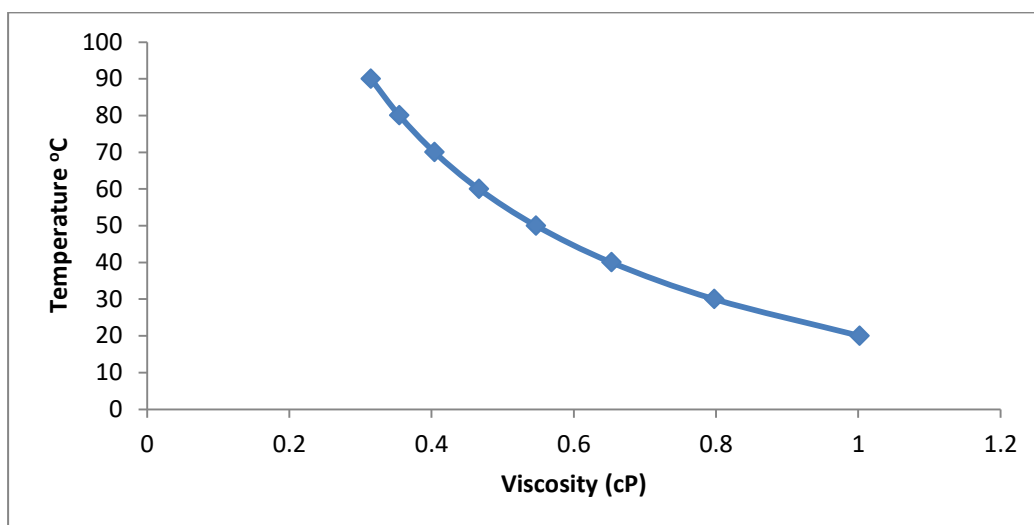
**Figure 4: Variation of Viscosity (Centipoise) of water with Temperature ($^{o}$C)**
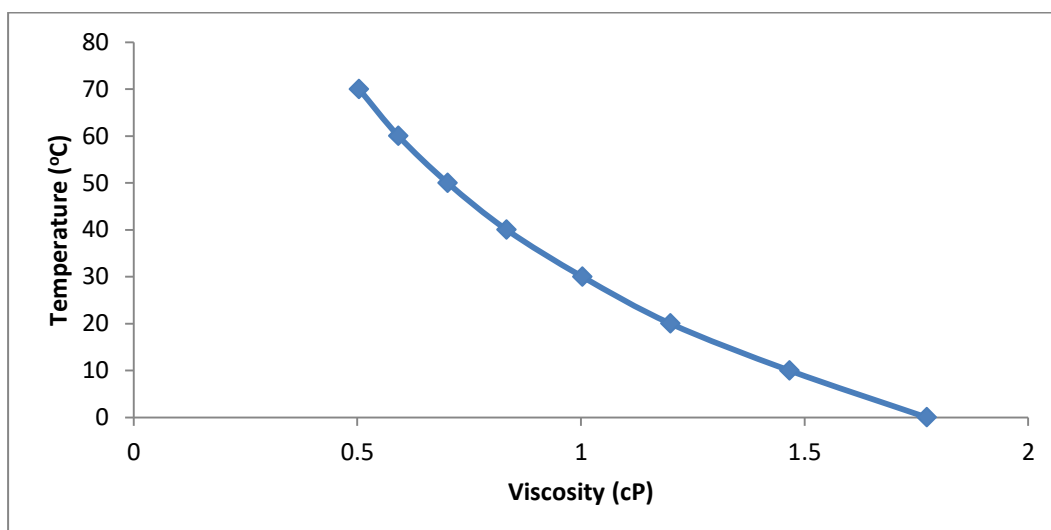


**Figure 5: Variation of Viscosity (Centipoise) of Ethanol with Temperature ($^{o}$C)**
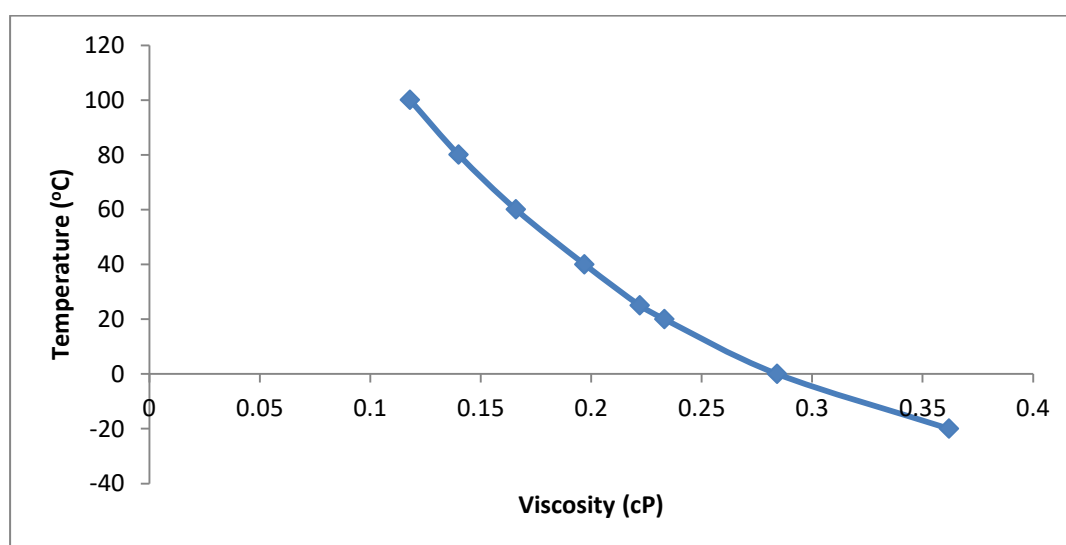


**Figure 6: Variation of Viscosity (Centipoise) of Diethyl Ether with Temperature ($^{o}$C)**

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine for instance must effectively lubricate effectively under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine. Viscosity decreases rapidly with increasing temperatures because (Figures 3 - 6) the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, oil that is thin enough to be a good lubricant in a cold engine will become too thin (have too low a viscosity) to be effective at high temperatures.

The above tables present viscosity data for water, ethanol, and diethyl ether over specific temperature ranges. Each data set is analyzed in order to investigate whether the liquid obeys the simple Arrhenius model, determine the activation energies $E_a$ and the pre-exponential factor A for the viscous flow of these liquids.

A plot of the natural logarithm of the viscosity of water versus the inverse of the successive temperatures (Figure 1) yields a straight line regression $In\eta = 29.04T^{-1} - 1.3033$ with $R^2 = 0.9$. This means that the average activation energy $E_a$ and the pre-exponential factor A are deduced from the slope and the intercept of the regression line respectively as 241.3224 J $mol^{-1}$ and 0.2716 cP.

Also, a plot of the natural logarithm of the viscosity of Ethanol versus the inverse of the successive temperatures (Figure 2) yields a straight line regression $In\eta = 5.4977T^{-1} - 0.2537$ with $R^2 = 0.1487$. This means that the average activation energy $E_a$ and the pre-exponential factor A can be deduced respectively as 45.6659 J $mol^{-1}$ and 0.7759 cP.

In another vein, a plot of the natural logarithm of the viscosity of Diethyl ether versus the inverse of the successive temperatures (Figure 3) yields a straight line regression $In \eta = -5.0843T^{-1} - 1.5286$ with $R^2 = 0.1744$. This means that the average activation energy $E_a$ and the pre-exponential factor A are respectively as -42.2505 J $mol^{-1}$ and 0.2168 cP. As observed from the graph plot (Figure 4), practically all the above parameters obey the linear Arrhenius behavior (Equation 4). Also, we found that there is significant statistical nonparametric correlation between the activation energy ($E_a$) and the entropic factor (A), as well as the Arrhenius temperature ($T_A$). Results showed that the model which best fits the relationship between the defined Arrhenius parameters is a logarithmic type correlating the activation energy ($E_a$) to the Arrhenius temperature ($T_A$). Concerning the hydraulic calculations of fluid transportations and for energy transfer (Aymen *et al.*, 2015), we have reduced the model using single variable without losing significant accuracy. The equation used in the present work allows for redefining the Arrhenius equation by using a single parameter (Ben Haj-Kacem *et al.*, 2012 and Kirkwood *et al.*, 1949) instead of two (Irving, 1977) by using experimental viscosity values at several temperatures. We hereby re-emphasize that this model would be very useful in different fields of physical and chemical sciences. Most interestingly, in engineering data and in estimating one unknown parameter when the second one is available (Das *et al.*, 2012) or evaluated by some relevant theories suggested in the literature (Viswanath *et al.*, 2007). The implication of the exponential term in equations 3 and 4 is that viscosity increases exponentially when the activation energy decreases. Because viscosity with small activation energy does not require much energy to reach the transition state, it should proceed faster than a reaction with larger activation energy.

In chemical reactions, the activation energy obtained above is the minimum energy required for the reaction to take place while the entropic factor expresses the fraction of reactant molecules that possess enough kinetic energy to go into reaction as governed by the Maxwell-Boltzmann law. In other words, the entropic factor is the fraction of molecules that would react if either the activation energy was zero, or if the kinetic energy of all molecules exceeded the activation energy; this is admittedly, an uncommon scenario although barrierless reactions have been characterized by this behavior.

## 4. CONCLUSION

In this paper, we have used statistical methods to analyze the correlation between the Arrhenius pre-exponential factor (A) and activation energy ($E_a$) for simple organic liquids. We found that there is significant statistical correlation between them. Results showed that the model which best fits the relationship between the defined Arrhenius parameters is a logarithmic type correlating the activation energy (Ea) to the Arrhenius temperature ($T_A$). We made use of an equation in modeling the relationship between the two parameters of viscosity Arrhenius-type equation, such as the activation energy (Ea) and the pre-exponential factor (A). The equation allows us to redefine the Arrhenius equation by using a single parameter (Ben Haj-Kacem *et al.*, 2014; Kirkwood, Buff and Green 1949) instead of two (Irving, 1977) by using

experimental viscosity values for organic liquids at several temperatures. We conclude that this model would be very relevant in several fields of the physical and chemical sciences.

The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating, ranging from SAE 5 to SAE 50 for engine oils; the lower the number, the lower the viscosity. The so-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or that the engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives "for improved engine performance" are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

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