Prediction of Viscosity Behavior (V) of Lubricants with Temperature Variation and its Influence on the Thermodynamic Parameters (TP) of Ngol MG-40 Oil

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Abstract

Looking at general technical literature, viscosity is indicated as the main commercial property of lubricating oils. The poor state of this property influences other product properties and vice versa. Lubricating oils are used between two moving or one fixed and a movable surfaces, form a protective film that has the function of minimizing contact between them and, consequently, reducing friction [1]. Its use involves constant variation of temperatures, and this variation leads to power changes in the behavior of lubricant properties. Among this group of properties, we highlight in this research thermodynamic properties of lubricating oils, such as Gibbs free energy, Enthalpy and Entropy and Activation Energy, which are quickly influenced by viscosity in scenarios of changes in lubricant use temperatures. In the case of the lubricant oil Ngol Mg-40 is produced by IMUL (Mulemba Lubricants Installation) in Luanda, which produces it with the aim of ensuring higher quality, high performance and meeting the requirements of the most reputable engine builders in the market, being the viscosity value one of the characteristics that most reveals the performance potential of this fuel. For the development of the study, we used a mixed methodology where laboratory tests were performed on samples of the Lubricant NGOL Mg-40 to verify the behavior of its viscosity (V) with the temperature variation. The results were submitted to a linear regression analysis and by the least squares method to verify the influence of viscosity behavior (V) on the thermodynamic parameters (TP) of the lubricant and we concluded that in the case in the study the viscosity positively influenced the thermodynamic properties, which makes us recommend temperature conditions of use of this lubricant for the maintenance of this quality.

Keywords: Prediction; Behavior; Viscosity; Variation; Temperature; Lubricating oils; Influence and thermodynamic parameters

Introduction

Together with the calorific power the behavior of thermodynamic properties dictate how high lubricating oil can be used, keeping it with good viscosity both in the use, handling, storage of the product, as well as the ability to transfer heat, especially in a sensitive way. The maintenance of this condition (temperature change, with little viscosity variation), will allow to prevent wear on the interior parts of the engines due to loss of properties of lubricants. In the Angolan consumer market, the lubricating oils with the highest share of the consumer market are the lubricating oils of Ngol brand. These oils are produced by Sonangol (Angolan oil company) through its installation called IMUL (Mulemba Lubricant Installation) that makes them available to the market. Among the various ranges of lubricants for various purposes, there are automotive engine lubricants such as Mg-40 oil. This particular oil is highly consumable in the Angolan market. Parallel to

it there are more imported brands (about 90%) [2] and it is necessary to ensure the quality of the product in particular that of national production in ways to ensure higher quality, high performance and meet the requirements of the most respected engine builders on the market. Given the availability of a wide range of lubricant products from different brands with high standards of quality and performance, national producers such as IMUL should seek to ensure that a lubricant that is in the same quality and performance standard. This guarantee is achieved through a good analysis of the quality of properties such as viscosity, and other properties that influence it. The research of techniques or measures, which promote monitoring and an adequate quality control of lubricating oil is a theme of extreme topicality at the level of the oil refining industry and in general, given the current requirements for lubricating oil, it is known that the automotive industry has offered the market increasingly powerful engines hence the need for industries to sail for lubricants that meet the needs of the

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market, by the use of techniques for monitoring the thermodynamic properties of oil activation and looking for technologies that allow you to walk with the advances ensuring greater efficiency and longer service life of the machines.

Thermodynamic Parameters for Lubricating Oil Activation

The thermodynamic properties of a product are those that are related to heat exchange, energy transformations and temperature variations. In this research, we highlight thermodynamic properties of lubricating oils, such as Gibbs free energy, Enthalpy, Entropy and Activation Energy.

Gibbs free energy: Gibbs free energy ($\Delta G°$) is a thermodynamic magnitude defined as the difference between enthalpy variation ($\Delta H°$) and temperature (T) times entropy variation ($\Delta S°$) in a reaction [3]. According to the equation below:

$$\Delta G° = \Delta H° - T\Delta S° \qquad (1)$$

where:

$\Delta H°$- enthalpy variation is a state function that informs the energy variation at constant pressure;

T - temperature is an intensive physical quantity that is influenced or suffer influence by energy variations during the movement of particles; $\Delta S°$-entropy variation is a state function that informs the energy variation depending on the state of freedom of the particles.

When we calculate Gibbs' free energy, we can have a negative or positive result, since a subtraction is made between the physical quantities involved. Thus, if the result is negative, the process is spontaneous ($\Delta G < 0$); however, if the result is positive, the process will not be spontaneous ($\Delta G > 0$).

The calculation of Gibbs' free energy, in addition to predicting whether a system is spontaneous, gives us an accurate sense of the amount of energy we can use from a chemical process to perform some kind of work. According to Gibbs, whenever a spontaneous chemical process occurs, it ends up releasing energy. However, part of this released energy is used by the system itself (substance) so that it can reorganize.

Enthalpy: Enthalpy is sometimes referred to as absolute enthalpy, it is a physical magnitude defined in the context of classical thermodynamics so that it measures the maximum energy of a thermodynamic system, theoretically able to be removed from this system in the form of heat. It is particularly useful in understanding and describing isobaric processes, constant pressure enthalpy variations are directly associated with the energies received by the system in the form of heat, these are easily measurable in calorimeters. According to the presented, absolute enthalpy or simply enthalpy H, is defined by:

$$H = U + PV \qquad (2)$$

Where:

U - represents the internal energy of the system;

PV - define the amount of energy associated with the neighborhood system set due to the fact that the system occupies a volume V when subjected to constant pressure P, that is, the maximum executable work by the neighborhood on the system.

Enthalpy (H) by itself is only a function of state, so it is the variation of enthalpy (ΔH) in a given thermodynamic process, that is, the difference between the enthalpy of the final state and the initial state ($\Delta H = H_f - H_i$) that retains real physical and practical significance. This means that it is the enthalpy variation that measures the heat absorbed by the system during thermodynamic processes as long as constant pressure is realized.

In particular, it is called the enthalpy of formation to the standard enthalpy ($\Delta H = \Delta H^0$)of a compound pure substance. Therefore, it is universally accepted that every simple substance in a standard state, that is, in the most stable physical and allotropic state, at 298.15 K (25°C) and 1 bar (100,000 Pa), has standard enthalpy by definition equal to zero even if its absolute enthalpy is not null in such state [3].

Entropy: Entropy is a thermodynamic magnitude that measures the degree of irreversibility of a system, being generally associated with what is called disorder of a thermodynamic system. According to the second law of thermodynamics, the work can be completely converted into heat, and likewise into thermal energy, but thermal energy cannot be completely converted into work. With entropy, we seek to measure the portion of energy that can no longer be transformed into work in thermodynamic transformations at a given temperature [3]. Calculating the disorder of a system by calculating the variation of entropy is something mathematically simple, just use the following formula:

$$\Delta S = S_p - S_r \qquad (3)$$

where:

ΔS - variation of the entropy of a system;

S_p- entropy of products;

S_r - entropy of reagents.

Whenever we use the ΔS formula to calculate the entropy variation, we will use cal/K.mol or cal.mol^{-1}·K^{-1}.

If the calculation results in a value greater than zero we have the indication of a spontaneous reaction; a value equal to zero the system has equilibrium and a value less than zero the reaction tends not to be spontaneous.

Activation energy: From the point of view of lubrication, knowledge of the viscosity behavior with temperature is important, as this property influences considerably the dimensions of the minimum lubricant thickness that promote the separation of surfaces in contact.

Viscosity is the property that determines the degree of resistance of the fluid to a shear force. There are several equations that correlate viscosity with temperature. For engineering applications, vogel's equation (eq.4) presents very accurate results [4].

$$\mu = a \cdot \exp(b/(T+C)) \qquad (4)$$

In which a, b, and c correspond to the empirical coefficients of the Vogel, T and μ equation, temperature and absolute viscosity respectively.

The determination of viscosity in liquids is based on Eyring's theory of activated state. This theory considers that a liquid is composed of molecules interspersed with unoccupied positions (variances), and these molecules even with the liquid at rest move for the purpose of occupying the variances (empty spaces) adjacent to them. Viscosity is related to the force that tends to object to this movement, being a measure of internal friction. This way the greater the potential barrier a molecule will have to overcome in order to jump into the adjacent vacancy, the greater the viscosity. This potential barrier is known as viscous activation energy or flow activation energy.

Activation energy is the minimum energy that the reagents need to initiate the chemical reaction. This minimum energy is necessary for the formation of the activated complex. The higher the activation energy the slower the reaction because it increases the difficulty for the process to occur. The lower the activation energy the lower the energy barrier, the more effective collisions and therefore a faster reaction. Temperature is a parameter related to the energy of a substance. Several studies have shown that the viscosity of a liquid is highly influenced by changes in temperature.

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Viscosity is directly proportional to the force of attraction between molecules. With the increase in temperature, this attraction force decreases, also decreasing viscosity. Thus, it is observed in liquids that viscosity decreases with the increase in temperature [5]. The reduction of the viscosity of liquids with the increase in temperature is attributed to the increase of intermolecular distances caused during heating. Increasing intermolecular distances reduces the attractiveness forces between molecules by decreasing viscosity [4,6].

The effect of temperature on viscosity is modeled by the Arrhenius equation, according to equation 5 [7].

$$\mu = \mu_w \cdot \exp(Ea/(R.T)) \tag{5}$$

Equation 5 can be rewritten in the form of:

$$\ln\mu = \ln\mu_w + (Ea/R). \ 1/T \tag{6}$$

In which E_a corresponds to the flow activation energy; R to the universal constant of the ideal gases; T at absolute temperature; μ to absolute viscosity $\mu\infty$ to absolute viscosity when temperature tends to infinity [4]. A graph $\ln\mu$ versus $1/T$ provides a line, where the angular coefficient is numerically equal to the ratio (Ea/R) and the linear coefficient, at the $\ln \mu\infty$ (Graph 1).
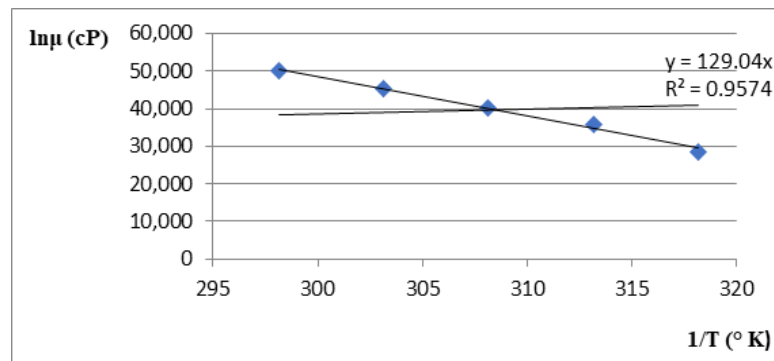
Graph 1: Dependence on the viscosity of a liquid depending on temperature.

Equation (6) indicates the dependence of the viscosity of a liquid with temperature and it can be used with experimental data of absolute viscosity, in the determination of the energy of flow activation and the $\mu\infty$ parameter, the knowledge of this parameter allows to verify the effects of temperature on viscosity, besides mathematically modeling the rheological behavior of this liquid.

With respect to flow activation energy (E_a), this magnitude indicates the sensitivity of viscosity due to temperature change so that the higher the flow activation energy, the greater the influence of temperature, i.e. high flow activation energy indicates a faster change in viscosity with temperature.

Considering equation 6, the increase in temperature has the effect of decreasing the viscosity of the liquid. Since the order of magnitude of the flow activation energy indicates the dependence of viscosity with temperature. Thus, in liquids with high flow activation energy they present great variation in viscosity as a function of temperature and vice versa [4,8].

Methodology

In addition to laboratory tests to gauge viscosities in Mg-40 lubricating oil samples for gasoline engines, the results found were treated and processed from mathematical models (linear regression method) where we determined the thermodynamic properties of activation (activation enthalpy, activation entropy and activation gibbs energy) of the lubricating oil under study.

For the determination of the viscosity of mg 40 Ngol oil as procedures it was necessary the following:

Sample collection (NGOL brand lubricating oil for petrol engines SAE 40);

- Becker cup with respective sample;
- Brookfield viscometer;
- Thermostat Apparatus;
- Picometer;
- Balance.

Results

According to API SJ or ACEA A3/B3 for lubricating oil in gasoline vehicles the method for performing the test is ASTM D445. The first step consisted of conducting tests to verify the viscosity as a function of temperature for further determination of the thermodynamic parameters of activation of lubricating oil.

The tests performed were possible through the use of the brookfield viscometer in a measuring range ranging from 5 - 40000 cP makes - if reading the value of the viscosity variation at different temperature intervals (25, 30, 35, 40 and 45°C) in centpoise. For this case did - if five trials in a time interval of five minutes. In the following table will be illustrated the reading made through the viscometer frame the viscosity values as a function of the temperature (Table 1).

The lower diagram of the equipment that allowed the test is performed below, and it consists of: thermostat apparatus, container containing water (water bath), viscometer apparatus and the beaker cup with the study sample suspended to a tripe (Figure 1).
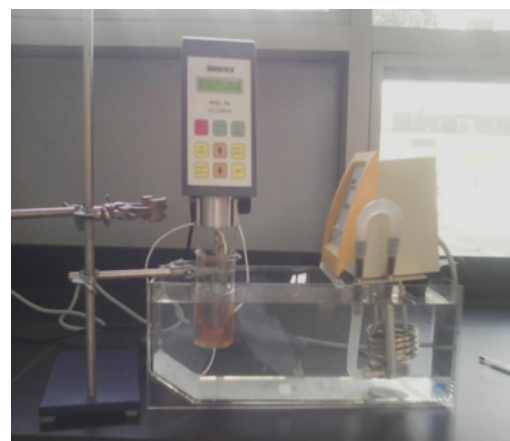

Figure 1: Assembled equipment ready for oil viscosity analysis.

Source: Image taken in the Laboratory Campus UAN (2021).

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Table 1: Determined viscosity values as a function of temperature.

N° of Readings	Te (°C)	η (cP)
1st	25	15
2nd	30	93
3rd	35	50.4
4th	40	43.2
5th	45	13.5

Viscosity Check

The values found in Table 6 will be transformed and the following formula was used for this:

$$=\ln \tag{7}$$

$$°k = (°c + 273,15) \tag{8}$$

where:

: Viscosity of lubricating oil determined in laboratory;

$\ln$: Natural logarithm of lubricating oil viscosity determined in laboratory;

°k: Temperature in kelvin degrees (Table 2).

Table 2: Experimental data on absolute viscosity provided by the test substance.

T (°K)	ln (cP)
298.15	5.01063
303.15	4.53261
308.15	4.08701
315.15	3.56504
318.15	2.80271

We can observe that as the temperature increases, the viscosity of the oil decreases. This is because as more heat is supplied to the system, the number of shock between the particles that form the oil molecule also increases, thereby decreasing the kinetic energy that favors the grouping of molecules, causing a decrease in viscosity.

Discussion

We passed the analysis and discussion on the influence of viscosity found in the most diverse temperatures, on the thermodynamic properties of lubricating oils, according to the results found in the tests.

Influence of Viscosity on Activation Energy

From the experimental data is constructed the viscosity graph as a function of temperature, which results in a tangent and this will allow the determination of the activation energy of the oil by means of the Equation of Arrhenius and by the least squares method (Graph 2).

The direction of the tangent direction of the graph means that for the determination of the activation energy the Arrhenius equation will be used.

Graph 2: Viscosity variation as a function of temperature.

$$\alpha = E\_a/R \tag{9}$$

This implies that:

$$E\_(a=) \alpha.R \tag{10}$$

By the method of the square minimums you have to:

$$y = a - bx \tag{11}$$

and

$$\ln = \ln\_\infty + E\_a/(R.T) \tag{12}$$

Assuming that:

$$y = \ln \quad \text{and} \quad x = 1/T \tag{13}$$

$$a = \ln\_\infty \quad \text{and} \quad b = E\_a/R \tag{14}$$
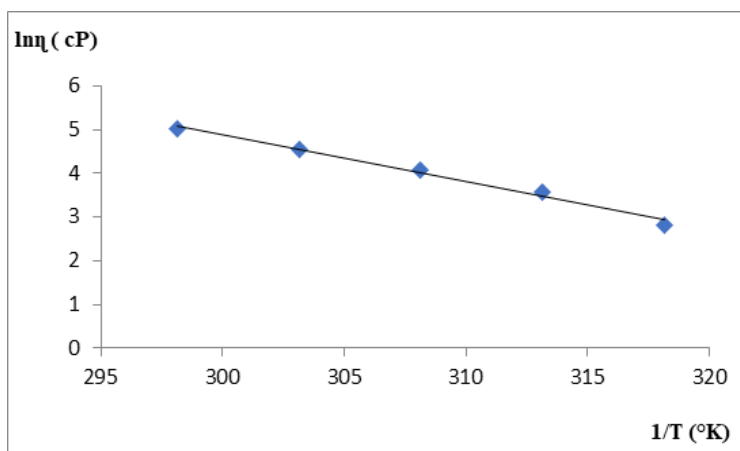
Where:

a: Represents the value where the tangent crosses on the y-axis and b the value where the tangent crosses on the x-axis.

Influence of Gibbs Free Energy

From the following formula will be determined the variation of gibbs energy of activation depending on viscosity and temperature.

$$\Delta G = (R\,T\,\ln\,V)/(h\,N\_a) \tag{15}$$

Graph 2: Viscosity variation as a function of temperature.

Where:

ΔG : Variation of the energy of activating gibbs;

R: Universal constant of real gases (8,314 J/mol °k);

T: Absolute temperature in °k;

ln : Natural logarithm of viscosity in cP;

V = V_P Picometer volume in m^3;

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h: Plank constant ($6,626.10^{-34}$ J.s);

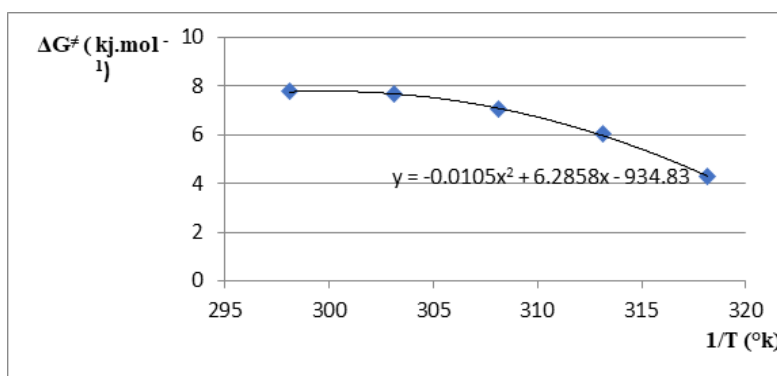N_a: Number of Avogadro ($6,023.10^{23}$ particules/mol).

In the table below are the energy variation values of activation gibbs determined from the formula (Table 3).

Gibbs' activation energy decreases as the temperature increases and this can be explained through the first law of thermodynamics or law of energy conservation applied to thermal processes, and it can be enunciated from the concept of internal energy and this can be understood as the energy associated with atoms and molecules in their movements and interactions internal to the system.

With this we can say that the higher the heat supplied to the system, the greater the shock between the particles and therefore the higher the internal energy consumption soon, the total activation energy of the system will decrease.

Table 3: Gibbs energy variation of activation as a function of temperature.

T (ºk)	ΔG (KJ.mol^{-1})
298,15	$7,78029.10^{-11}$
303,15	$7,65605.10^{-11}$
308,15	$7,04044.10^{-11}$
313,15	$6,04162.10^{-11}$
318,15	$4,27519.10^{-11}$

Influence of Enthalpy

For the determination of the variation of activation entropy (ΔS) and variation of the activation enthalpy (ΔH) by the linear regression method, With the data from the Table 3 the graph $\Delta G = f(T)$ is constructed and as a result will give a linear equation that will allow to determine the constants (Graph 3).

Given the following linear equation:

$$y=-0,010x^2+6,285x-934,8 \qquad (16)$$

Knowing that:

$$\Delta G =-a_2 T^2+a_1 T+a_0 \qquad (17)$$

This implies that:

$$a_0 +a_1 T-a_2 T^2=\Delta G \qquad (18)$$

From the equation (16) we have the values of the constants represented in the Table 4.

Starting from the equation:

$$\Delta G =\Delta H -T\Delta S \qquad (18)$$

Where :

$$\Delta H =a_0-a_2 T^2 \qquad (19)$$

Determines - whether the parameter ΔH by the linear regression according to the Table 4 & Table 5.

Graph 3: Gibbs energy variation as a function of temperature.

Table 4: Values of constants a0, a1 and a2 determined.

Constants	Value of Constants
a_0	- 934,8
a_1	6,285
a_2	- 0,010

Influence of Entropy

Starting from the equation:

$$\Delta G =\Delta H -T\Delta S \qquad (20)$$

$$\Delta S =-a_1-2a_2 T \qquad (21)$$

Determines the parameter ΔS by the linear regression method according to Table 6.

Certain parameters all are displayed the following Table 7:

In the table are represented the thermodynamic parameters that were determined taking into account the theory of absolute velocities of Eyring where ΔG is energy variation of viscous flow activation gibbs, Na the number of avograde, h planck constant, Vm molar volume of the liquid, Constant R of the ideas gases, T temperature and ln the logaritimo of viscosity; It is observed that the variation of the activation gibbs energy (ΔG) decreases as the system heat increases, ΔH increases with the increase in temperature and for the variation of activation entropy (ΔS) decreases with the increase in temperature, all of which have significantly influenced the behavior of lubricating oil.

The data in Table 6 of the Thermodynamic Parameters of lubricant oil activation will be used in the preparation of the statement graphs.

An increase in the activation energy of the viscous flow is observed with the reduction of the viscosity of the lubricating oil studied and the increase in temperature. This increase in activation energy is due to the fact that as the viscosity of the oil decreases by increasing temperature, the number of molecules in solution that restrict their own movements and thus prevents them from occupying the adjacent empty spaces causing an increase in the activation energy (Graph 4).

This graph results in the tangent that allowed to determine the value of the activation energy of the viscous flow. Ea = 90547,774 J/mol°k (Graph 5).

The positive values of the variation of the free energy activation (ΔG) of the viscous flow show that by increasing the temperature the process occurs in a very spontaneous environment, so to make the process favor what had to be spontaneous, more energy will be needed from external sources, thus allowing more interaction between the molecules leading to more associations of them and thus causing a greater number of empty spaces and this will cause there to be an increase in viscous flow (Graph 6).

It turns out that as the temperature increases, the variation of activation enthalpy (ΔH) also increases, which means that when the temperature increases, the thermal energy of the molecules also increases, just as the variances exist in the liquid, in this way, when a liquid seeps are the layers of the molecules that slide over each other, to overlap with intermolecular forces, which cause resistance to runoff (Graph 7).
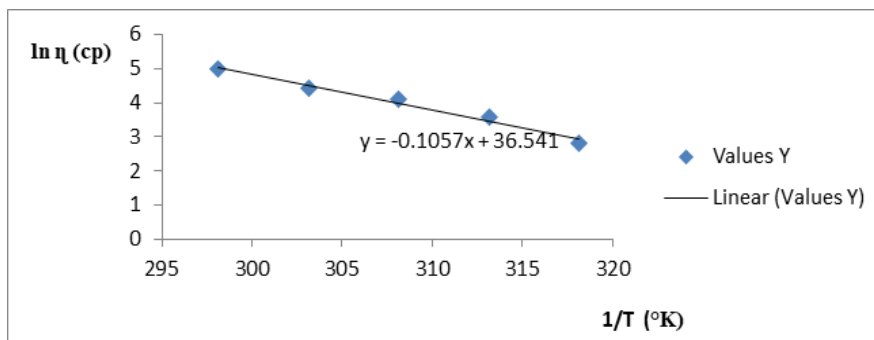
Graph 4: Viscosity versus temperature variation.
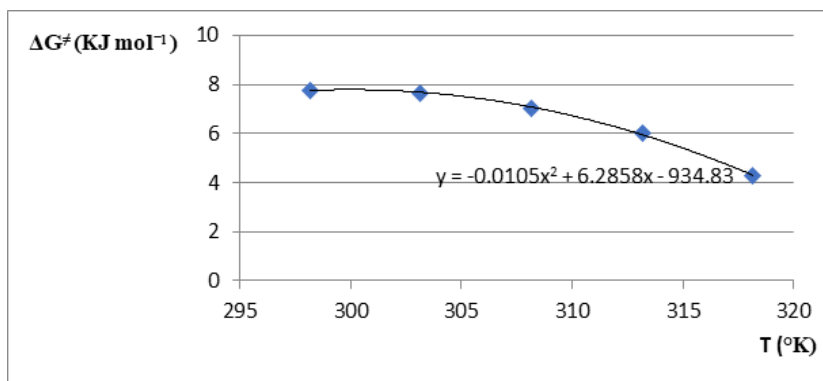
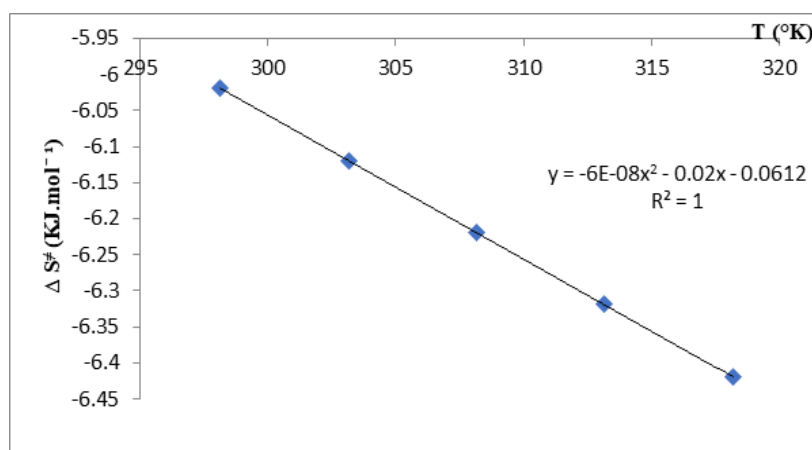**Graph 5:** Variation of the energy of activating gibbs as a function of temperature.
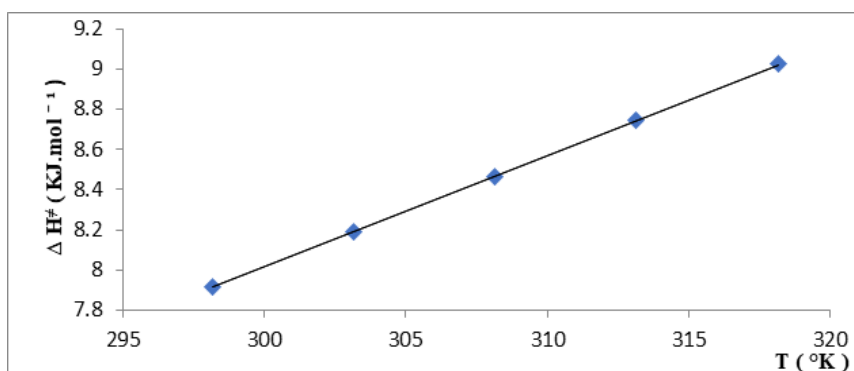
Graph 6: Variation of the activation enthalpy according to temperature.

Table 7: Thermodynamic oil activation parameters as a function of temperature.

T(°K)	$\Delta G \neq (KJ.mol^{-1})$	$H \neq (kJ.mol^{-1})$	$\Delta S \neq (kJ.mol^{-1})$
298,15	$7,78029.10^{-11}$	7,917398	-6,01893
303,15	$7,15605.10^{-11}$	8,187983	-6,11893
308,15	$7,04044.10^{-11}$	8,463068	-6,21893
313,15	$6,14162.10^{-11}$	8,742653	-6,31893
318,15	$4,27519.10^{-11}$	9,026738	-6,41893

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Graph 7: Variation of activation entropy as a function of temperature.

The increase in the variation of activation entropy (ΔS) with the increase in temperature for the system means that the transition state occurs by formation and not by rupture of the solution structure, also demonstrating that the viscous flow behaves as an orderly process involving the adjacent parts of the liquid, from which they must maintain their structural configuration as they pass into the transition state with formation of the activated complex.

Conclusion

Given the results found on the viscosity influence on the thermodynamic properties of the Lubricant Oil Ngol Mg-40, we can consider that changes in viscosity due to temperature, directly influence on the thermodynamic properties of lubricating oil. And in our case study this influence was positive.

The tests and their results indicate that the prediction of the viscosity behavior in relation to temperature allows to monitor the evolution of the behavior of thermodynamic properties during the use of lubricant. This dictates the range of optimum temperatures in which the lubricant should be used without losing its energy quality. In the case of study of Ngol Mg-40 lubricating oil, the recommended range for use is 25°C to 45°C.

In order to determine the thermodynamic properties of activation (activation enthalpy, activation entropy and activation gibbs energy) of the lubricating oil study also allowed to prove that the application of mathematical models (linear regression method) and the least squares method are effective to analyte the influence of viscosity behavior (V) on the thermodynamic parameters (TP) of the lubricant.

Acknowledgements

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